NT-MDT Spectrum Instruments

Nanoscale IR Microscopy and Spectroscopy

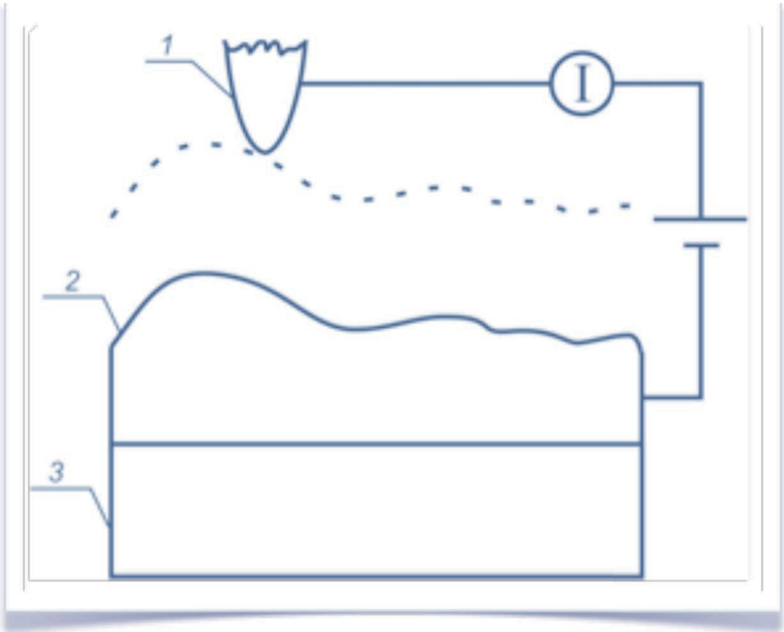
V.V. Polyakov[1], A.V. Shelaev[1]

1 – NT-MDT Spectrum Instruments, Moscow, Zelenograd, Russia

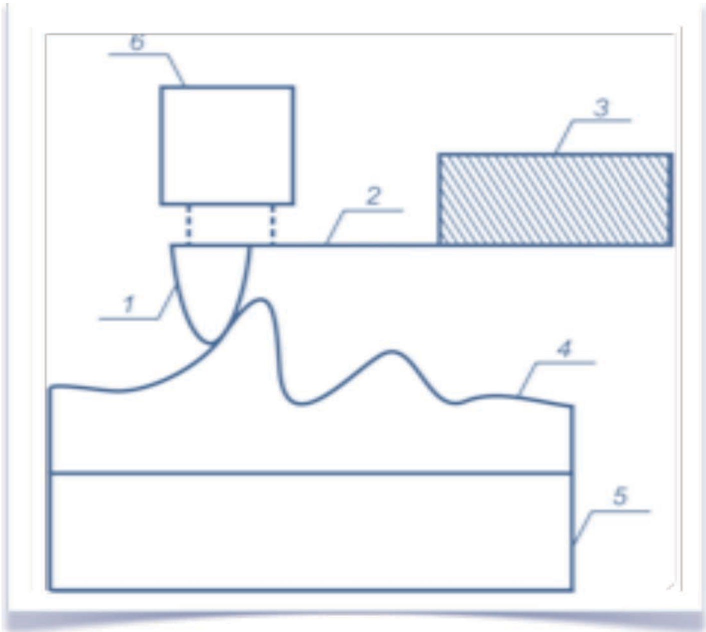
Agenda

- Introduction
- Combination of AFM and optical spectroscopy techniques
- Nanoscale IR microscopy
- Conclusions

SPM history and background

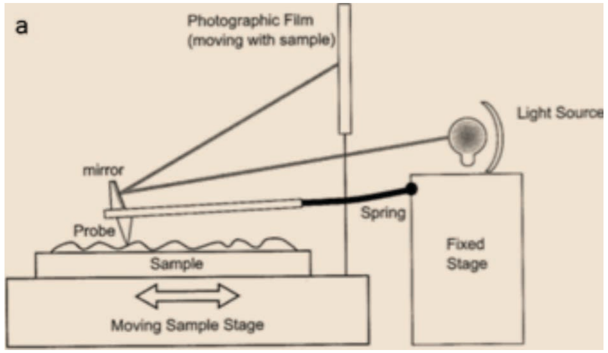


Scanning tunneling microscope:
1 - tip, 2 – conductive sample, 3 - scanner



Atomic force microscope:
1 - tip, 2 – cantilever, 3 – chip, 4 – sample,
5 – scanner, 6 – deflection sensor

SPM history and background



Surface stylus profiler
G. Schmaltz, U. Glätte , Zeitschrift des Vereins deutscher Ingenieure, Oct 12, 1929, pp. 1461-1467

1966 – tunnel effect used for sample topography research (R. Young, J. Ward, F. Scire)

1981 – STM atomic resolution achieved (G. Binnig and F. Rohrer, Nobel prize 1986)

1985 – first AFM introduced (G. Binnig et. al.)

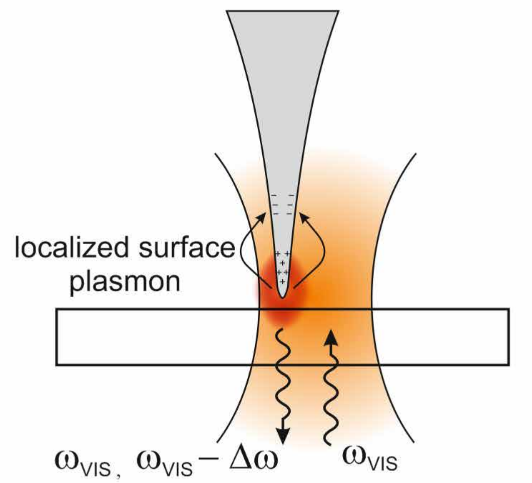
1998 – first combined AFM-Raman system introduced (NT-MDT)

VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

Atomic Force Microscope

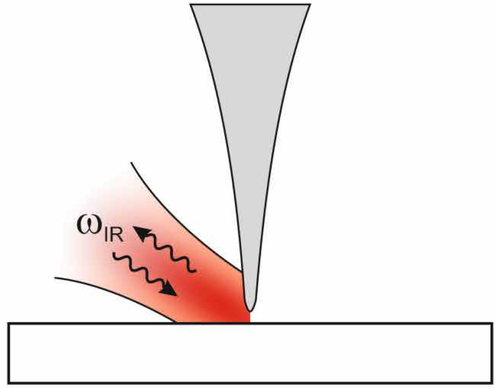
G. Binnig[a] and C. F. Quate[b]
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305
and
Ch. Gerber[c]
IBM San Jose Research Laboratory, San Jose, California 95193
(Received 5 December 1985)

Super-resolution imaging using scanning optical antennas



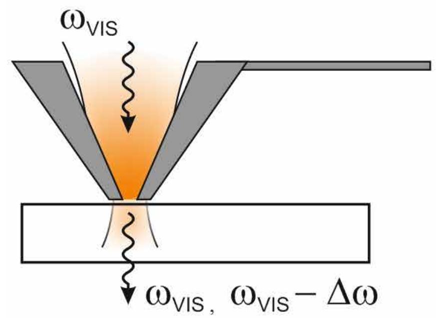
Tip enhanced near-field optical microscopy

Light localization and enhancement by localized surface plasmon



Apertureless (scattering) scanning near-field optical microscopy (s-SNOM); **nano-IR**

Infrared (& Vis) light scattering by non-resonant antenna

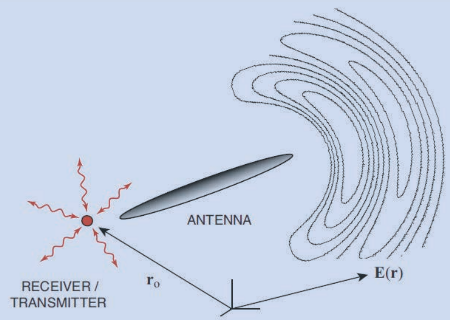


Aperture scanning near-field optical microscopy (SNOM)

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.

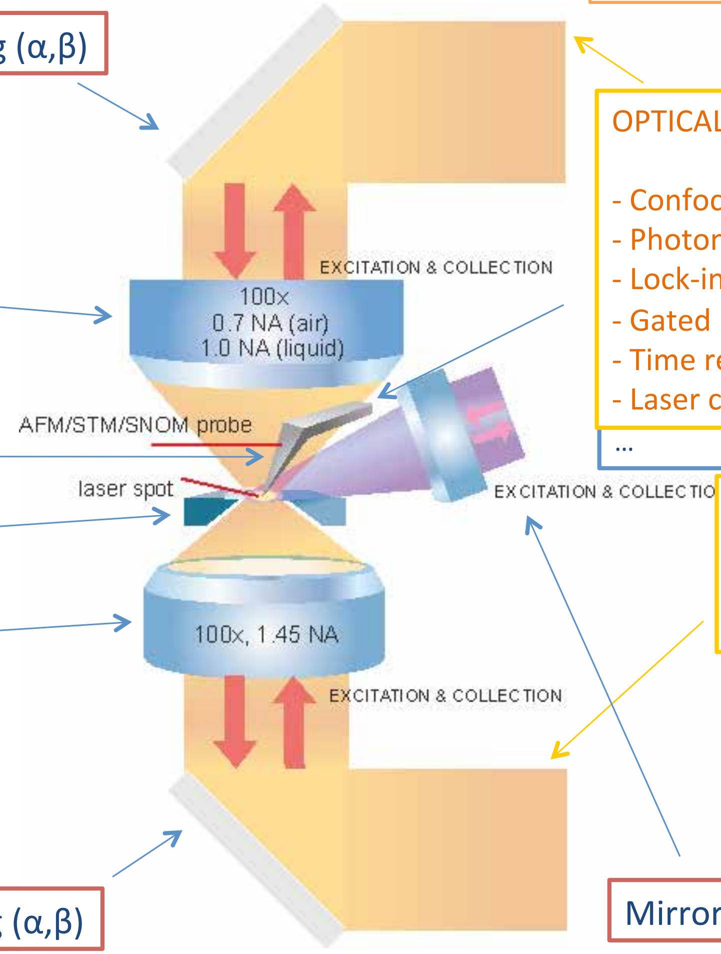
- *L. Novotny, N. van Hulst, Nature photonics 5, 89 (2011)*
- *P. Bharadwai, B. Deutch, L. Novotny, Adv. In Opt. Phot. 1, 438 (2009)*
- *Pohl D. W., Optics, Principles and Applications (World Scientific, 2000).*



AFM integration with LIGHT

PIEZO SCANNING COORDINATES (CLOSED LOOP):

- Mirror scanning (α,β)
- Objective, Z
- Tip, XYZ
- Sample, XYZ
- Objective, Z
- Mirror scanning (α,β)
- Mirror scanning (α,β)



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

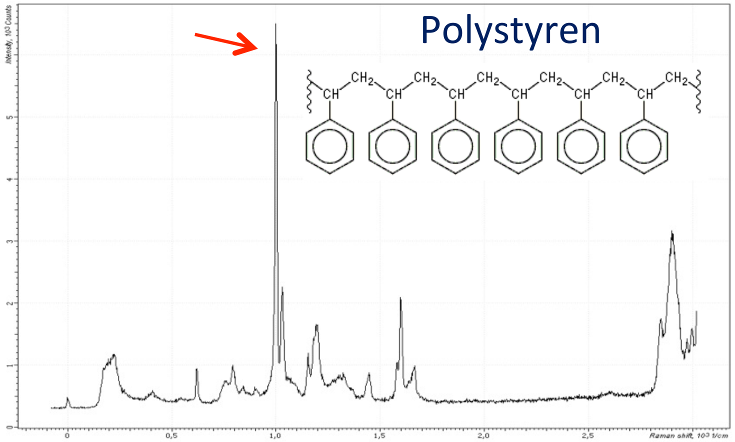
...

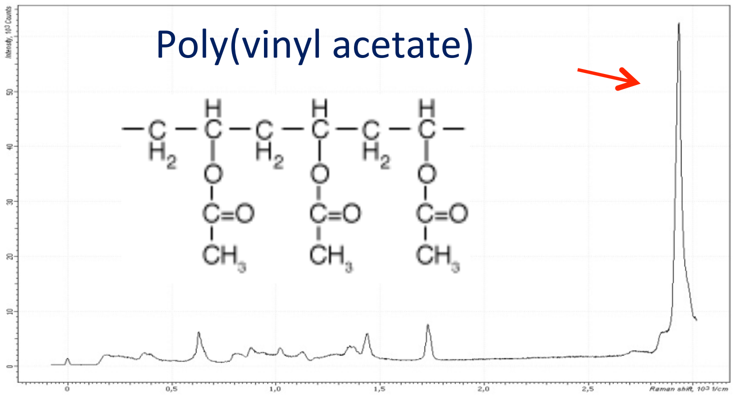
WAVELENGTH RANGE

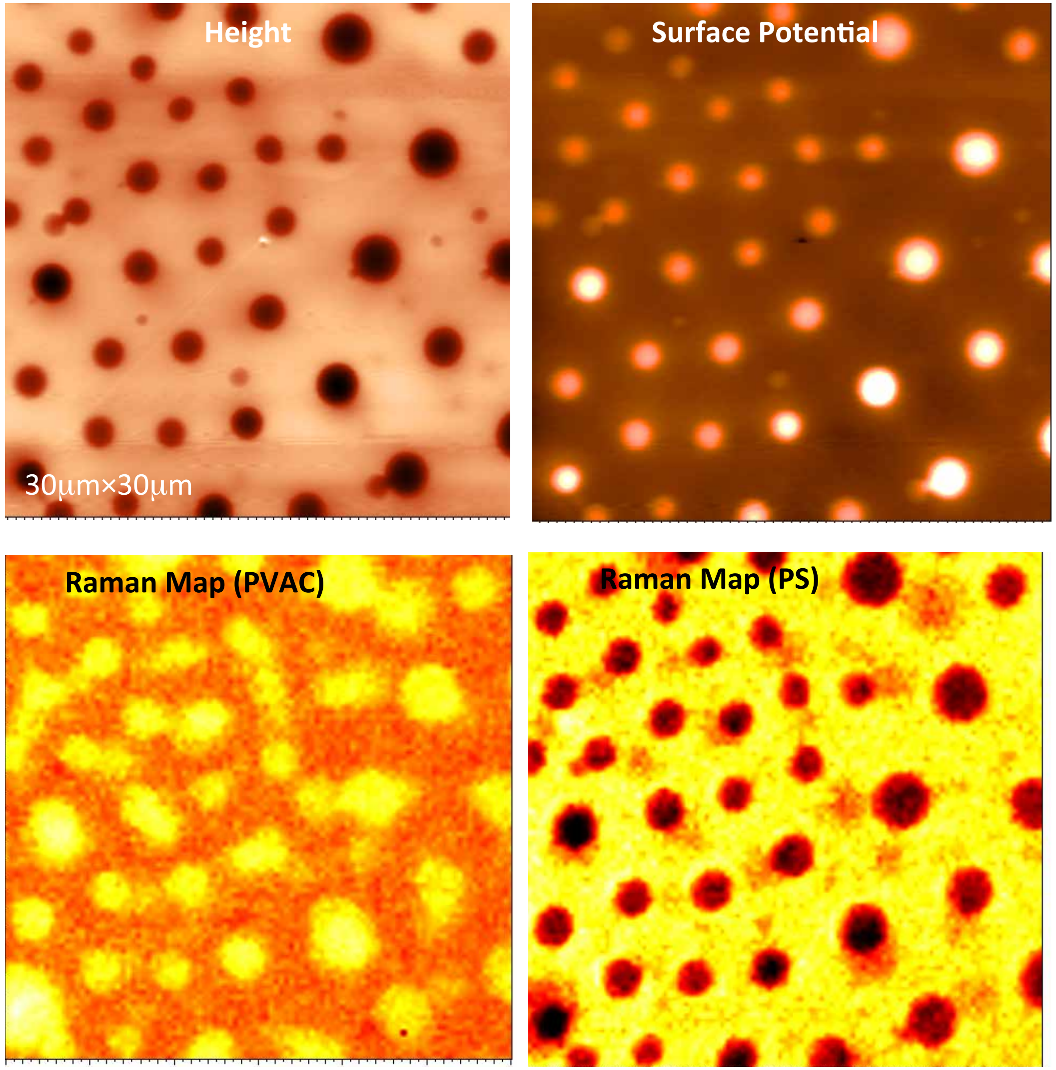
- UV, VIS, near-IR
- Mid- and Long- Infrared (1-20 μm)

KFM-Raman Studies of Polymer Blends

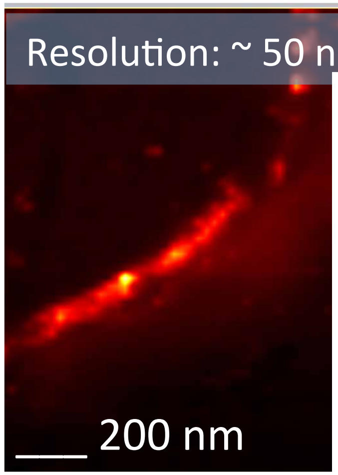
Polymer Blend PS-PVAC: Thick Film on ITO glass



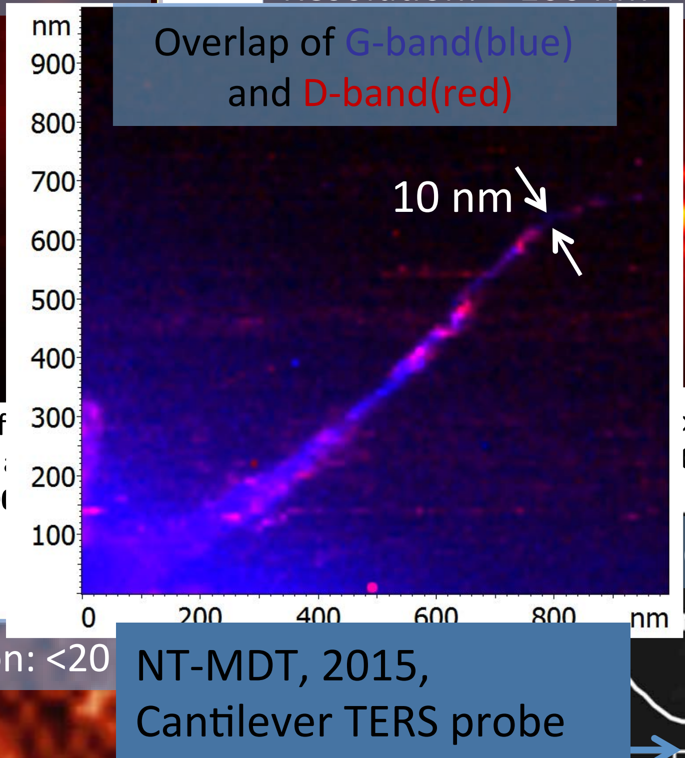


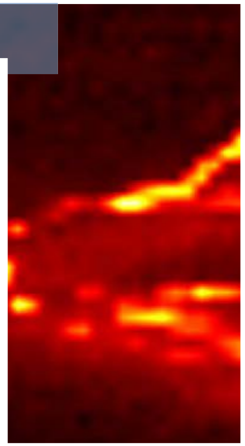


TERS on carbon nanotubes

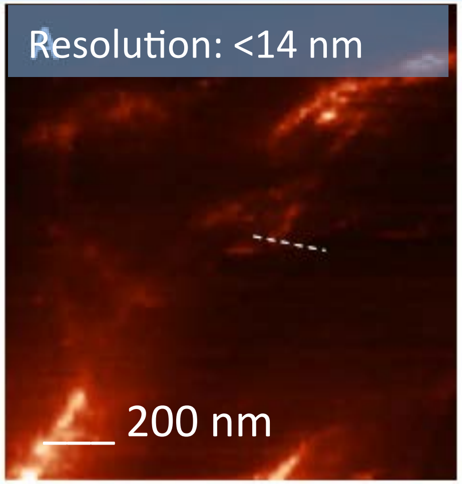


S.S. Kharintsev, G. Hoff
Dorozhkin, G. de With,
Nanotechnology 18 **(20**

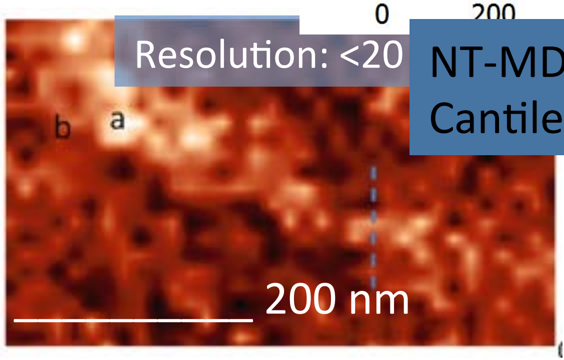




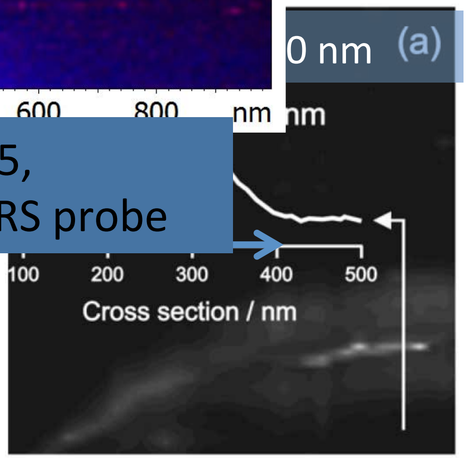
os, R. Zenobi
008)



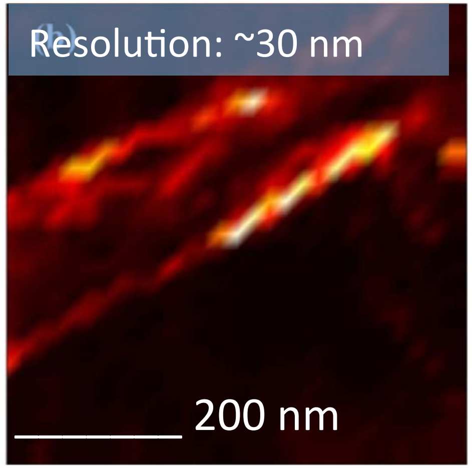
Chan K.L., Kazarian S.G., Nanotechnology 21, 445704 **(2010)**



Chan K.L., Kazarian S.G., Nanotechnology 22, 175701 **(2011)**

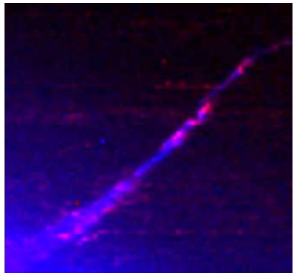


S. Kharintsev, G. Hoffmann, A. Fishman. & M. Salakhov J. Phys. D: Appl. Phys. 46 **(2013)** 145501

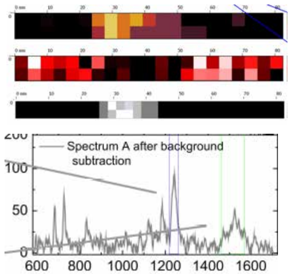


M. Zhang, J. Wang, Q. Tian, Optics Communications 315, 164 **(2014)**

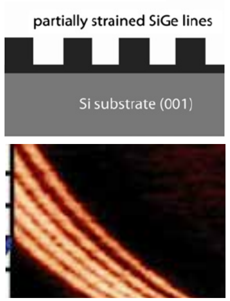
TERS results on various types of samples



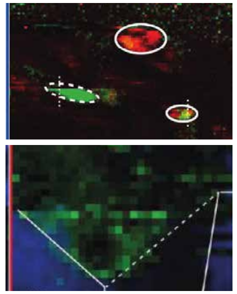
Carbon nanotubes
Resolution: ~10 nm
Nanotechnology, 2011
& ~10 other papers



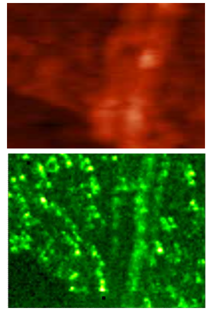
DNA molecule
Resolution: ~15 nm
Ang. Chem. Int., 2014,
E. Lipiec et. al



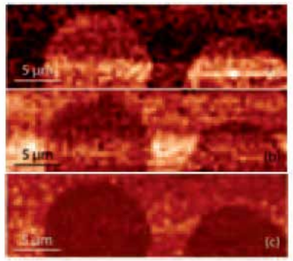
Si/SiGe structures
Resolution: <50 nm
Ultramicroscopy,
2010
P. Hermann et al.



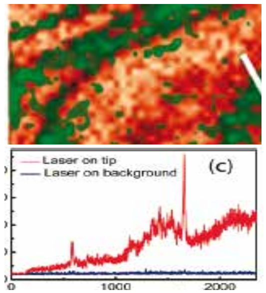
Graphene
Resolution: ~12 nm
ACS Nano, 2011
R. Zenobi et. al.



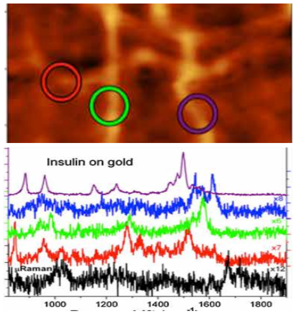
Graphene Oxide
Resolution: ~15 nm
A. Shelaev, et. al.,
2014



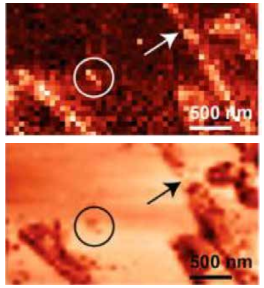
Thiol monolayers
Resolution: ~50 nm
Beilstein J. Nano, 2011
R. Zenobi et. al.



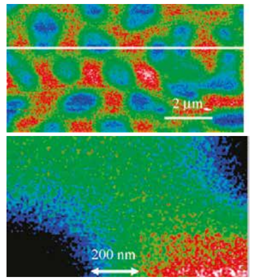
Thin molecular layers
Resolution: ~15 nm
NanoLett., 2010
R. Zenobi et. al.



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.

Overview of TERS (nano-Raman) results

TERS tips (nanoantennas)

- Ag, Au, Al etched wires
- Ag, Au - coated Si cantilevers
- Ag, Au - coated SiN, SiO cantilevers
- "Smart" probes (FIB processed): photonic crystal assisted plasmonic probes, etc.

AFM feedback regimes

- Non-contact (cantilevers)
- Contact (cantilevers)
- HybriD (cantilevers)
- Tunneling current (metal wires)
- Shear force tuning fork (metal wires)
- Normal force tuning fork (metal wires)

Illumination/detection geometries

- Top illumination/ top collection
- Bottom illumination/ bottom collection
- Side illumination / top collection
- Top illumination / bottom collection (and vice versa)

Laser wavelengths

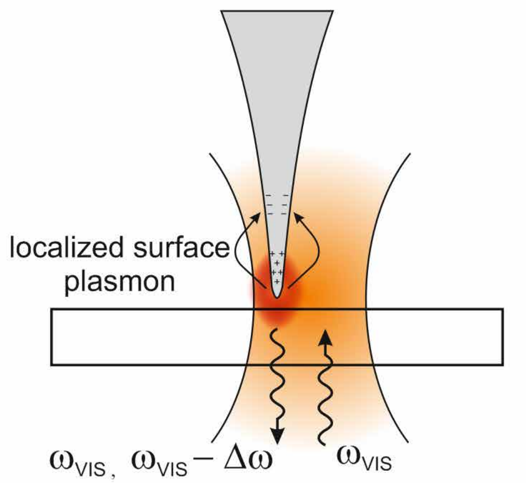
- 355 nm
- 473/488 nm
- 532 nm
- 633 nm

Samples (>15 types)

- **Carbon nanotubes, nanowires**
- **Graphene, Graphene Oxide**
- **Si, SiGe nanostructures (stress mapping)**
- **Polymers**
- **Thin organic layers (BCB, NB, phthalocyanine, fullerenes, thiol monolayers)**
- **Amyloid fibrils, peptide nanotapes, lipid monolayers**
- **Individual DNA molecules**

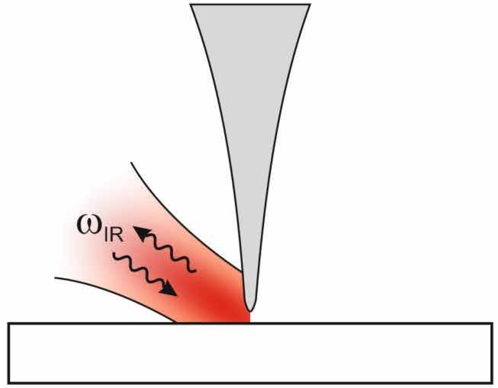
In most of experiments: high resolution 2D TERS mapping

Super-resolution imaging using scanning optical antennas



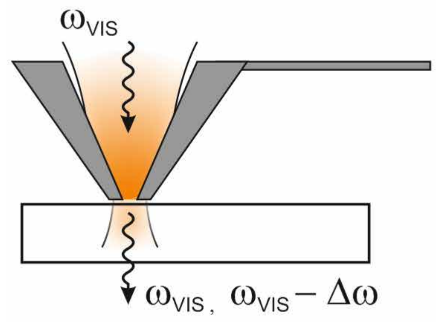
Tip enhanced near-field optical microscopy

Light localization and enhancement by localized surface plasmon



Apertureless (scattering) scanning near-field optical microscopy (s-SNOM); nano-IR

Infrared (& Vis) light scattering by non-resonant antenna

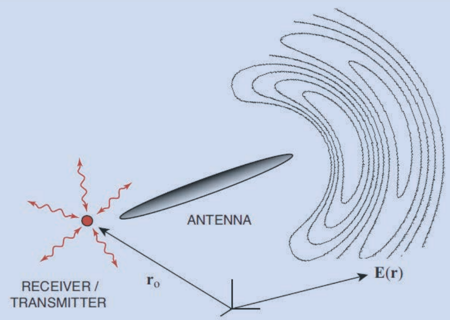


Aperture scanning near-field optical microscopy (SNOM)

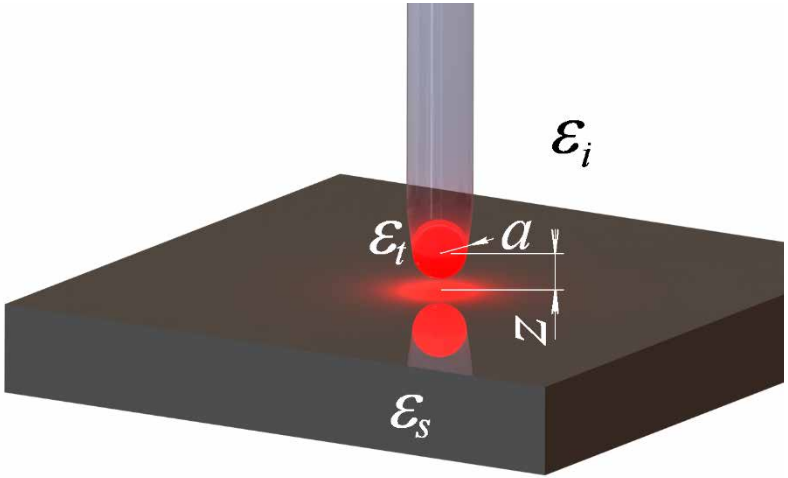
Light transmission through non-resonant subwavelength aperture

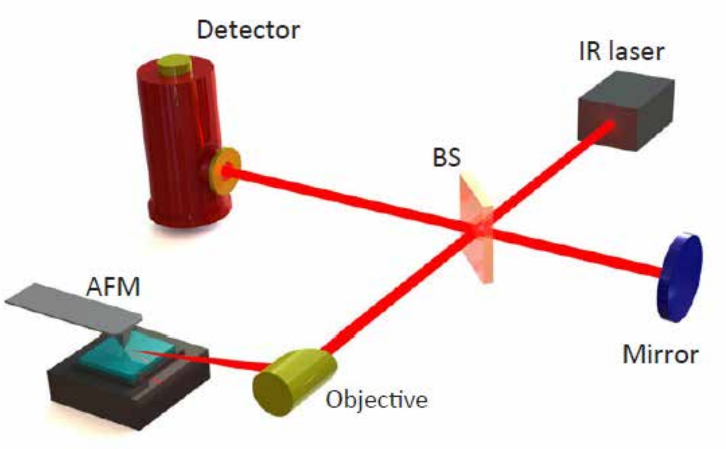
Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa.

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



s-SNOM Physical Principles





NTEGRA IR principal scheme

$$E_{scatt} \approx E_{loc}\alpha_{eff}$$

$$\alpha_{eff} = \frac{\alpha(1-\beta)}{1 - \frac{\alpha\beta}{32\pi(z+a)^3}}$$

$$\beta = \frac{\varepsilon_s - 1}{\varepsilon_s + 1}$$

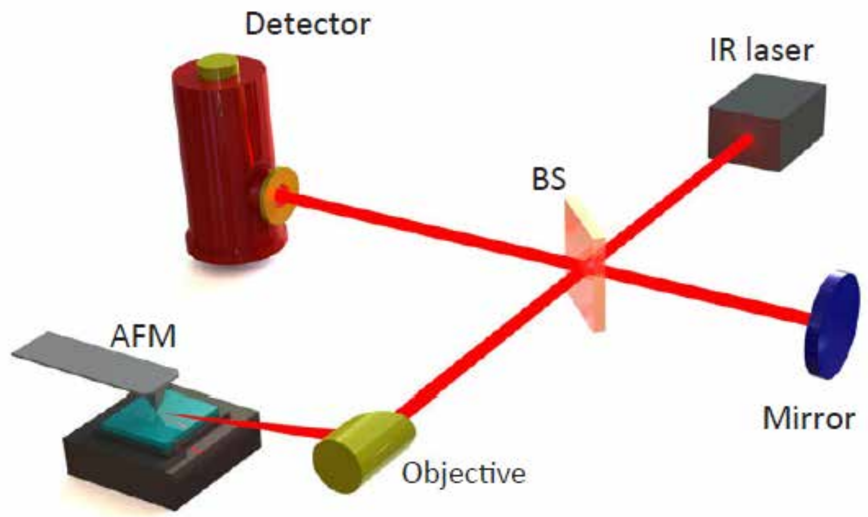
$$\alpha = 4\pi a^3 \frac{\varepsilon_t - \varepsilon_i}{\varepsilon_t + 2\varepsilon_i}$$

IR vibrational microscopy and spectroscopy

There are two approaches to integration of IR micro-/ spectroscopy and AFM:

- By measuring mechanical/electrical/thermal/etc. response of AFM cantilever to IR radiation
- By measuring the scattered IR radiation with Michelson interferometer and/or Fourier spectrometer (s-SNOM)

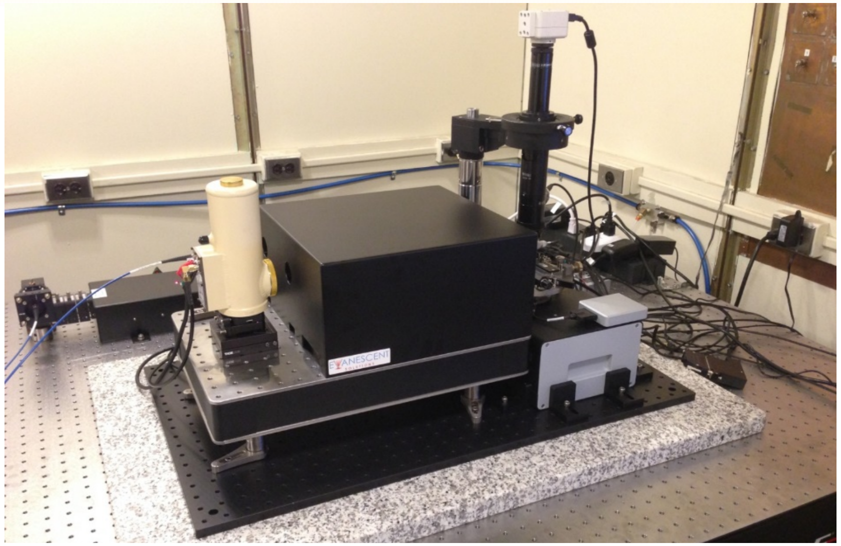
NTEGRA Nano IR: IR s-SNOM measurements



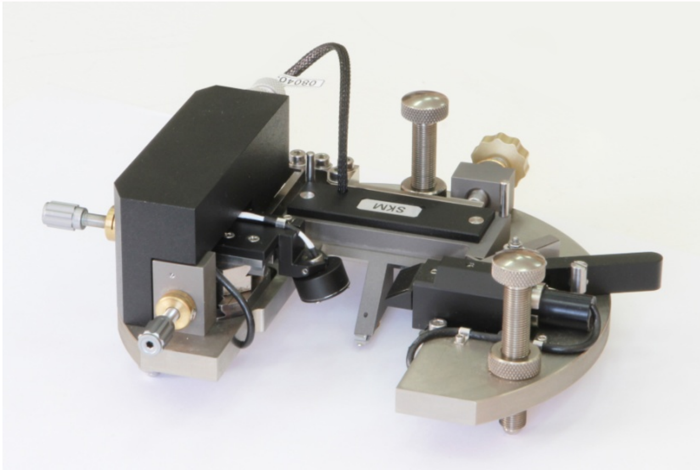
NTEGRA IR principal scheme

- IR s-SNOM microscopy and spectroscopy with 10 nm spatial resolution
- Wide spectral range of operation: 3-12 µm
- Incredibly low thermal drift and high signal stability
- Versatile AFM with advanced modes: SRI (conductivity), KPFM (surface potential), SCM (capacitance), MFM (magnetic properties), PFM (piezoelectric forces)
- HybriD Mode™ - quantitative nanomechanical mapping
- Integration with microRaman (optional)

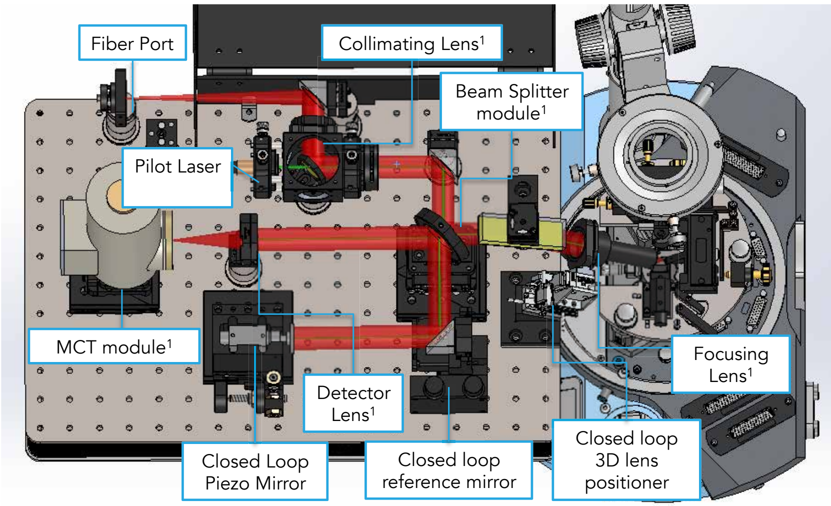
NTEGRA Nano IR

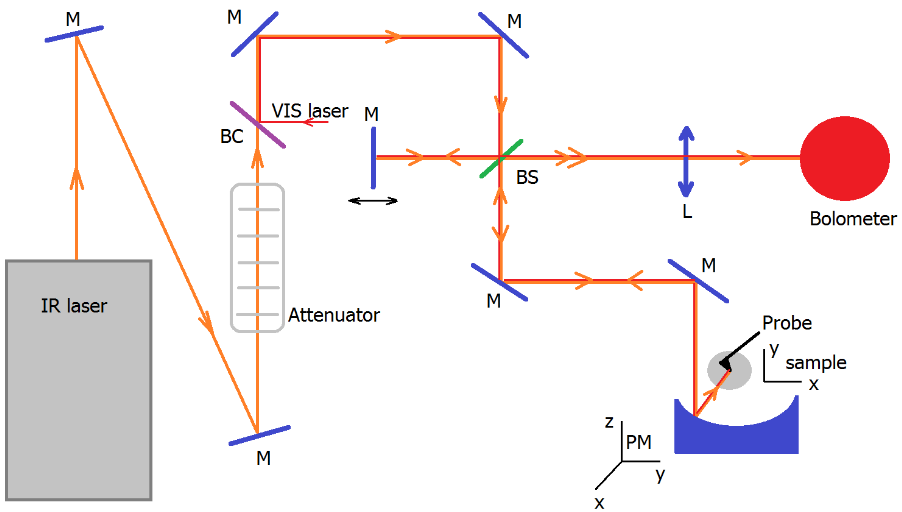


NTEGRA Nano IR, **Stony Brook Univ., NY, USA**



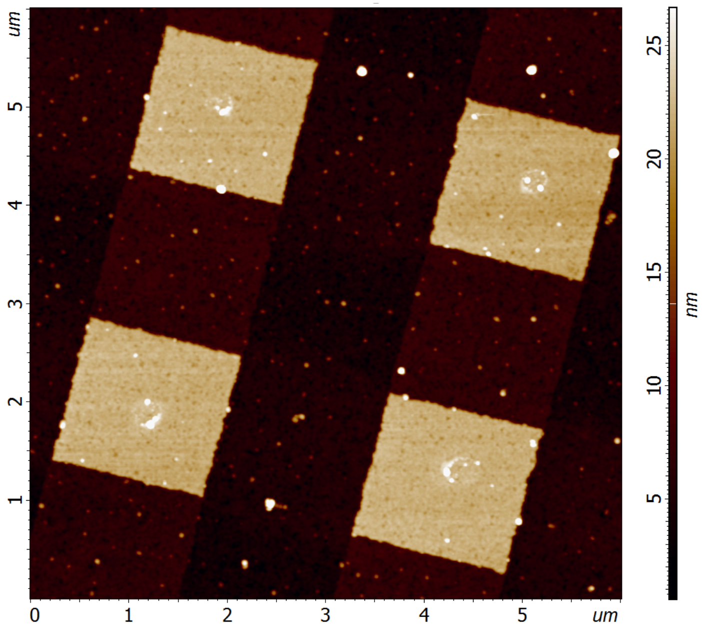
Measuring head

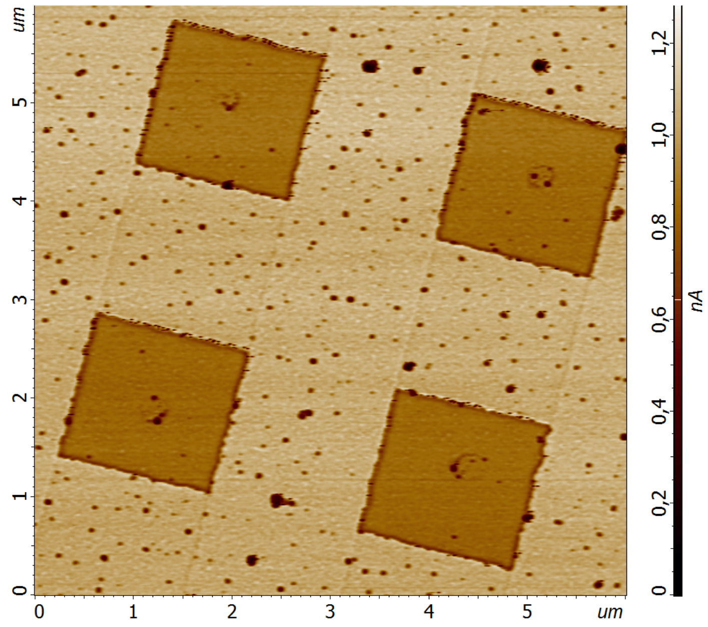


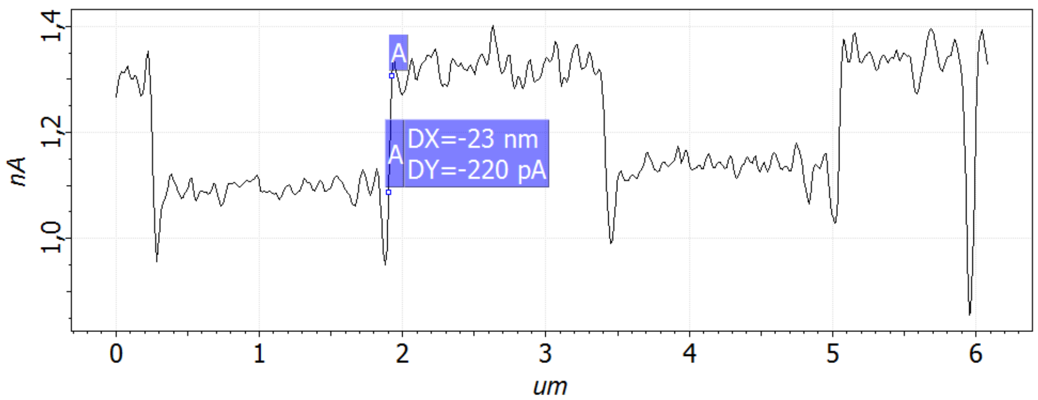


Optical schemes

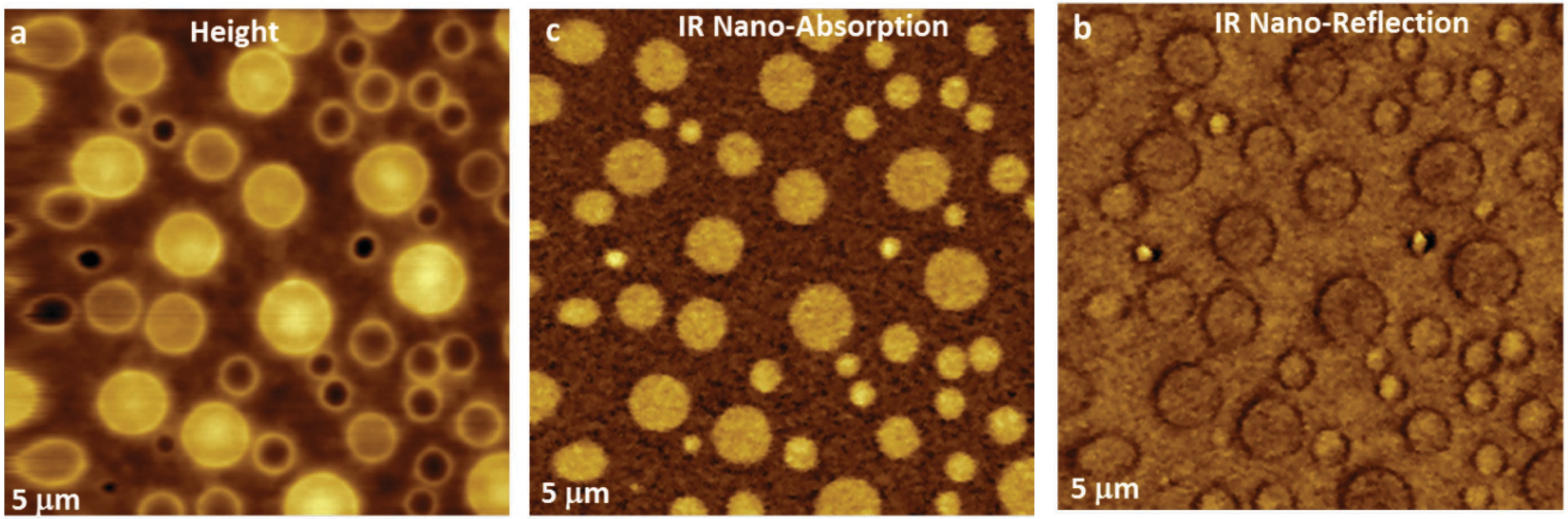
Si/SiO_2 Calibration Grating





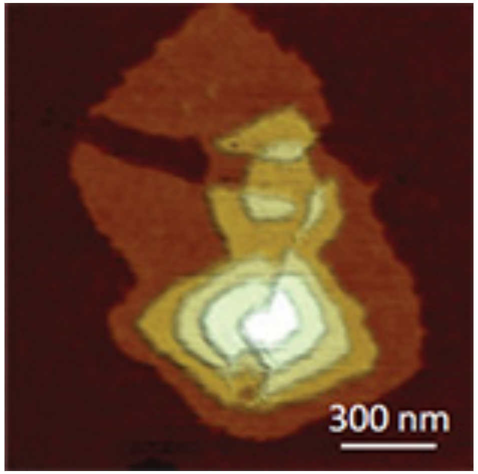


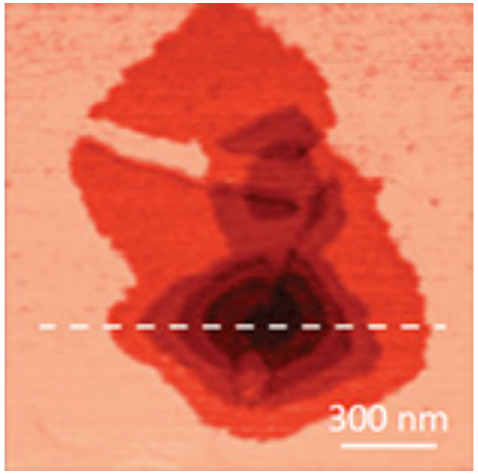
Thin layer of PS/PVAC polymer blend on ITO

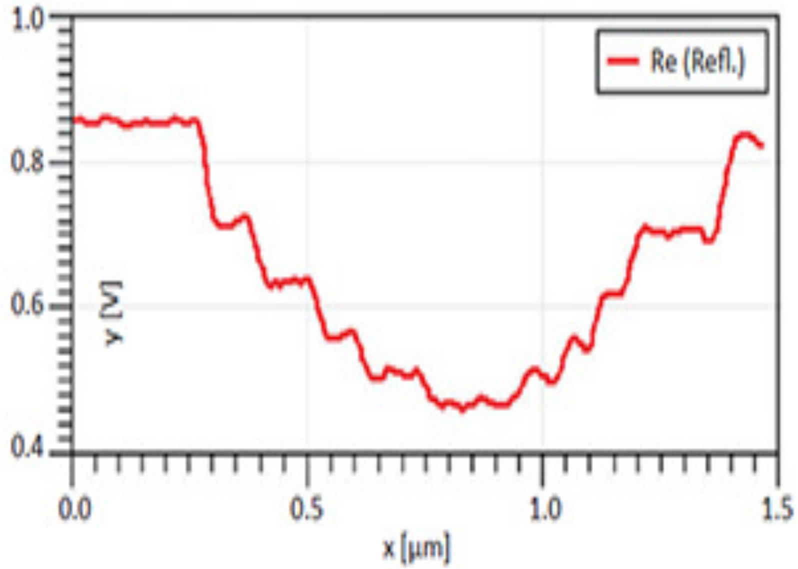


Height (a), nano-reflection (λ = 10.6 mm), (b) and nano-absorption (λ = 10.6 mm) (c) images of a PS/PVAC film on ITO substrate.

Ultrathin films: oligothiophene monolayers on silicon







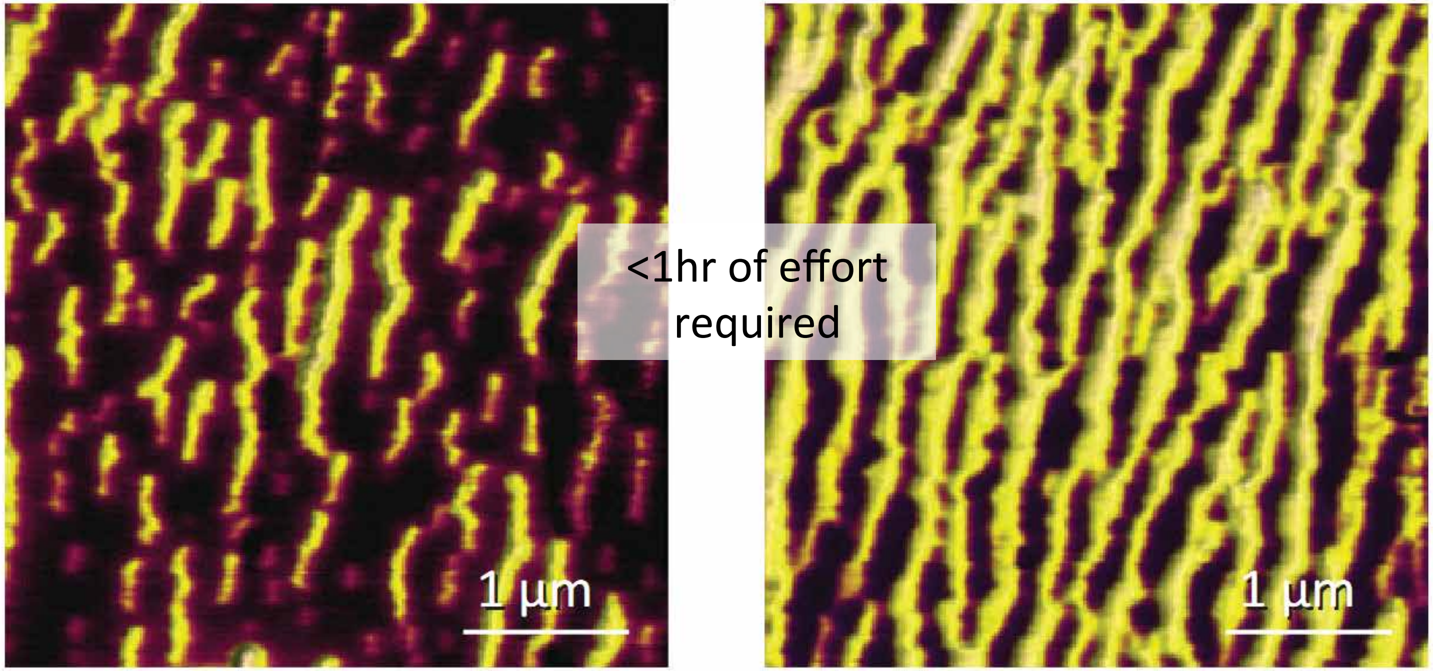
IR reflection contrast of thin and soft structures easily detectable. Each of five 3.4 nm steps is resolved. Spatial resolution is better than λ/1000.

Sample courtesy to Dr. A. Mourran (DWI, Aachen, Germany). Measured by Dr. G. Andreev (EVS Co)

High Temperature AFM and sSNOM on a phase changing material: VO2

IR sSNOM Reflection

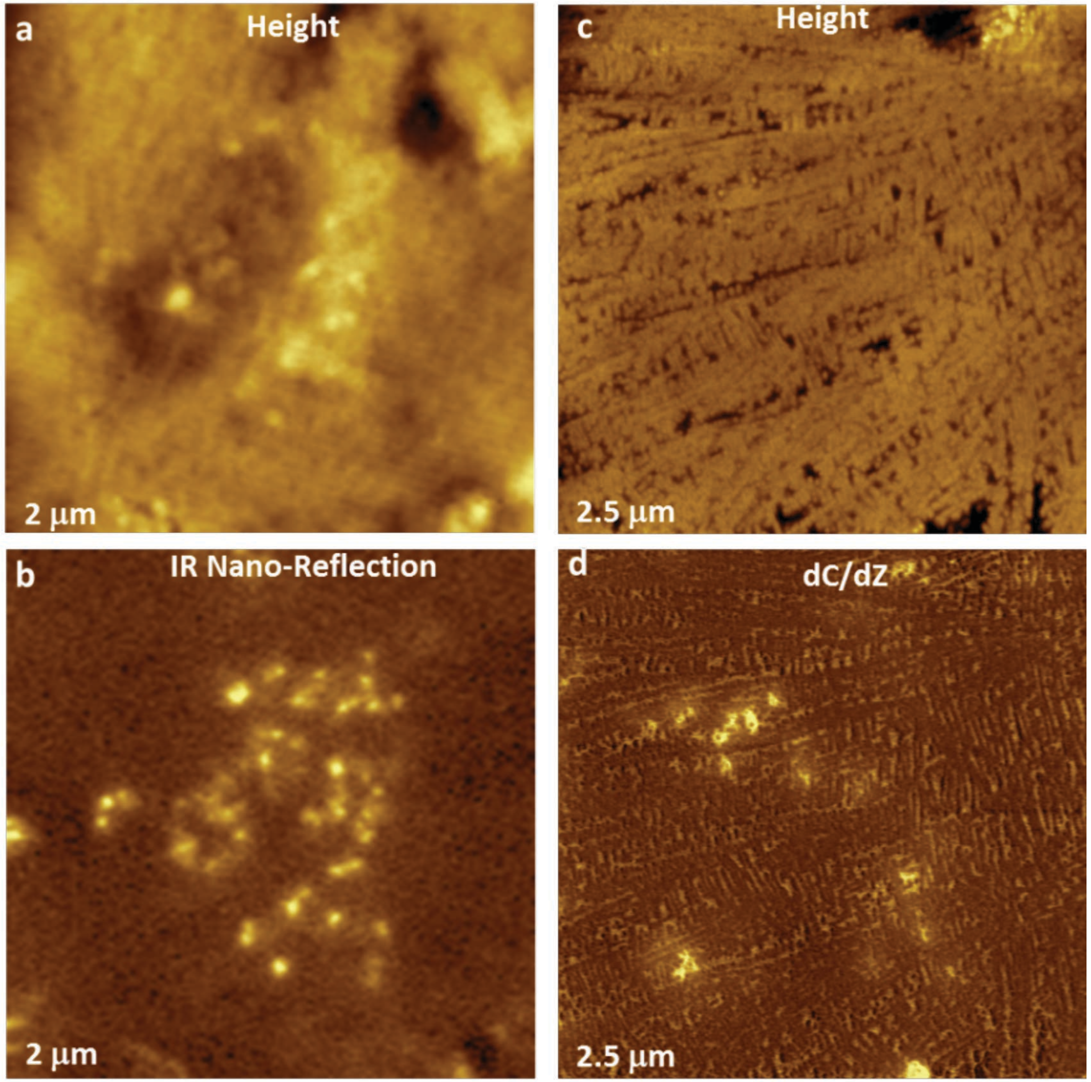
27C 67C



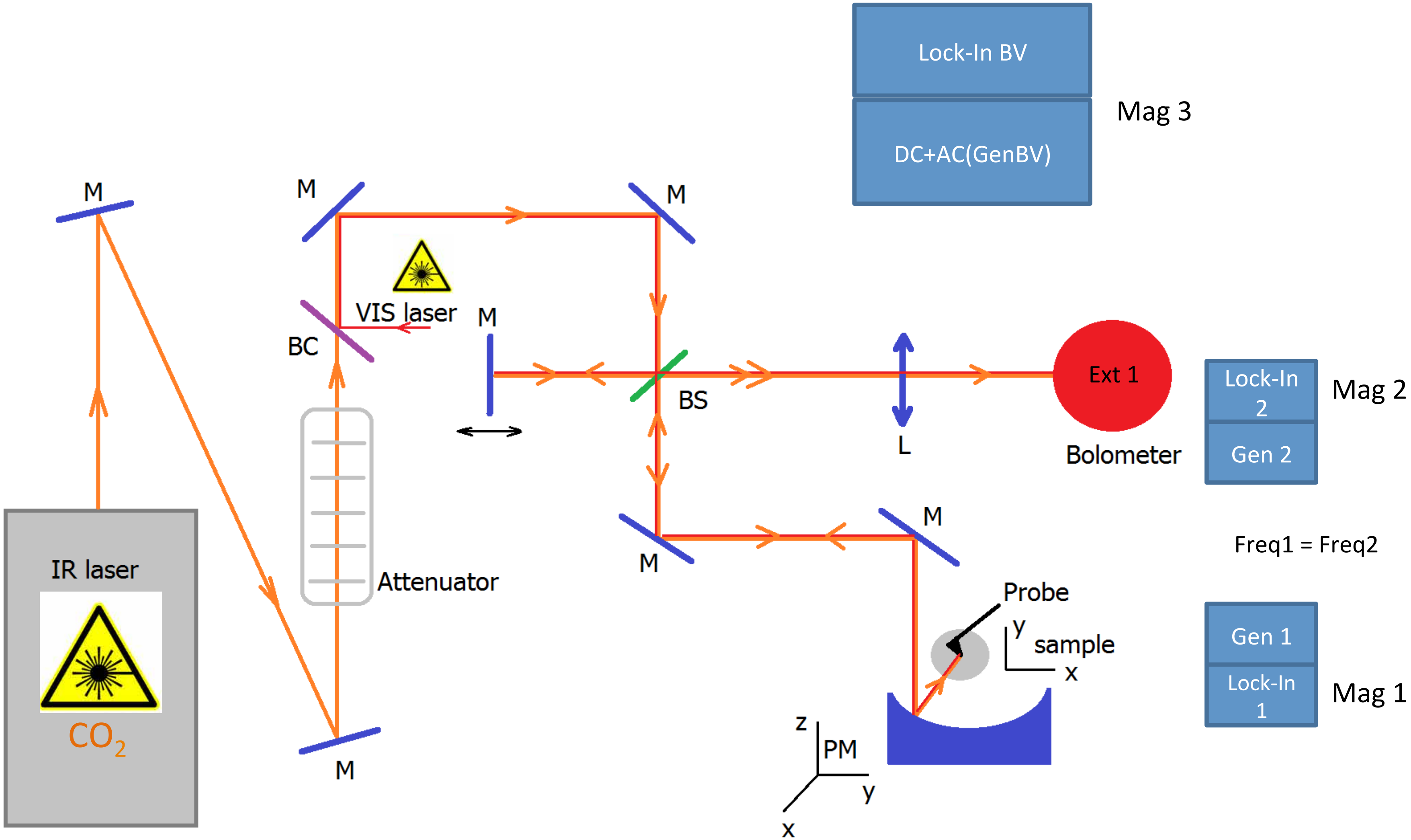
- Superior high temperature performance: under 1 hour needed to acquire images 40C apart. Compare to days on competitor’s system
- Low drift and high signal stability: <1um XY drift from 27 to 67C, no realignment of nanoReflection optics needed

Sample courtesy to prof. Liu (Stony Brook University, New York, USA)

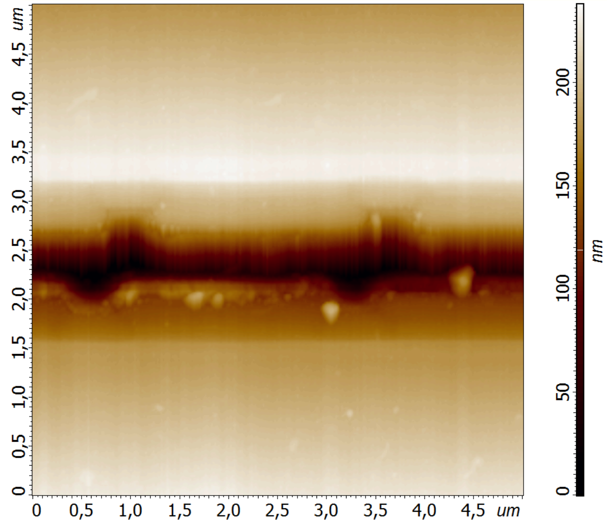
AFM/IR measurements of thermoplastic vulcanizate (TPV)



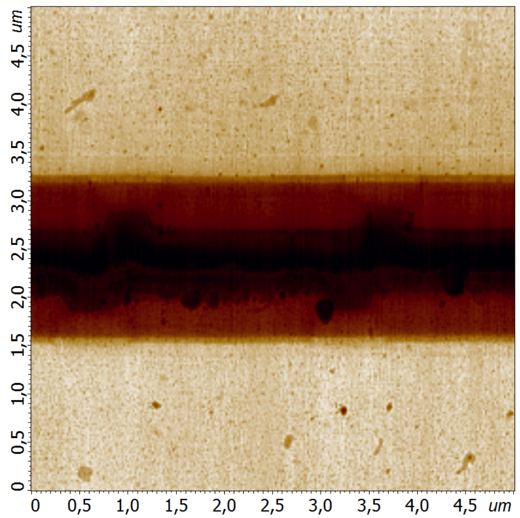
NTEGRA Nano IR: Phase locked homodyne mode



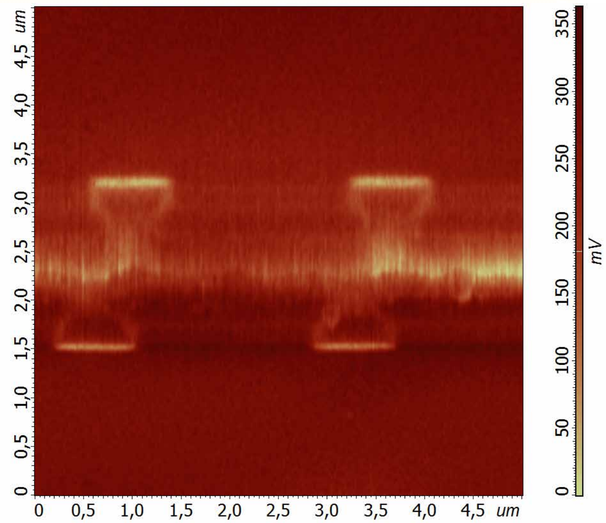
Semiconductor structure mapping



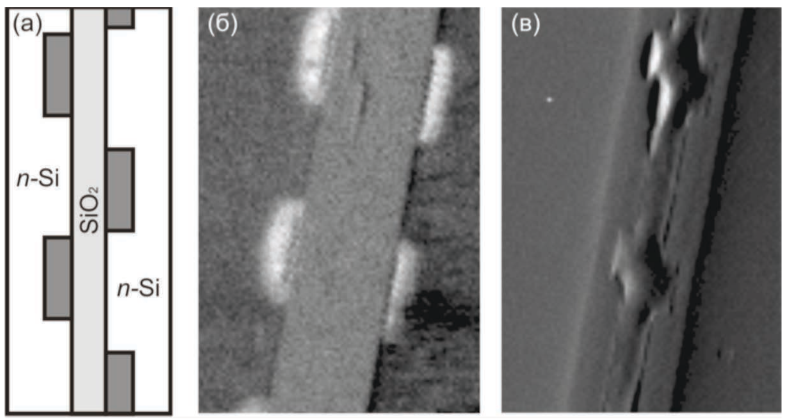
AFM topography



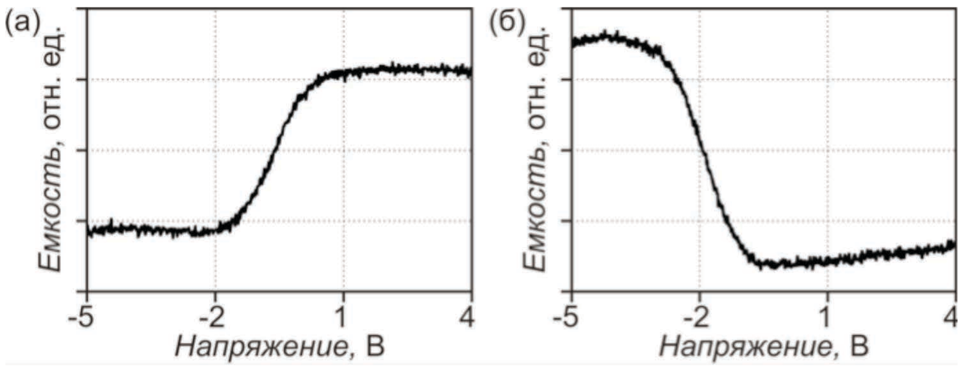
s-SNOM signal, Amplitude



s-SNOM signal, Phase



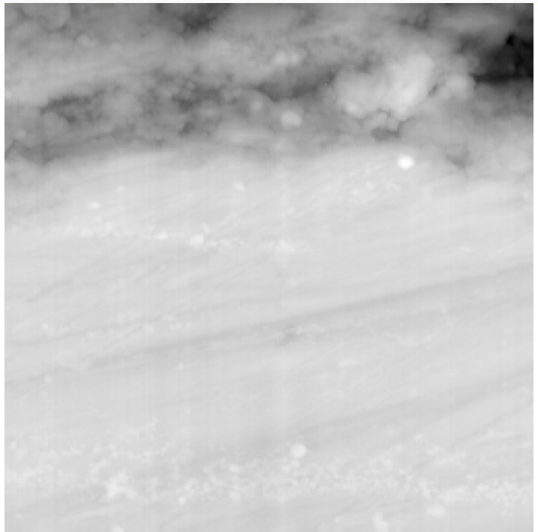
(a) – sample structure, (б) – capacitance contrast dC/dV, (в) – topography (*measured separately*)
Scan size 3.5x5 um



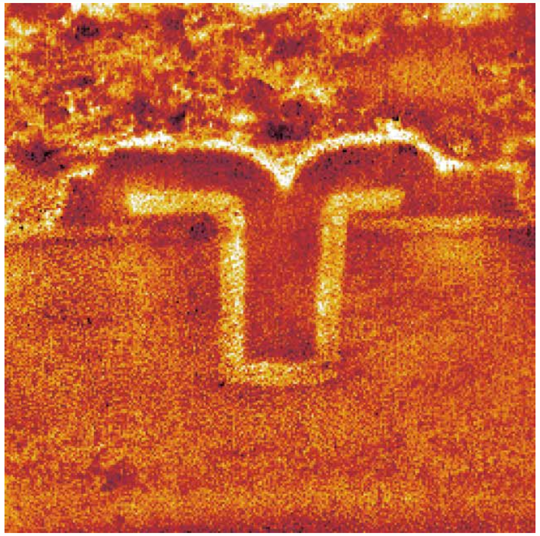
C-V curves measured on the wafer (right) and in the doped region (left)

Sample: two cleavages of diffraction grating clued together. Grating of n-type Si was doped with BF2 ions p=10^20

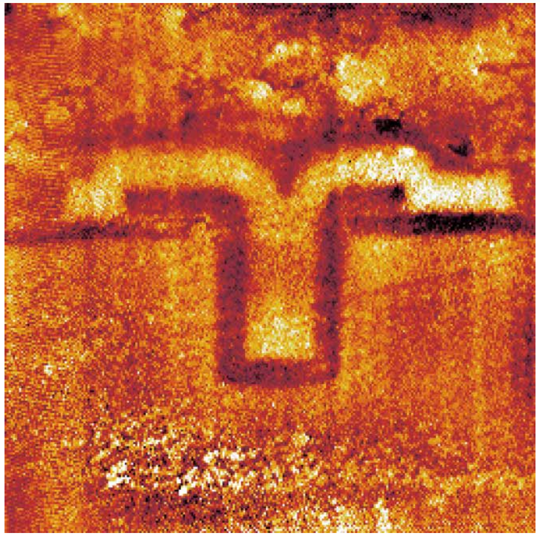
MOS Transistor mapping



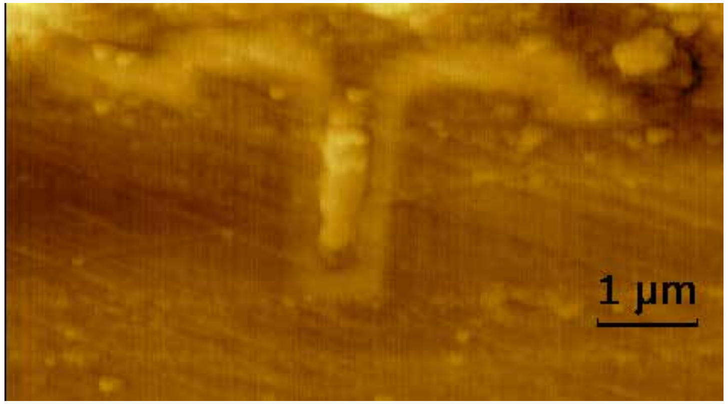
AFM topography



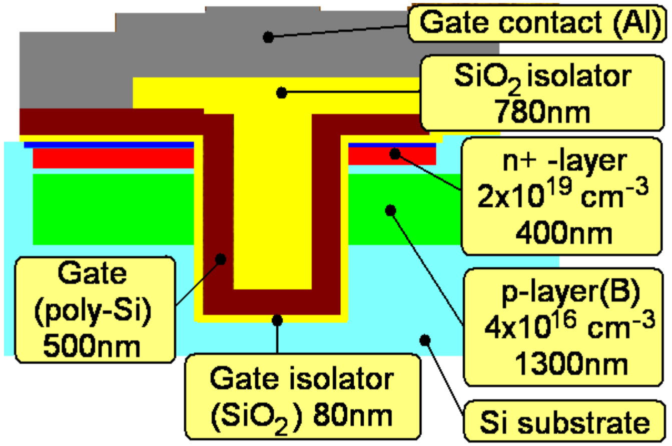
s-SNOM signal, Amplitude



s-SNOM signal, Phase

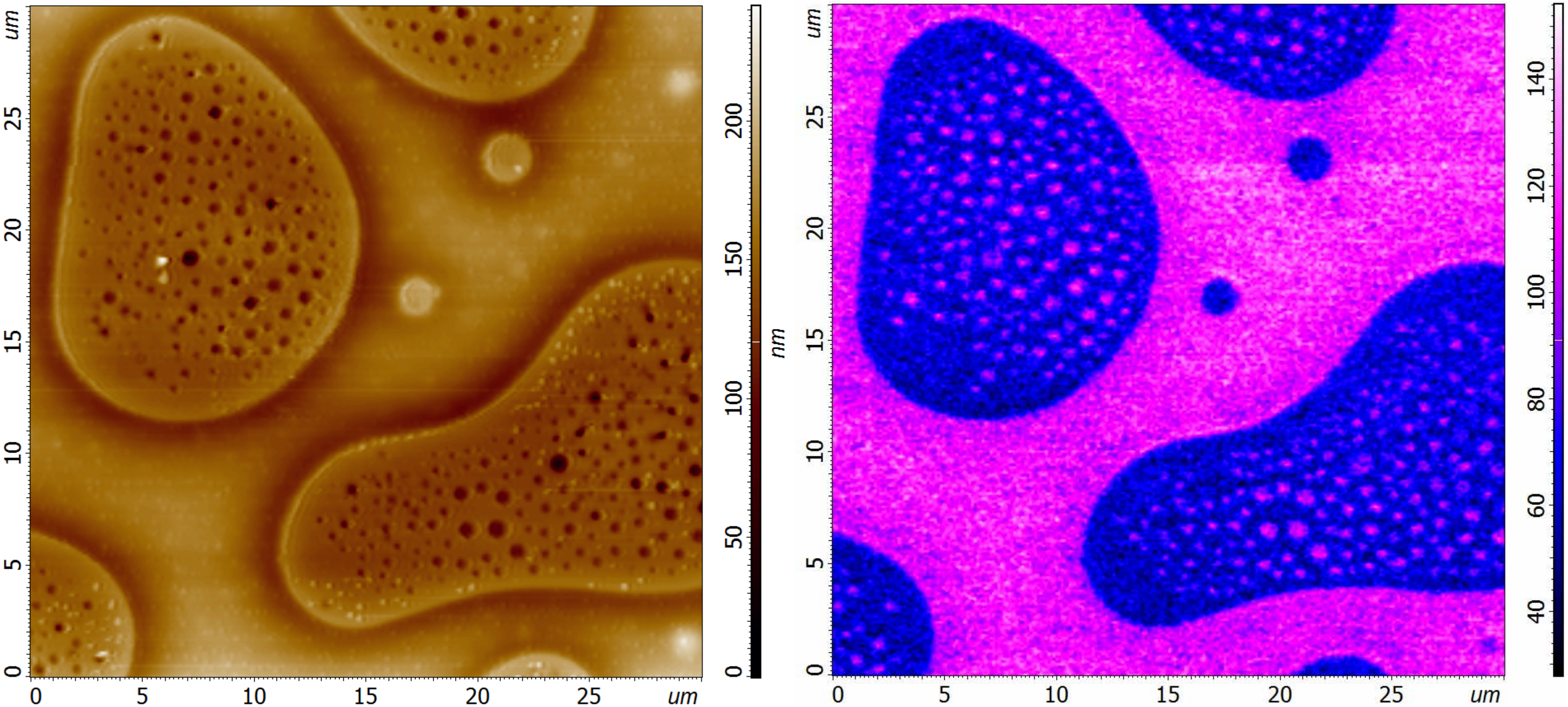


Kelvin probe microscopy, surface potential
(*measured separately*)



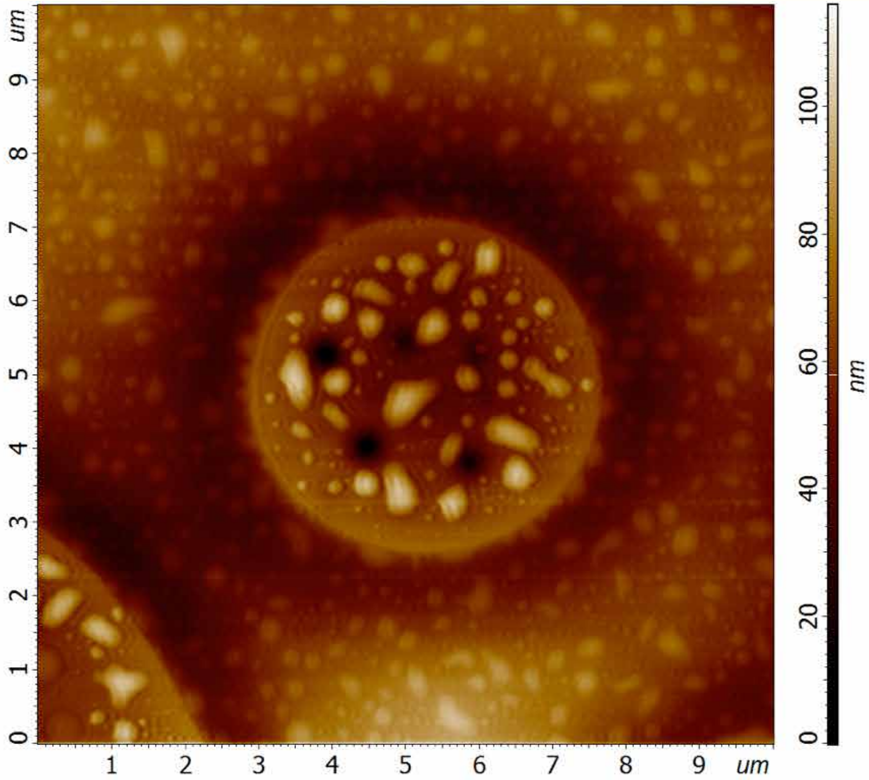
Sample: Si trench defined MOS transistor. Excitation laser: 10.8 µm (923 cm^{-1}). Image size: 10x10 µm
Measurement mode: s-SNOM optical signal (Amplitude and Phase) by interferometric homodyning. Measured by D. Kazantsev

IR thermal expansion response – AFM IR

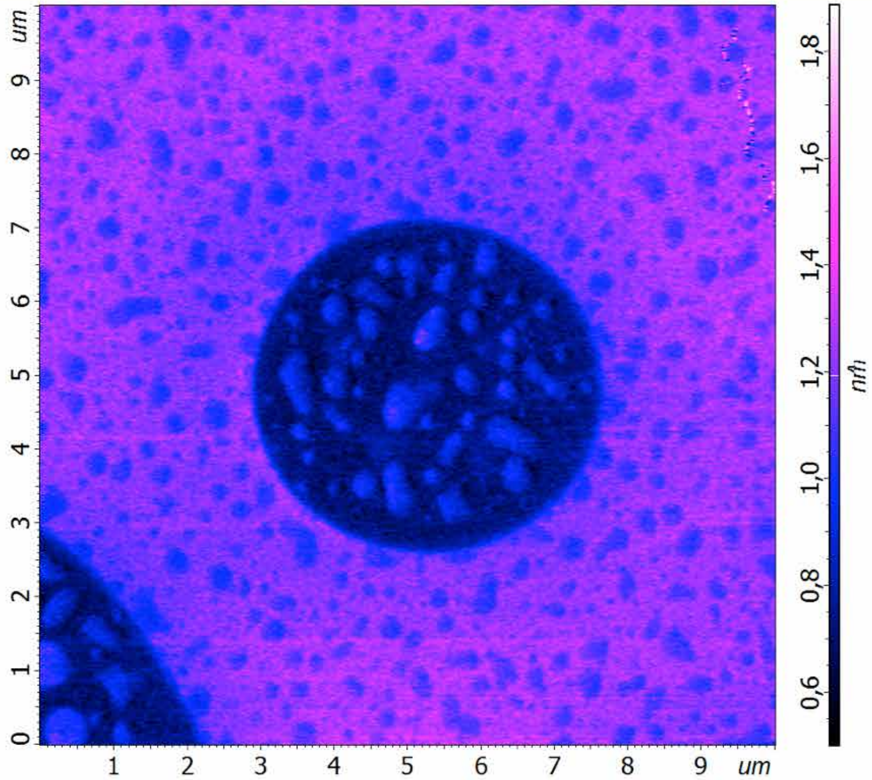


Sample: PS/PVAC. Excitation laser: 10.8 μm (923 cm^{-1}). Image size: 10x10 μm

IR thermal expansion response – AFM IR



AFM topography



AFM IR response

Sample: PS/PVAC. Excitation laser: 10.8 µm (923 cm^{-1}). Image size: 10x10 µm

Conclusions

- Combination of AFM with IR microscopy/spectroscopy opens the prospective way for chemical analysis of samples with nanometer spatial resolution
- We are AFM company and we have low drift low noise AFM with wide range of AFM techniques
- We offer the only solution which is able to integrate sSNOM IR and Raman

Thank you!

Questions?