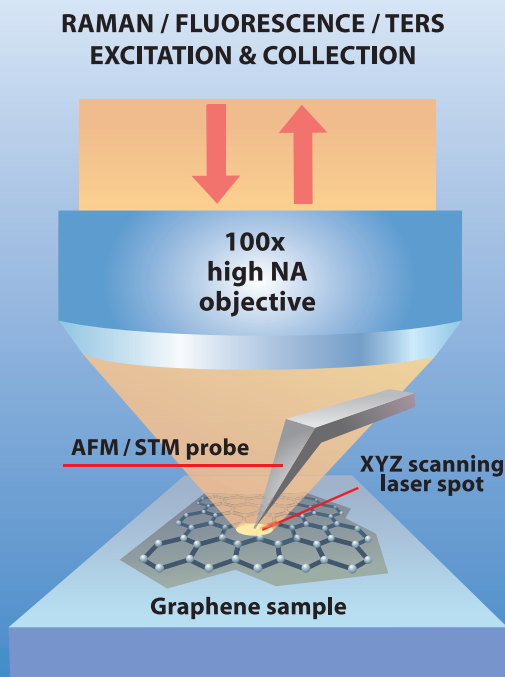
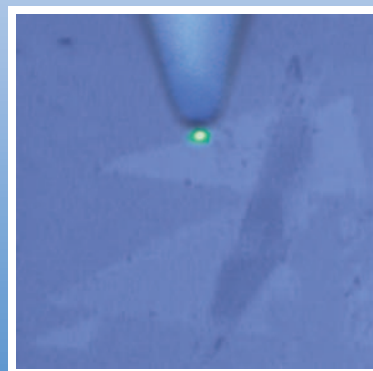


Graphene

**Comprehensive AFM / Optical / Raman / TERS*
Characterization in the Single Experiment**



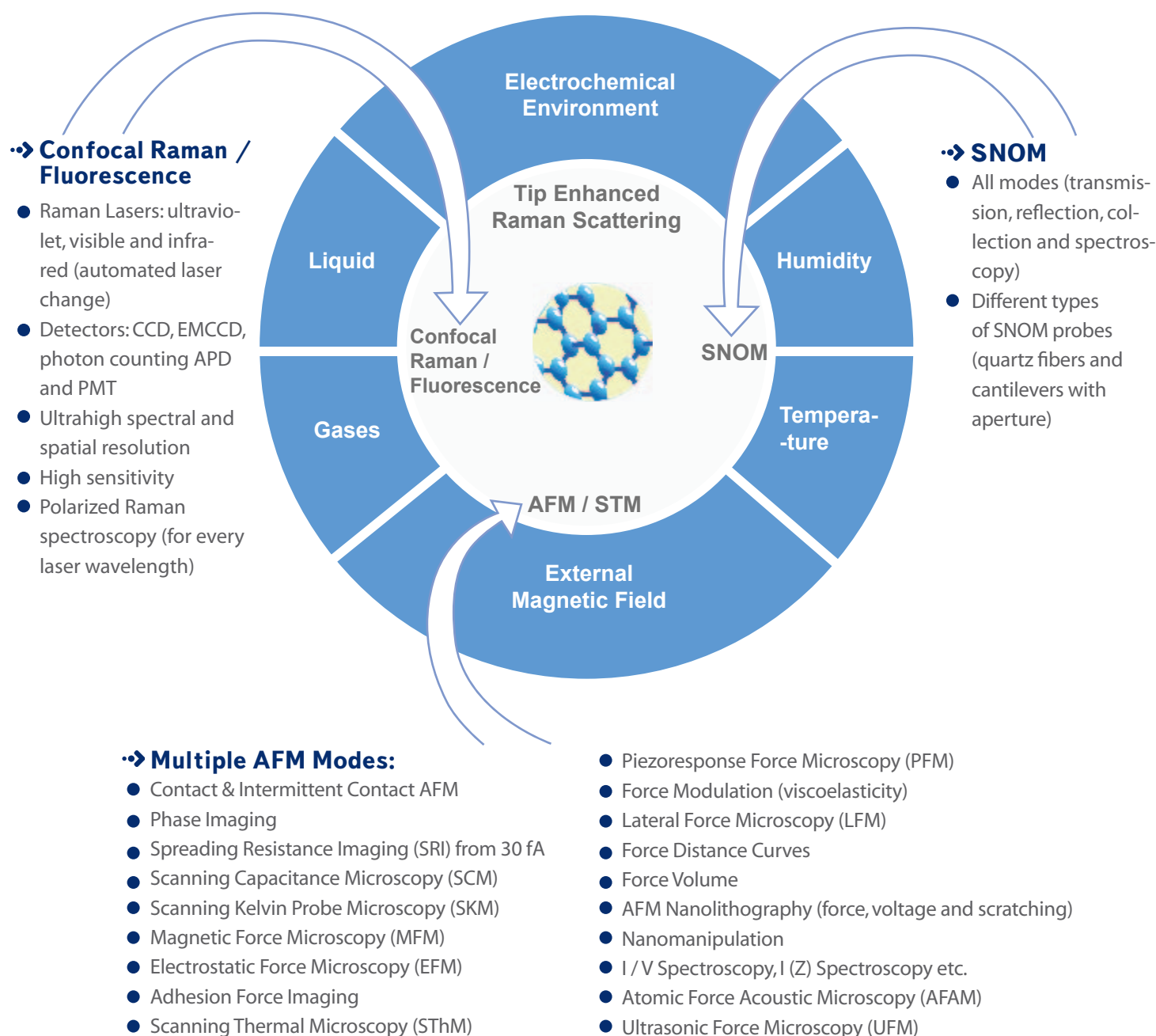
White light image of the graphene flake
with AFM tip and Raman laser spot



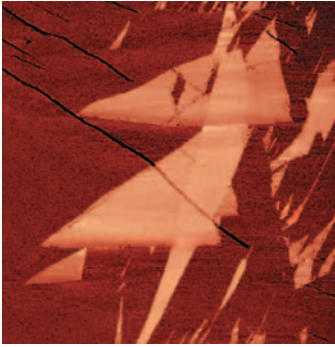
In this issue, Graphene was investigated by:

- High resolution AFM and STM imaging
- Ultrasonic Force Microscopy (UFM),
Scanning Thermal Microscopy (S_{Th}M)
- Advanced AFM modes: EFM, FMM, SKM, LFM etc.
- Nanomanipulations
- Confocal Raman and Rayleigh Microscopy
- *Tip Enhanced Raman Scattering (TERS)

Combination of Atomic Force Microscopy (AFM), confocal Raman / Fluorescence / Rayleigh microscopy and Scanning Near-Field Optical Microscopy (SNOM) provides unique opportunities for graphene investigation. Different AFM techniques allow studying mechanical, electrical, magnetic, and even elastic properties of graphene flakes. Studies of local work function, conductivity, capacitance, piezoresponse, and many other surface properties are available. At the same time, Raman microscopy (available *simultaneously* with AFM) provides information about flake thickness, structural uniformity, presence of impurities, and defects etc. Additionally, Rayleigh imaging and SNOM measure local optical properties of the sample providing further information about flake structure. Importantly, most of the measurements can be performed under environmental control: at variable humidity and temperature, in controlled atmosphere, in liquid and even (in some configurations) in electrochemical environment and at the external magnetic field.



AFM, Optical and Confocal Raman Characterization of Graphene — All in the Single Experiment



AFM: Force modulation
(elastic properties)



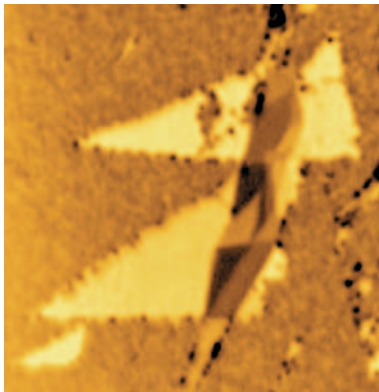
AFM: Electrostatic force (charge
distribution)



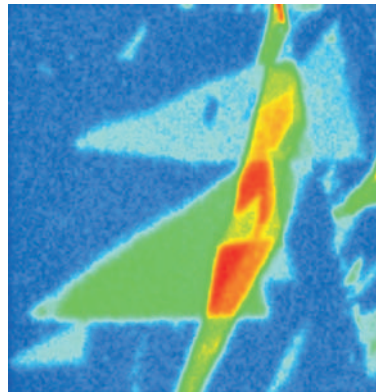
AFM: Kelvin probe microscopy
(surface potential)



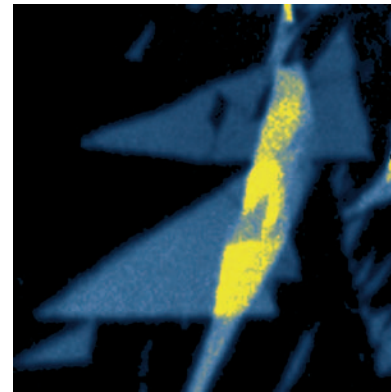
AFM: Lateral force (friction)



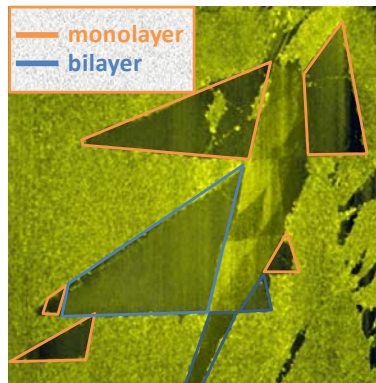
Rayleigh light intensity
(473 nm laser)



Confocal Raman map:
G-band intensity



Confocal Raman map:
2D (G') band mass center



AFM: Height (topography)
Size: 30*30 μm
Substrate: gold

AFM topography is used to identify single, double and multiple layer graphene flakes and to study flakes shape, uniformity, adsorbates etc. Confocal Raman and confocal Rayleigh microscopy confirm information about flakes thickness and provide further information about sample electronic structure, defects etc. Advanced AFM imaging techniques correlate sample physical properties (friction, elasticity, localized charge, surface potential) with the number of layers in graphene.

Data courtesy:

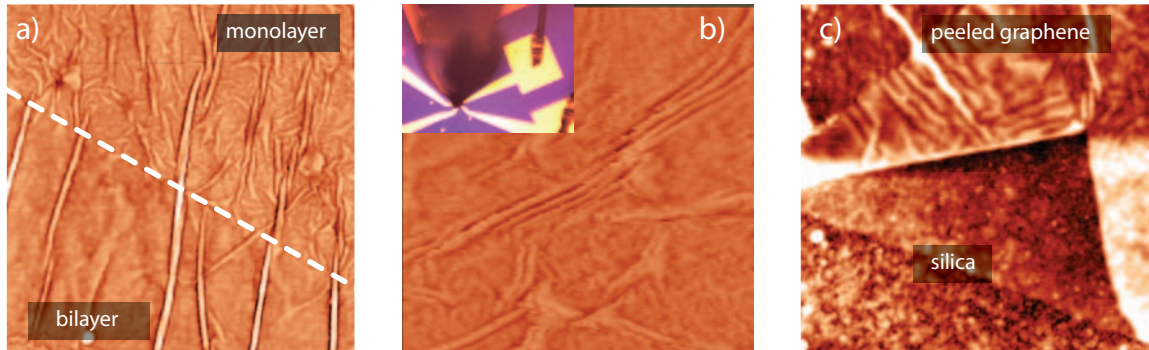
E. Kuznetsov, S. Timofeev,
and P. Dorozhkin, NT-MDT Co.

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Graphene Topography by AFM and STM

Image 1



a) The graphene crystal is not perfectly flat. On silica it is seen to ripple with height ~ 0.3 nm and width ~ 10 nm. Rippling in bilayer is significantly smaller. (Scan: $1.5 \mu\text{m}$ square, phase contrast, 10° full colour scale).

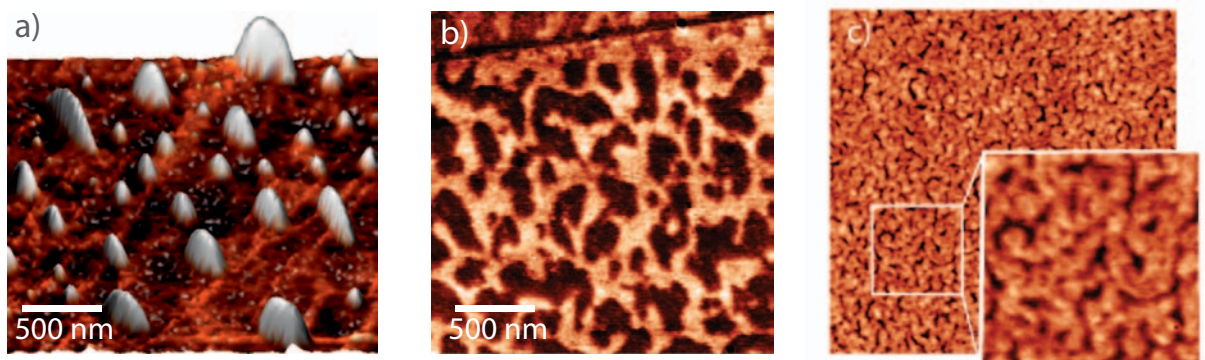
b) STM scans show that some of these ripples are correlated. Inset shows an optical image of the experiment, the graphene crystal grounded via 4 gold electrical contacts. (Scan: $0.8 \mu\text{m}$ square, 5 nm full colour scale).

c) Graphene can be peeled off the substrate by an AFM tip. The peeled crystal shows stronger, >0.6 nm, ripples than the attached crystal. The origin of the ripples is also revealed: the graphene is supported on spikes in the silica substrate, which has a roughness of ~ 0.5 nm. (Scan: $0.8 \mu\text{m}$ square, semi-contact topography, 4 nm full colour scale, 3 mbar dry nitrogen environment, NT-MDT NSG01_DLC cantilever).

Graphene under Controlled Environment

Graphene topography features as well as its physical properties depend highly on environmental conditions. For quantitative reproducible studies, measurements have to be performed under a controlled environment. The figure below shows monolayer graphene AFM images taken under different environmental conditions. Bubbling on graphene surface (a) is observed when measured in ambient conditions - caused by a thin water layer between graphene and the silica substrate. Heating above 100°C decreased the size of the bubbles (b) and changed their structure; however, the bubbles could not be removed completely. After exposure to toluene vapor (c), graphene topography substantially changed confirming the possibility of using graphene monolayer as a practical sensor.

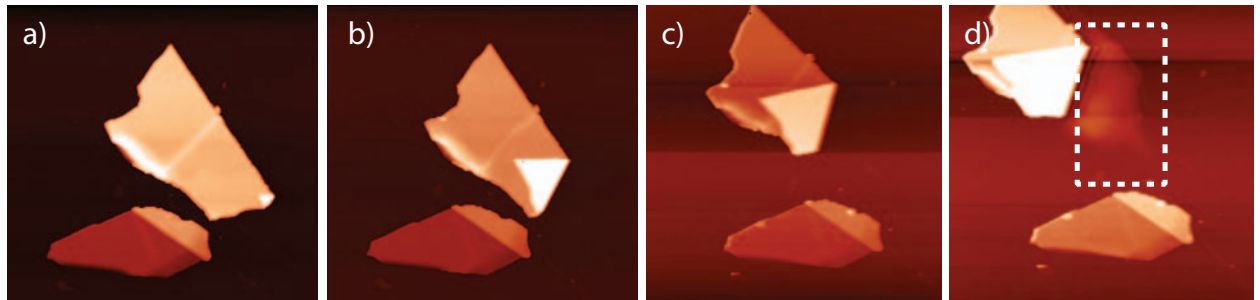
Image 2



Graphene Nanomanipulation by AFM

Graphene (multilayer) folded in successive steps (image 3, scans a-d) by an AFM cantilever. The graphene is attached to a silica / silicon substrate. The degenerately doped silicon is separated from the graphene by 300 nm silica. Between each fold, 10 V is applied between the silicon and the tip held at the centre of the graphene crystal. After folding, a 'ghost' of the graphene is left behind (see white highlighted region in scan (d)). This is from charge built up in the silica from the applied voltage: charge from the tip is dispersed across the conductive graphene crystal then charges impurities in the silica. Even in ambient conditions, this effect lasts for several hours.

Image 3



Data courtesy of images 1-3: Dr. David W. Horsell, Center of Graphene Science, University of Exeter, UK. For more information, see: D. W. Horsell, P. J. Hale and A. K. Savchenko, *Microscopy and Analysis* 25(1), 15 (2011), and F. V. Tikhonenko, D. W. Horsell, R. V. Gorbachev, and A. K. Savchenko, *Phys. Rev. Lett.* 100, 056802 (2008)

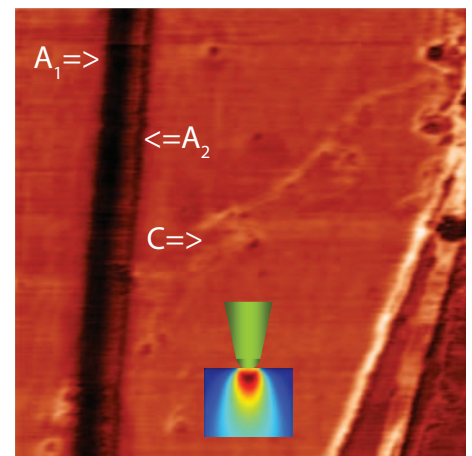
Mapping of Graphene Nanomechanical and Thermal Properties with Ultrasonic Force Microscopy and Scanning Thermal Microscopy

Nanoscale mechanical and thermal properties of graphene materials and devices are often as vital for successful implementation of graphene fragile two-dimensional structures (often with high energy dissipation) as their electronic properties.

Elastic moduli of graphene can range from kPa flexural moduli of suspended graphene sheets to hundreds GPa and TPa of supported film in-plane moduli.

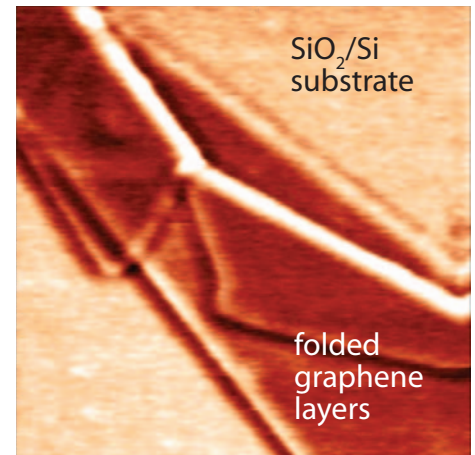
In order to image this vast range, we use Ultrasonic Force Microscopy (UFM) that deploys very small amplitude (few Å), but very high frequency ultrasonic vibration of 10 – 100 MHz. That makes the cantilever infinitely rigid and able to probe moduli of any material from soft to the hardest. This vibration is then detected thanks to extreme nonlinearity of tip-surface nanoscale contact, in a similar way to radio frequency detected by the semiconductor diode.

An UFM image of a few layer graphene on Si / SiO₂ substrate shows its elasticity in the areas of intricate contact with trench edges (arrows A₁, A₂) as well as map attachment of graphene to the substrate over wider area (arrow C). UFM also has a unique feature of zeroing the tip-surface friction (so called "ultrasonic superlubricity") that practically eliminates damage to the tip and making it a good alternative to Intermittent Contact imaging.



UFM image. Image size: 2.5 x 2.5 μm
Image 4

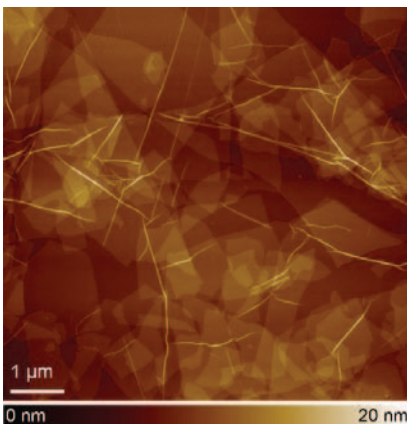
Scanning Thermal Microscopy (SThM) using ambient or a high vacuum NT-MDT scanning probe microscope, allowed to observe heat conductivity within the graphene film, heat transfer to the underlying substrate as well as image peculiarities of heat transfer in folded graphene layers (right image, SThM w/ heated tip, brighter contrast corresponds to higher contact temperature).



SThM image. Image size: 2.5 x 2.5 μm
Image 5

Data courtesy of images 4, 5: O. Kolosov, M. Pumarol, P. Tovee, M. Rosamond and D. Zeze,
University of Lancaster, UK and www.nano-science.com

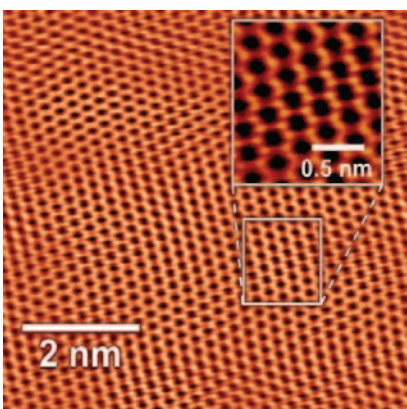
High-Resolution Imaging of Single-Layer Graphene



The high-resolution image was taken by AFM and shows an assembly of single-layer, functionalized graphene sheets on a surface. Some of the sheets are many square micrometers large. The thickness of each sheet is less than 1 nm.

Image 6

Atomic-Resolution Lattice Images of Graphite



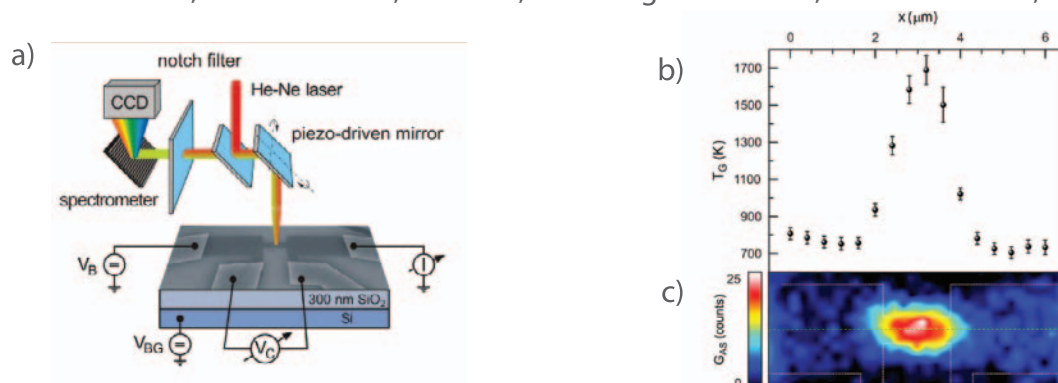
The picture shows a graphite (HOPG) sample that was imaged by Scanning Tunneling Microscopy (STM). The scan range of the entire image is less than 7 nm. Excellent atomic resolution is achieved.

Image 7

Data courtesy of images 6, 7:
Prof. Hannes Schniepp, The College of William & Mary, USA

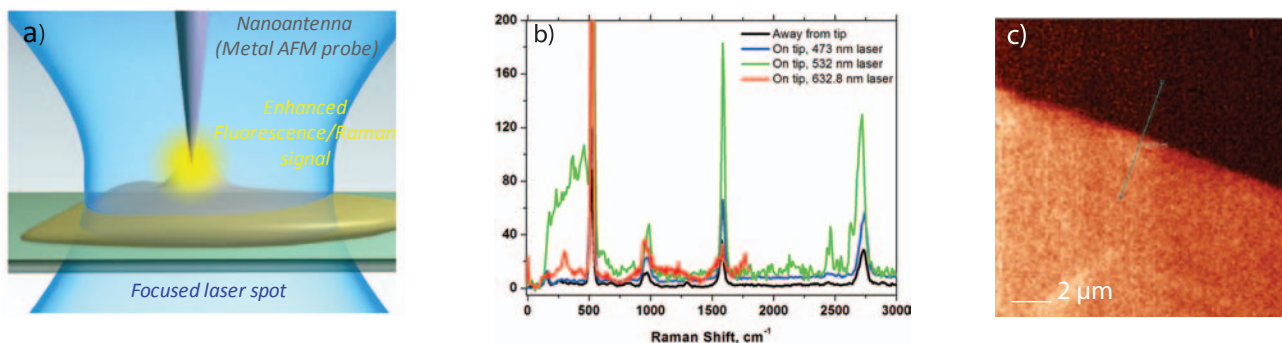
Hot Phonons in an Electrically Biased Graphene Constriction

Confocal Raman microscopy can be used to measure phonon temperature distribution in graphene. In fig. (a) laser spot is scanned across electrically biased graphene constriction while Raman spectra are measured. G-phonon effective temperature (T_G) is calculated from the ratio of Stokes and anti-Stokes components of Raman G-peak. Sample is kept in 3×10^{-6} mbar vacuum to avoid contamination. The measured spatial profile of T_G across the device is shown in fig. (b), at a dissipated electric power of 2.4 mW. The effective temperature reaches >1600 K at the center of the constriction and is significantly higher than in the wide graphene regions close to electrodes. Colour map on fig. (c) shows intensity of anti-Stokes G-band reflecting temperature distribution of the sample. Red (blue) corresponds to a high (low) intensity value and hence high (low) temperature. The white dotted line on (c) demarcates the etched graphene flake. For more information, see: D.-H. Chae, B. Krauss, K. Klitzing and J. Smet, Nano Lett. 2010, 10, 466



Tip Enhanced Raman Scattering of Graphene

In Tip Enhanced Raman Scattering (TERS), fig. (a), a metalized AFM probe is used to enhance light locally around the tip apex. Power density of the focused laser light can be increased by a few orders of magnitude in the vicinity (~ 10 nm) of the tip if the light frequency is in resonance with localized surface plasmon at the tip apex. Effectively, the tip acts as a “nano-source” of light. If the sample is now scanned below the tip, lateral resolution of resulting Raman / fluorescence maps are defined by the localization volume of the surface plasmon field rather than by light wavelength. Fig. (b) shows Raman spectra of a multilayer graphene flake. Black spectrum is taken in the absence of the TERS tip; red, green and blue are TERS spectra taken with lasers of corresponding wavelengths. TERS enhancement effect is resonant and reaches maximum ($\sim 10\times$ enhancement for G-band) at 532 nm laser wavelength. Fig. (c) shows corresponding TERS map of the graphene edge (intensity of Raman G-band).

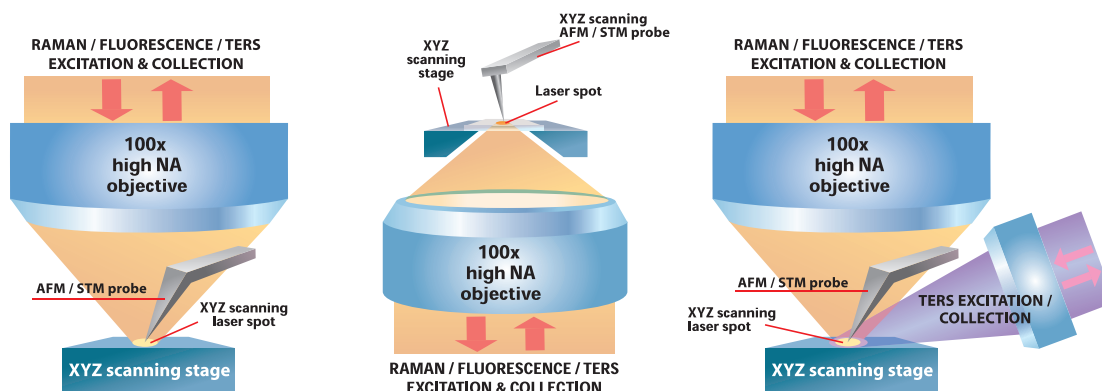


Data courtesy: A. Schokin, P. Dorozhkin, NT-MDT Co.

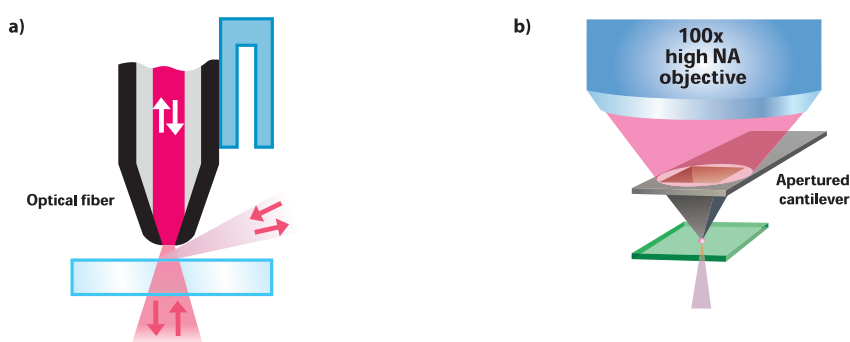
NTEGRA Spectra AFM / Confocal Raman / SNOM / TERS One Sample — Different Experimental Geometries, Techniques and Conditions

NTEGRA Spectra provides opportunity to carry out all the measurements by the same instrument, on the same sample during the same experiment. It is possible to obtain AFM / Raman / Fluorescence / Rayleigh maps exactly from the same area during one sample scan. All AFM and spectral data analysis are performed with the same software.

Solution for all possible excitation/detection and TERS geometries



Scanning Near-Field Optical Microscopy



a) Based on quartz SNOM fiber, shear-force feedback
b) Based on silicon cantilevers with nanofabricated aperture

→ Modes

- AFM (mechanical, electrical, magnetic properties and nanomanipulation – more than 30 modes)
- Confocal Raman Imaging and Spectroscopy
- Confocal Fluorescence Imaging and Spectroscopy
- Scanning Near-Field Optical Microscopy
- Tip Enhanced Raman and Fluorescence Microscopy (TERS, TEFS)
- White Light Microscopy and Reflected Laser (Rayleigh) Confocal Imaging

→ Controlled Environment

- Temperature
- Humidity
- Gases
- Liquid
- Electrochemical environment
- External magnetic field

Confocal Raman / Fluorescence microscopy

Confocal Raman / Fluorescence / Rayleigh imaging runs simultaneously with AFM (during one sample scan)

Diffraction limited spatial resolution:
< 200 nm in XY,
< 500 nm in Z (with immersion objective)

True confocality;
motorized confocal pinhole for optimal signal
and confocality

Motorized variable beam expander / collimator: adjusts
diameter and collimation of the laser beam individually
for each laser and each objective used

Full 3D (XYZ) confocal imaging with powerful image
analysis

Hyperspectral imaging (recording complete
Raman spectrum in every point of 1D, 2D or 3D confocal
scan) with further software analysis

Optical lithography (vector, raster)

AFM / STM: Integration with spectroscopy

Upright and Inverted optical AFM configurations (opti-
mized for opaque and transparent samples correspond-
ingly); side illumination option

Highest possible resolution (numerical aperture) optics
is used simultaneously with AFM:
0.7 NA for Upright, 1.3–1.4 NA for Inverted

AFM / STM and confocal Raman / Fluorescence images
are obtained simultaneously (during one scan)

All standard SPM imaging modes are supported (>30
modes) — combined with confocal Raman / Fluores-
cence

Low noise AFM / STM (atomic resolution)

Vibrations and thermal drifts originating from optical mi-
croscope body are minimized due to special design of
optical AFM heads

Focus track feature: sample always stays in focus due to
AFM Z-feedback; high quality confocal images of very
rough or inclined samples can be obtained

Software

Seamless integration of AFM and Raman; all AFM / Ra-
man / SNOM experiment and further data analysis is per-
formed in one and the same software

Powerful analysis of 1D, 2D and 3D hyperspectral images

Powerful export to other software
(Excel, MatLab, Cytospec etc.)

Spectroscopy*

Extremely high efficiency 520 mm length
spectrometer with 4 motorized gratings

Visible, UV and IR spectral ranges available

Echelle grating with ultrahigh dispersion;
spectral resolution: 0.007 nm (< 0.1 1/cm)**

Up to 3 different detectors can be installed
- TE cooled (down to -100°C) CCD camera. EMCCD cam-
era is optional — for *ultrafast imaging*
- Photon multiplier (PMT) or avalanche photodiode APD
in photon counting mode
- Photon multiplier for fast confocal laser (Rayleigh) im-
aging
Flexible motorized polarization optics in excitation and
detection channels, cross-polarized Raman measure-
ments

Fully automated switching between different
lasers — with a few mouse clicks

Scanning Near Field Optical Microscopy (SNOM)

Two major SNOM techniques supported: (i) based on
quartz fiber probes, (ii) based on silicon cantilever probes

All modes are supported: Transmission, Collection,
Reflection

All SNOM signals are detected: laser intensity,
fluorescence intensity, spectroscopy

SNOM lithography (vector, raster)

Optimized for Tip Enhanced Raman Scattering (TERS) and other tip-related optical techniques (S-SNOM, TEFS, STM-LE etc.)

All existing TERS geometries are available: illumination /
collection from bottom, from top or from side

Different SPM techniques and TERS probes can be used:
STM, AFM cantilever, quartz tuning fork in tapping and
shear force modes

Dual scan (for Hot Point Mapping in TERS): scan by sam-
ple AND scan by tip / by laser spot

Motorized polarization optics to produce
optimal polarization for TERS

AFM-Raman measurements can be run in air, in a controlled atmosphere or in liquid — all with variable temperature

Some features listed are *optional* — not included into basic system
configuration

* NT-MDT AFM can be integrated with Renishaw inVia or with NT-MDT
spectrometer. Specifications are given for the latter. Renishaw specifica-
tions can be found at www.renishaw.com/AFM-Raman

** Exact value of spectral resolution highly depends on how “resolution”
is defined

NTEGRA Spectra

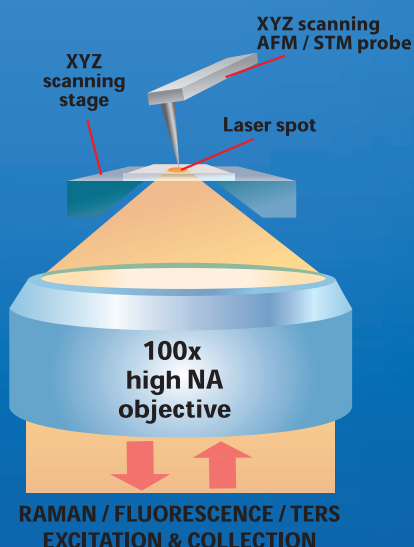
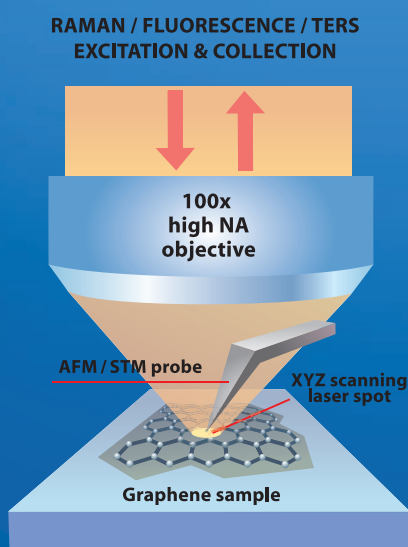
AFM + Confocal Raman + SNOM



Upright Setup



Inverted Setup



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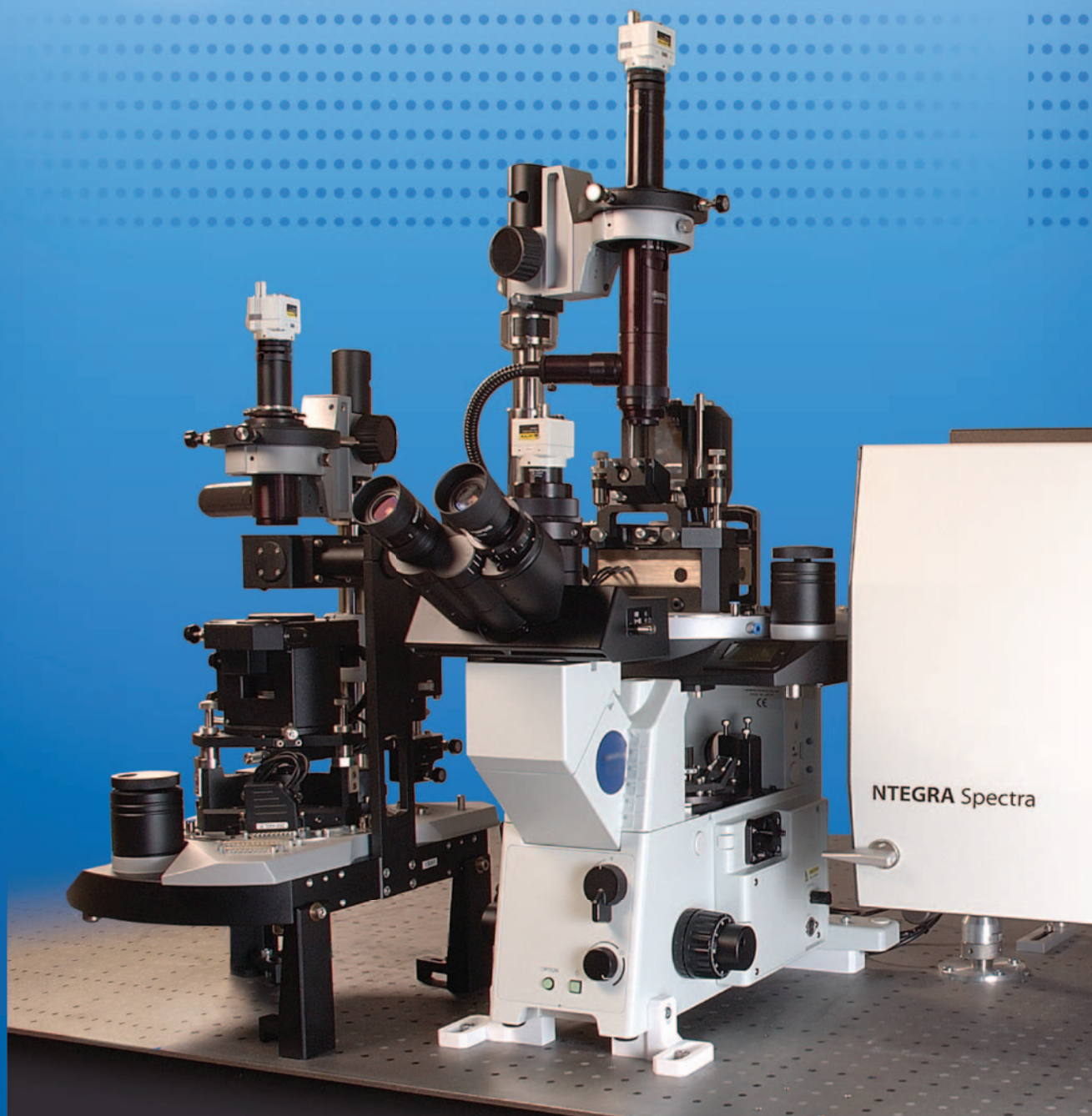
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NTEGRA Spectra

AFM + Confocal Raman + SNOM



Inverted + Upright Setup



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