



Nanoscale IR Microscopy and Spectroscopy

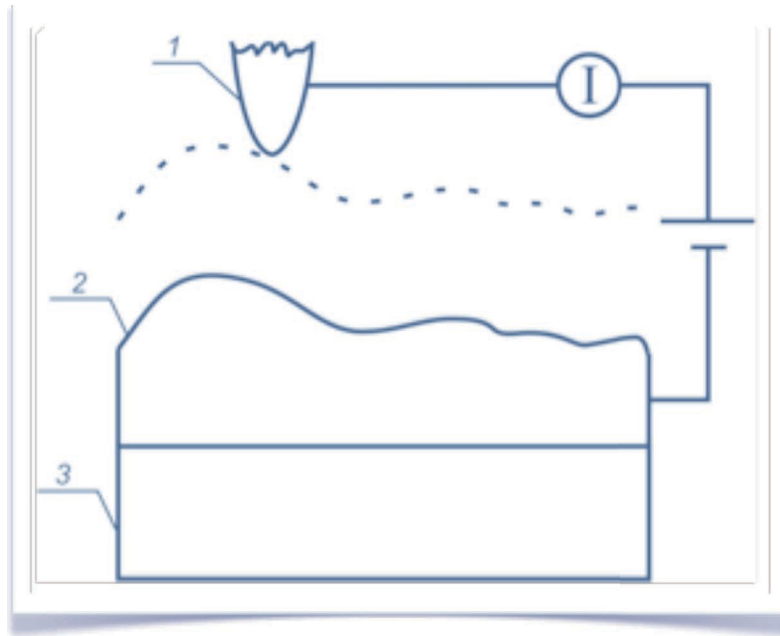
V.V. Polyakov¹, A.V. Shelaev¹

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

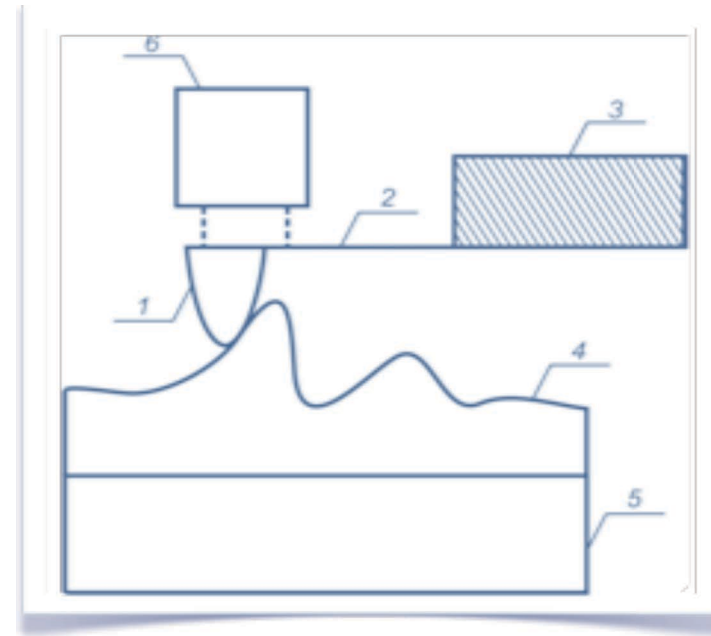
Agenda

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

SPM history and background

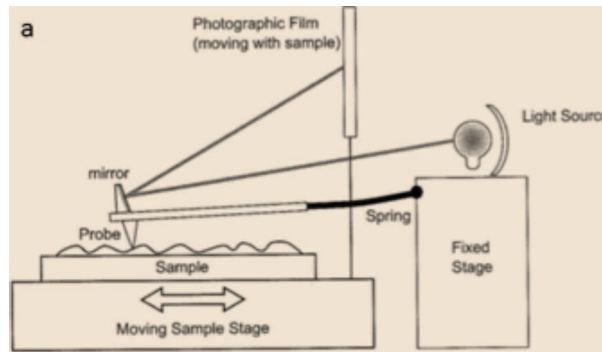


Scanning tunneling microscope:
1 - tip, 2 – conductive sample, 3 - scanner



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

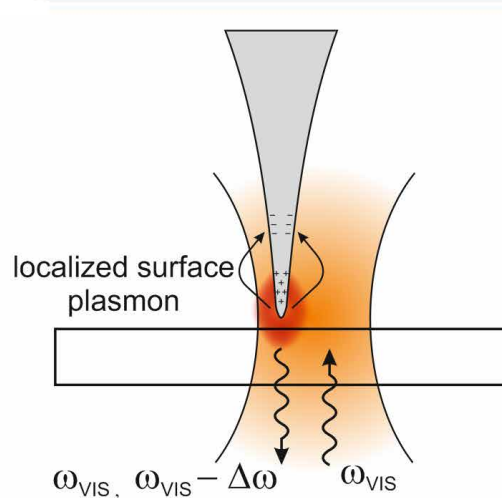
and

Ch. Gerber^(c)

IBM San Jose Research Laboratory, San Jose, California 95193

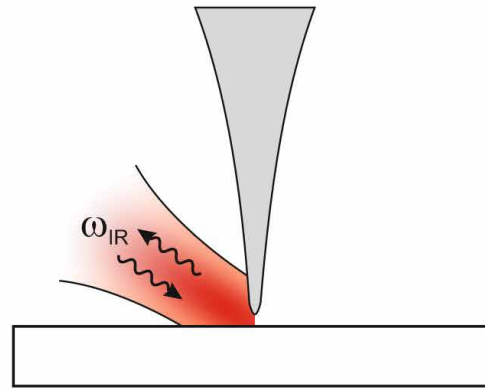
(Received 5 December 1985)

Super-resolution imaging using scanning optical antennas



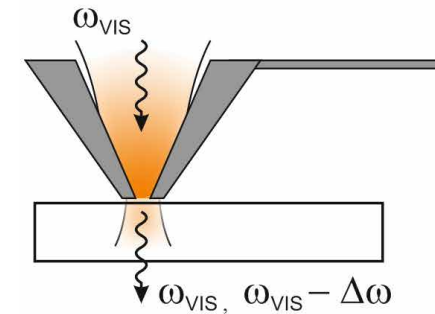
Tip enhanced near-field optical microscopy

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

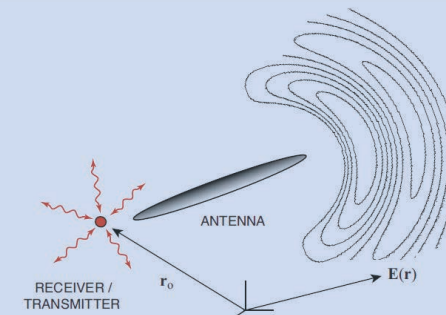


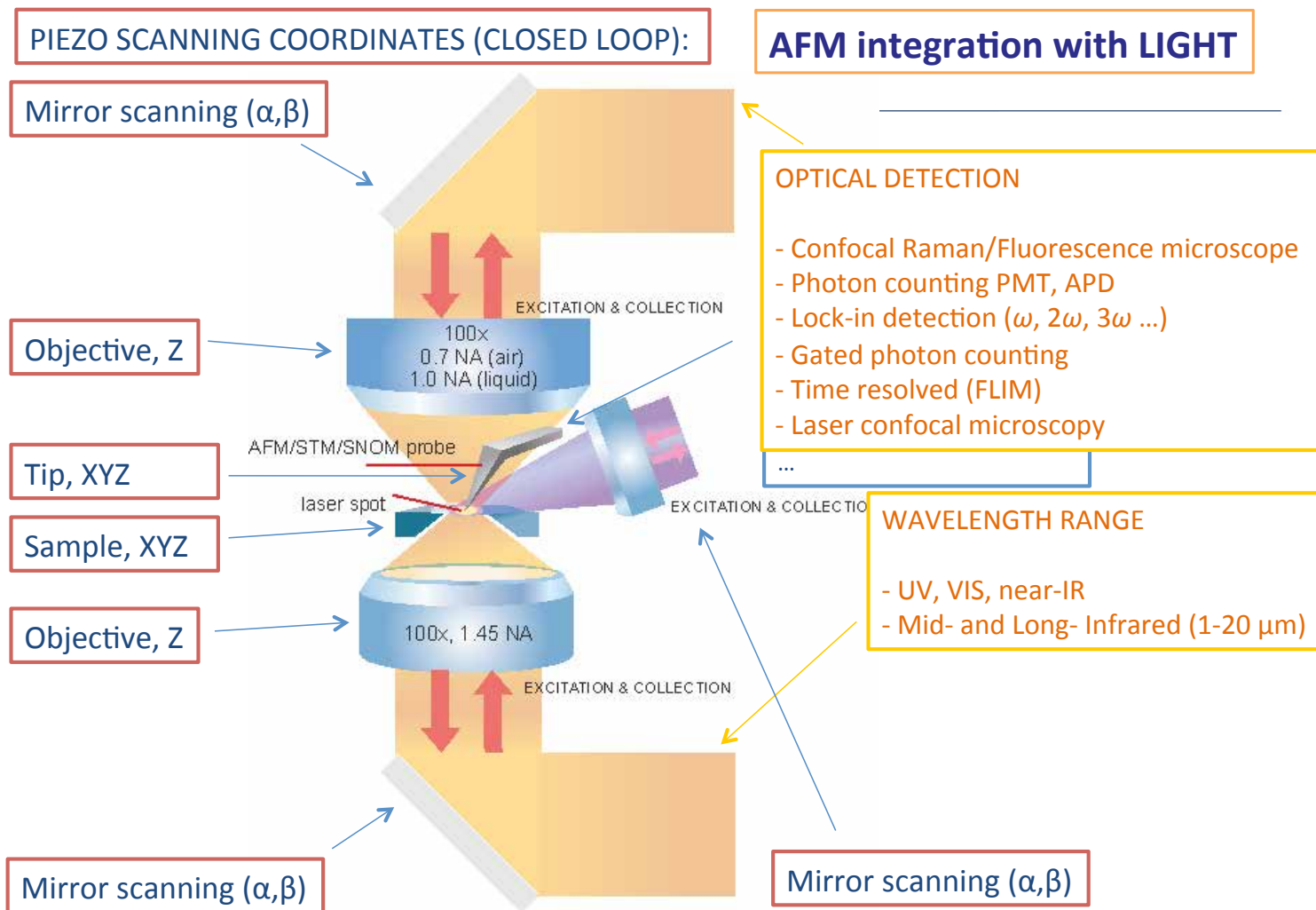
Aperture scanning near-field optical microscopy (SNOM)

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.

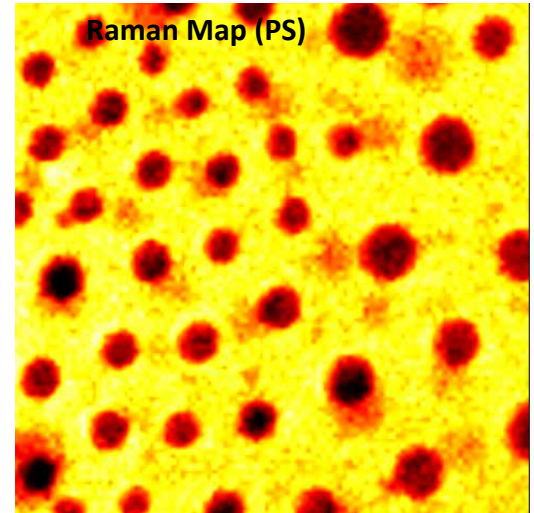
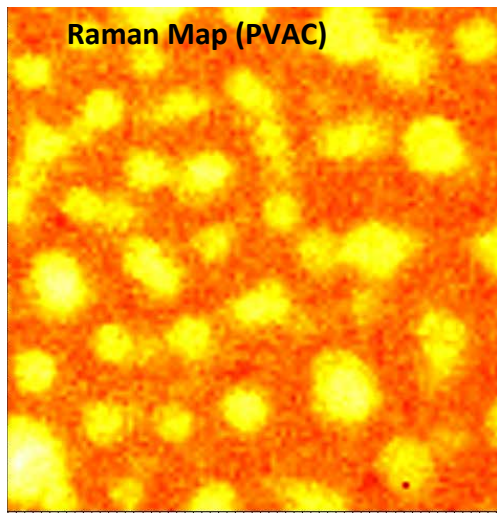
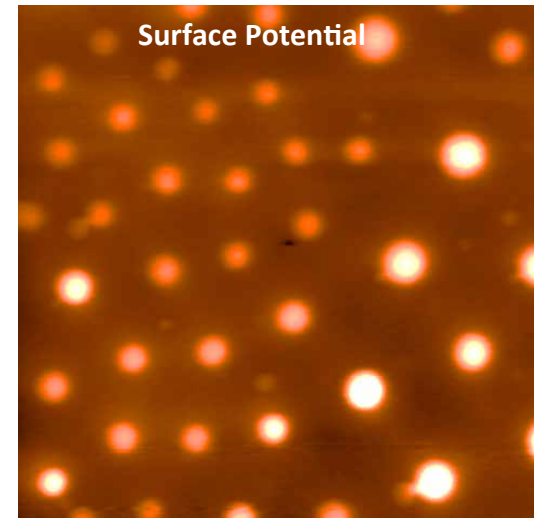
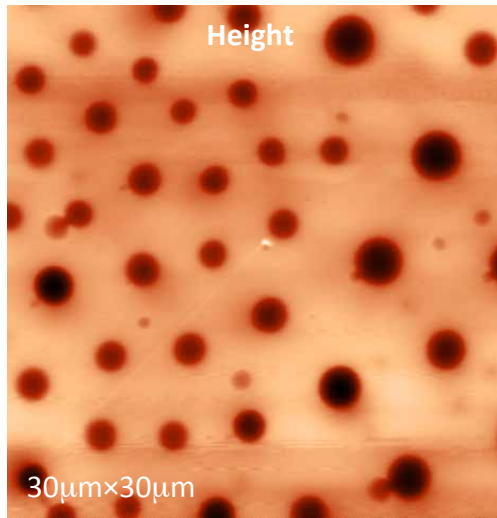
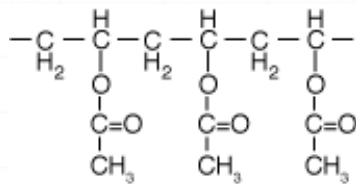
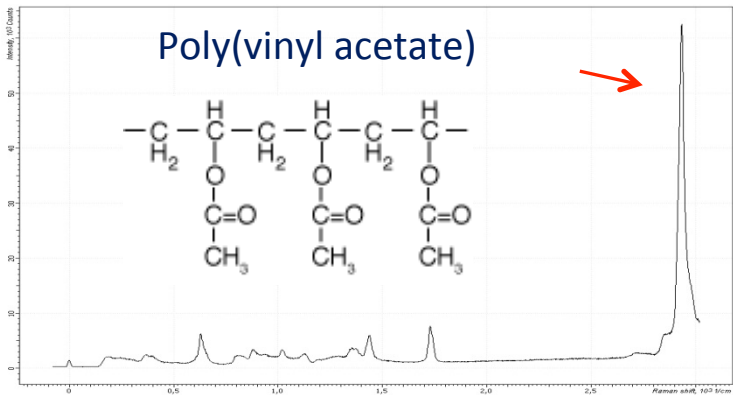
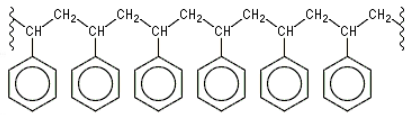
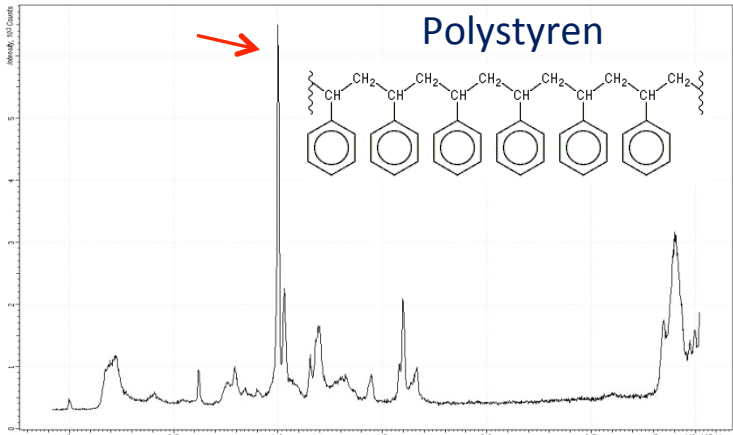
- L. Novotny, N. van Hulst, *Nature photonics* 5, 89 (2011)
- P. Bharadwaj, B. Deutch, L. Novotny, *Adv. In Opt. Phot.* 1, 438 (2009)
- Pohl D. W., *Optics, Principles and Applications* (World Scientific, 2000).



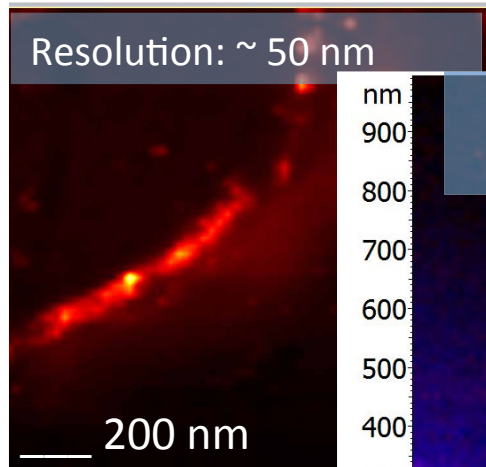


KFM-Raman Studies of Polymer Blends

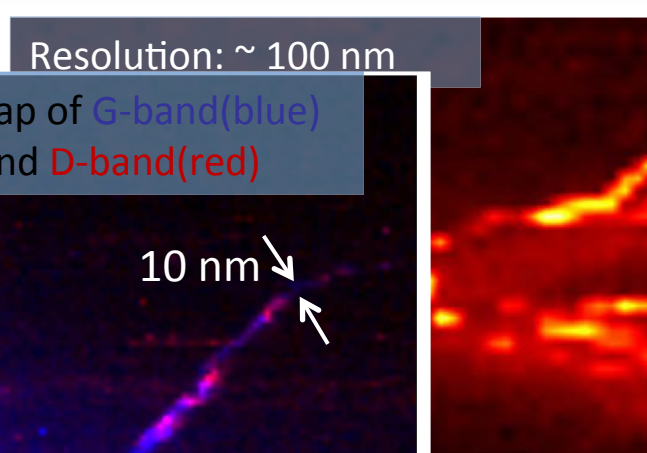
Polymer Blend PS-PVAC: Thick Film on ITO glass



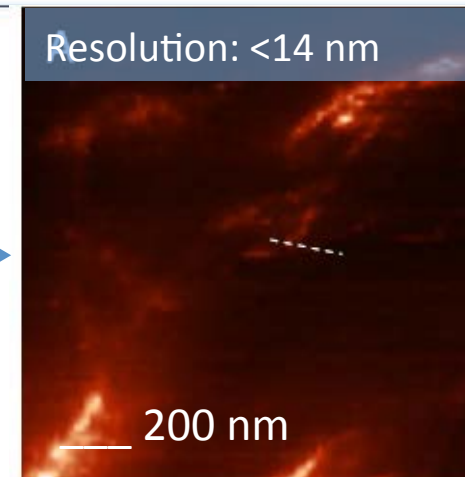
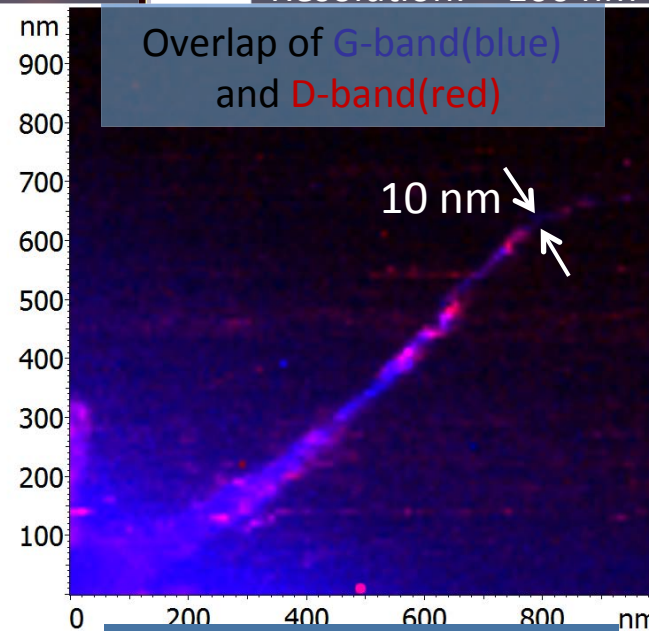
TERS on carbon nanotubes



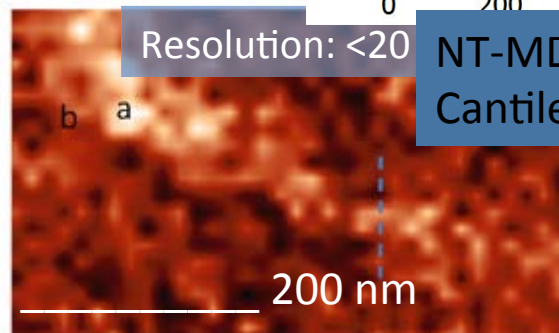
S.S. Kharintsev, G. Hoffmann, G. Dorozhkin, G. de With, Nanotechnology 18 (2007) 175701



Yos, R. Zenobi (2008)

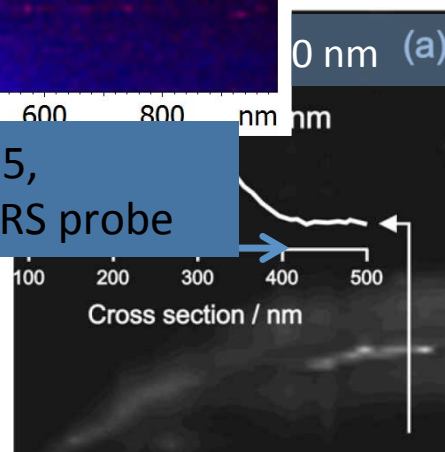


Chan K.L., Kazarian S.G., Nanotechnology 21, 445704 (2010)

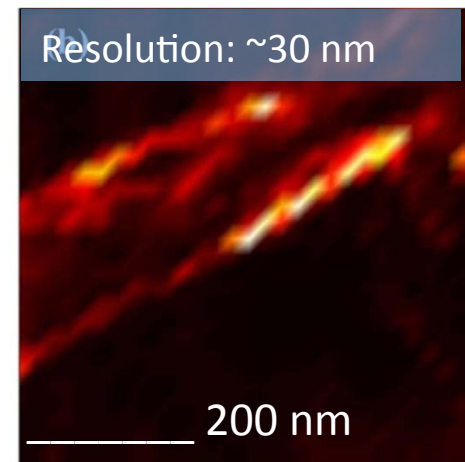


Chan K.L., Kazarian S.G., Nanotechnology 22, 175701 (2011)

NT-MDT, 2015, Cantilever TERS probe

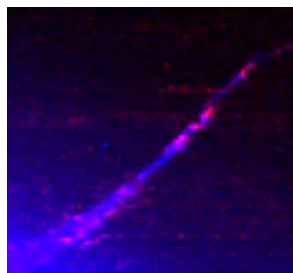


S. Kharintsev, G. Hoffmann, A. Fishman. & M. Salakhov J. Phys. D: Appl. Phys. 46 (2013) 145501

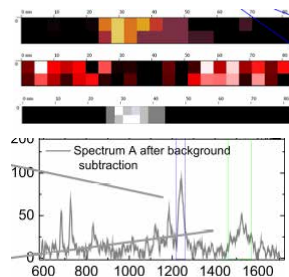


M. Zhang, J. Wang, Q. Tian, Optics Communications 315, 164 (2014)

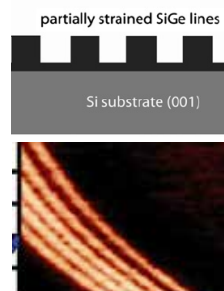
TERS results on various types of samples



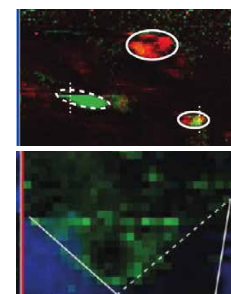
Carbon nanotubes
Resolution: ~10 nm
Nanotechnology, 2011
& ~10 other papers



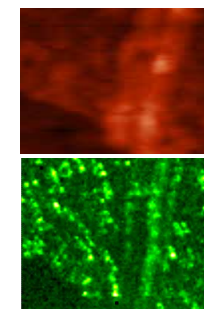
DNA molecule
Resolution: ~15 nm
Ang. Chem. Int., 2014,
E. Lipiec et. al



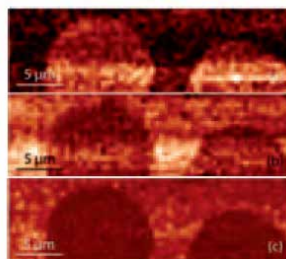
Si/SiGe structures
Resolution: <50 nm
Ultramicroscopy,
2010
P. Hermann et al.



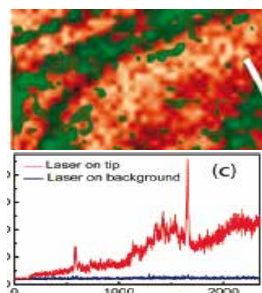
Graphene
Resolution: ~12 nm
ACS Nano, 2011
R. Zenobi et. al.



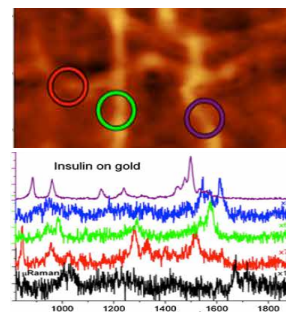
Graphene Oxide
Resolution: ~15 nm
A. Shelaev, et. al.,
2014



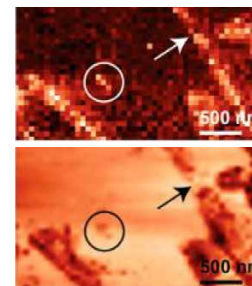
Thiol monolayers
Resolution: ~50 nm
Beilstein J. Nano, 2011
R. Zenobi et. al.



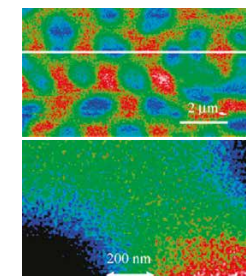
Thin molecular layers
Resolution: ~15 nm
NanoLett., 2010
R. Zenobi et. al.



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

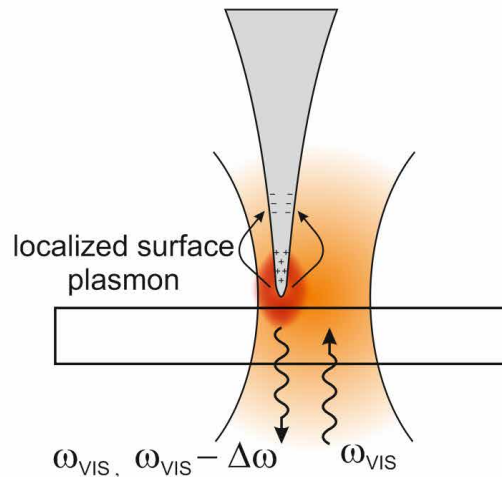
- 355 nm
- 473/488 nm
- 532 nm
- 633 nm

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**

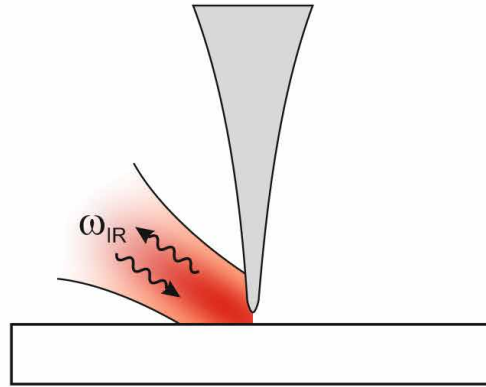
In most of experiments: high resolution 2D TERS mapping

Super-resolution imaging using scanning optical antennas



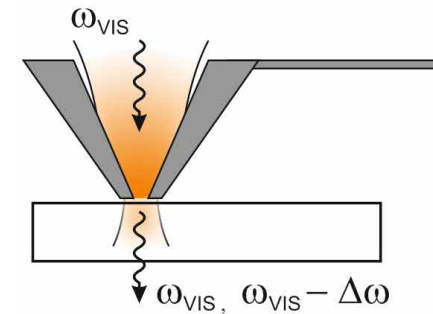
Tip enhanced near-field optical microscopy

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

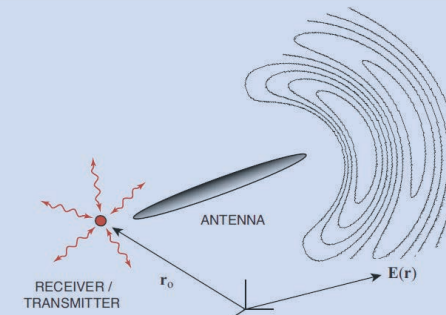


Aperture scanning near-field optical microscopy (SNOM)

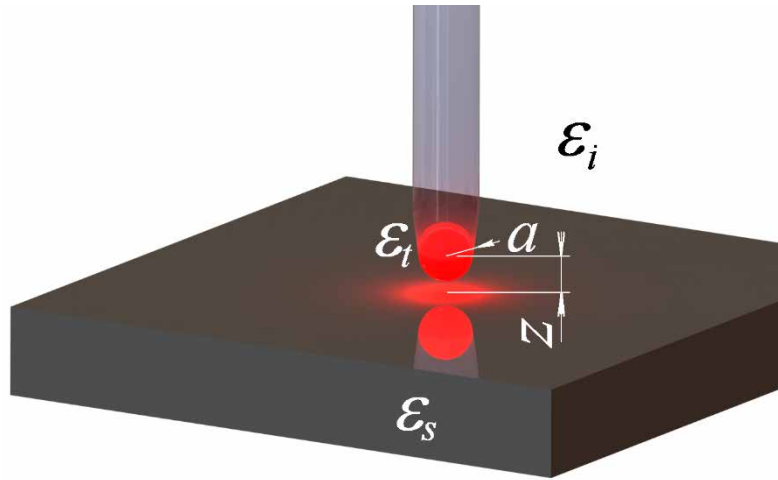
Light transmission through non-resonant subwavelength aperture

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- L. Novotny, N. van Hulst, *Nature photonics* 5, 89 (2011)
- P. Bharadwaj, 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

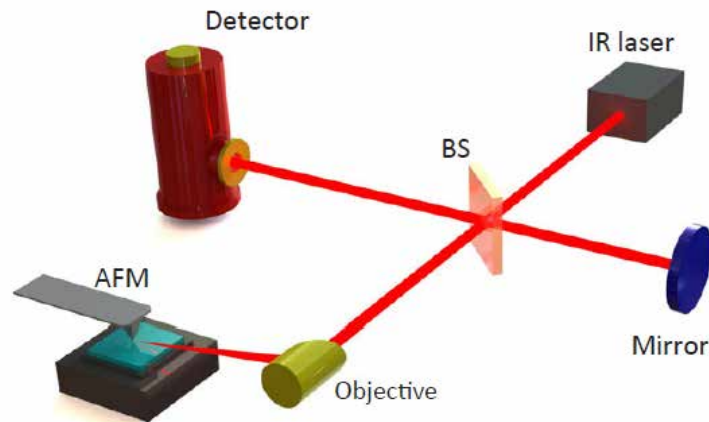


$$E_{scatt} \approx E_{loc} \alpha_{eff}$$

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

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

$$\alpha = 4\pi a^3 \frac{\epsilon_t - \epsilon_i}{\epsilon_t + 2\epsilon_i}$$



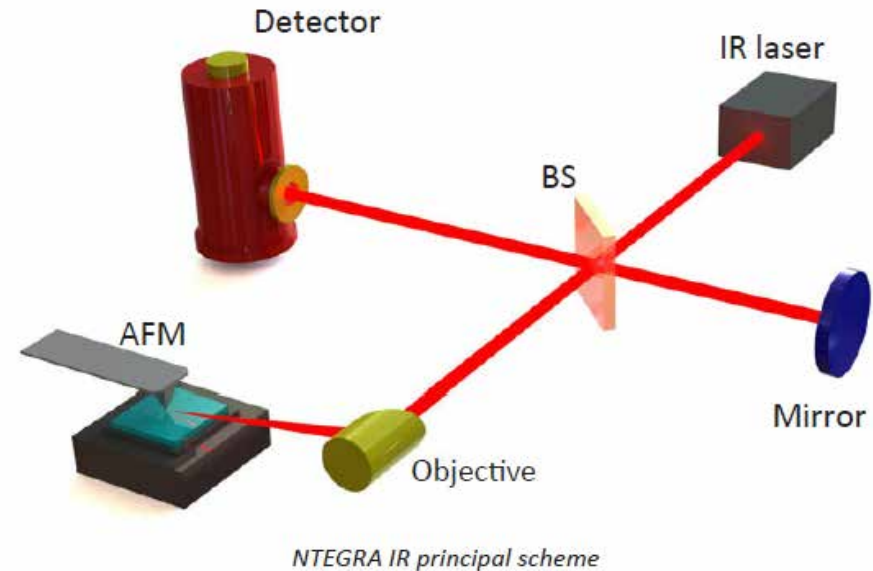
NTEGRA IR principal scheme

IR vibrational microscopy and spectroscopy

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

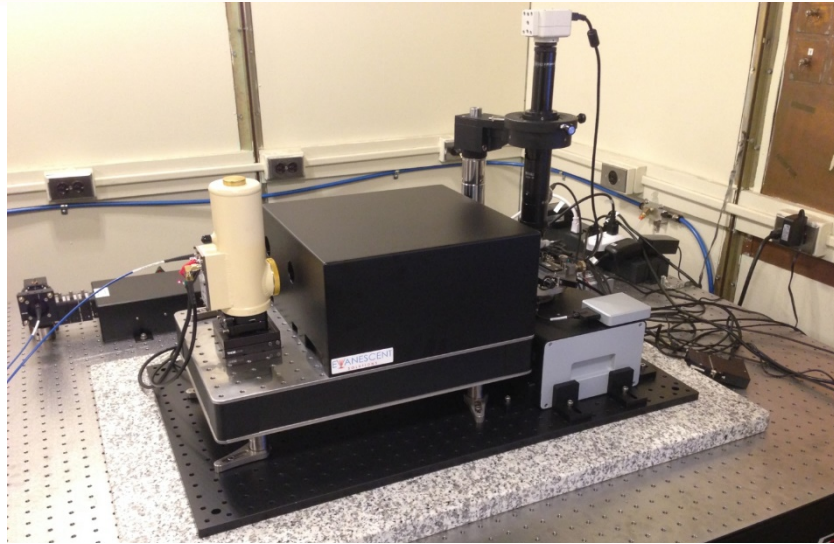
- By measuring mechanical/electrical/thermal/etc. response of AFM cantilever to IR radiation
- By measuring the scattered IR radiation with Michelson interferometer and/or Fourier spectrometer (s-SNOM)

NTEGRA Nano IR: IR s-SNOM measurements

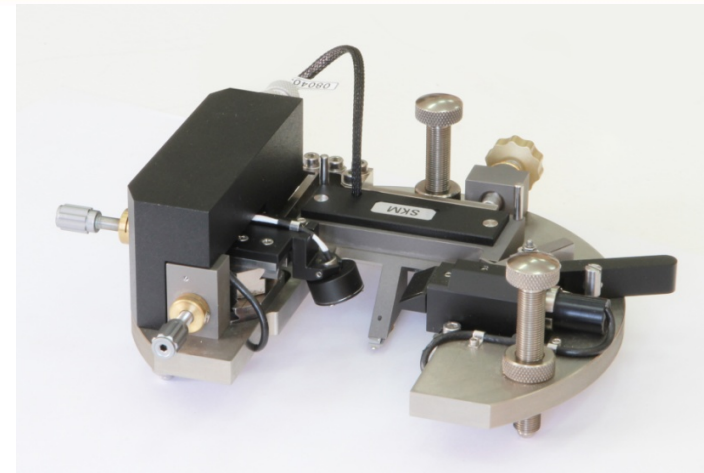


- IR s-SNOM microscopy and spectroscopy with 10 nm spatial resolution
- Wide spectral range of operation: 3-12 μm
- Incredibly low thermal drift and high signal stability
- Versatile AFM with advanced modes: SRI (conductivity), KPFM (surface potential), SCM (capacitance), MFM (magnetic properties), PFM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

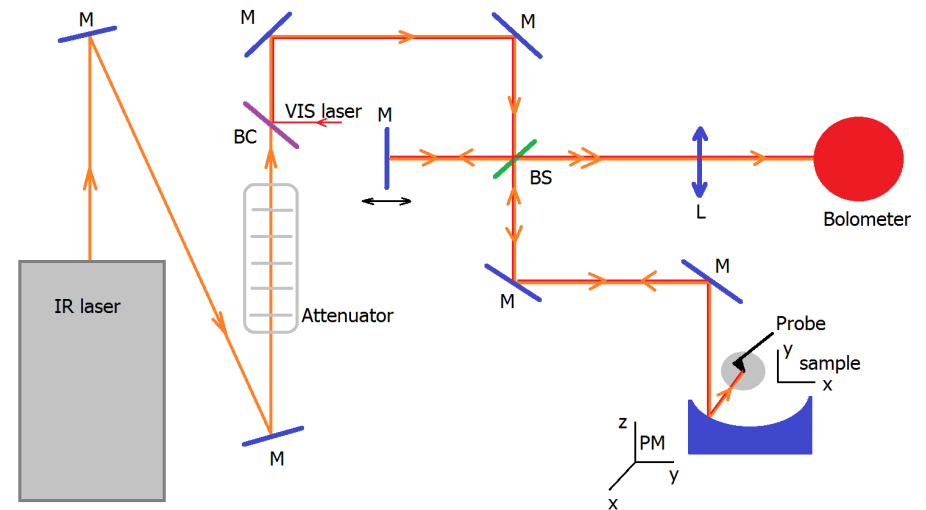
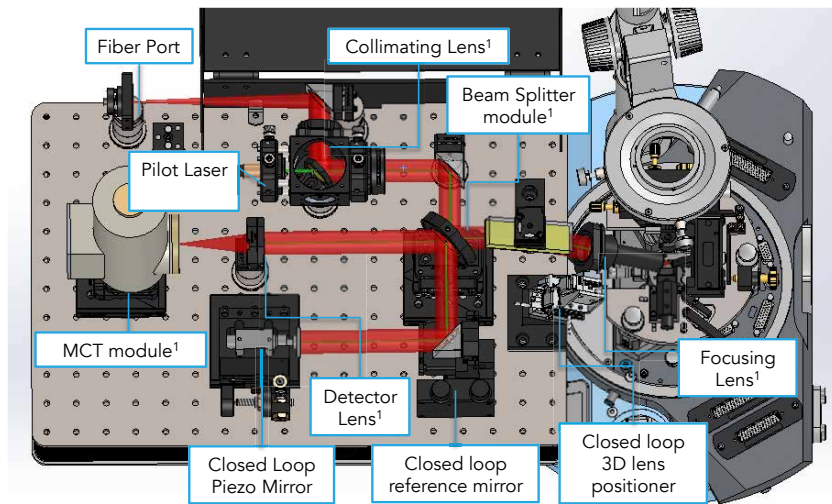
NTEGRA Nano IR



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

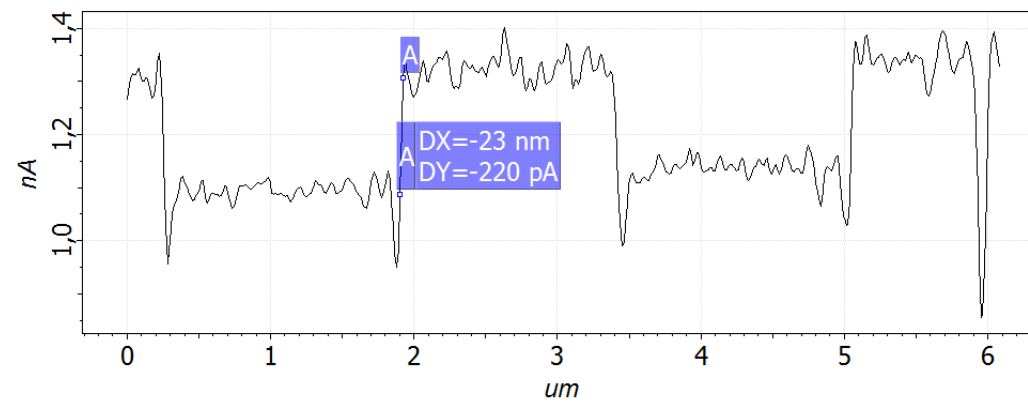
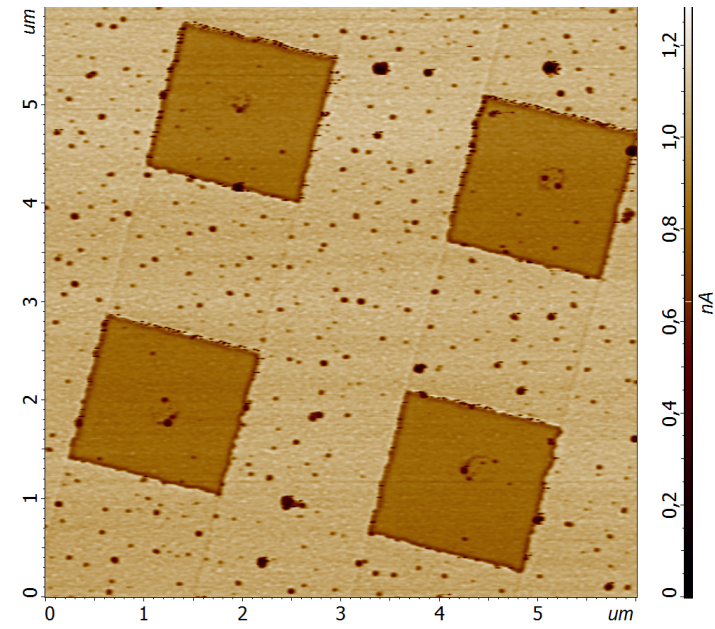
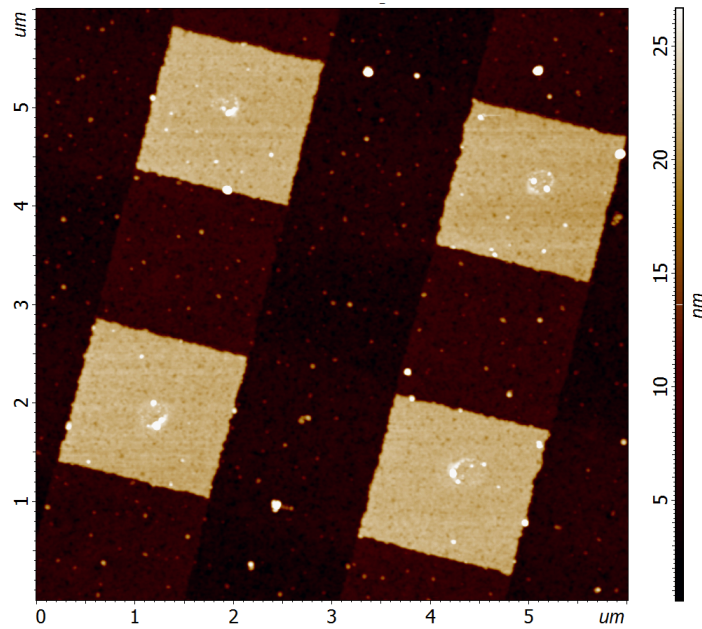


Measuring head

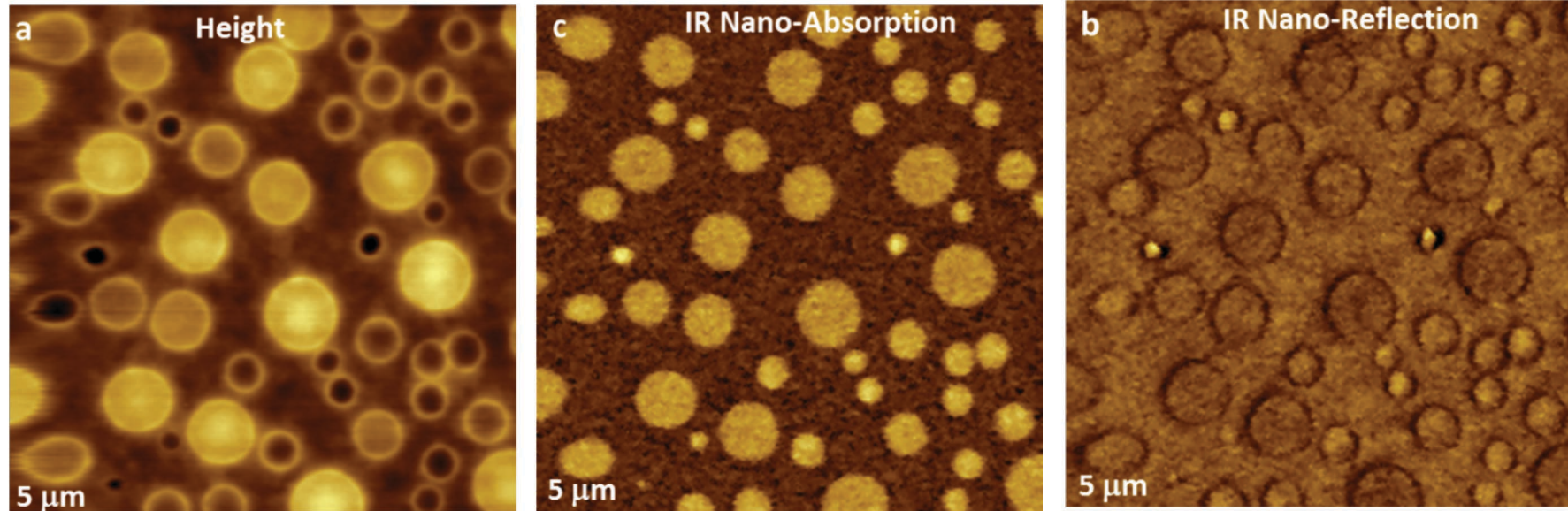


Optical schemes

Si/SiO₂ Calibration Grating

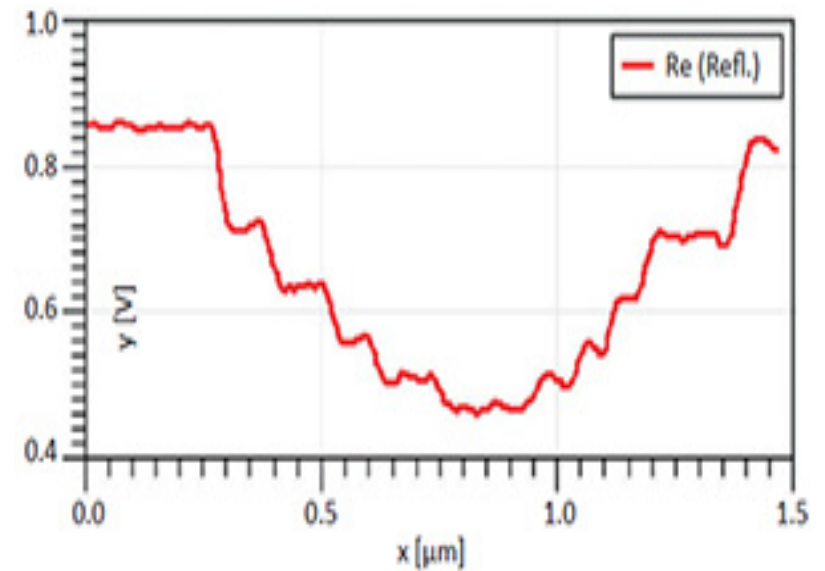
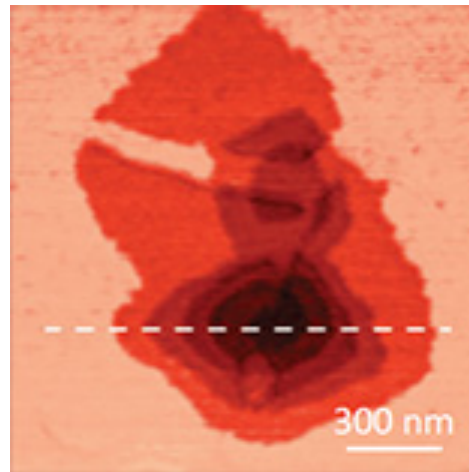
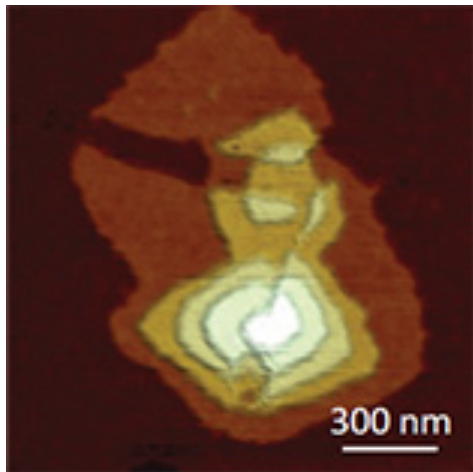


Thin layer of PS/PVAC polymer blend on ITO



Height (a), nano-reflection ($\lambda = 10.6 \text{ mm}$), (b) and nano-absorption ($\lambda = 10.6 \text{ mm}$) (c) images of a PS/PVAC film on ITO substrate.

Ultrathin films: oligothiophene monolayers on silicon



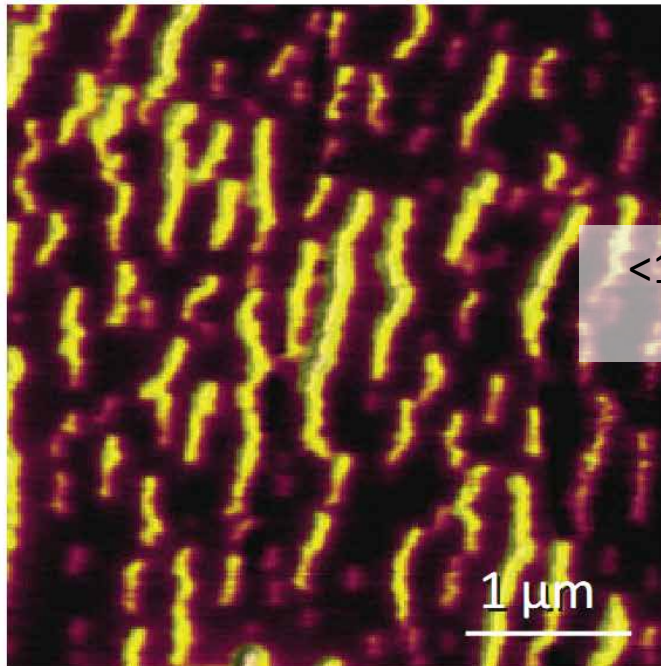
IR reflection contrast of thin and soft structures easily detectable. Each of five 3.4 nm steps is resolved. Spatial resolution is better than $\lambda/1000$.

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

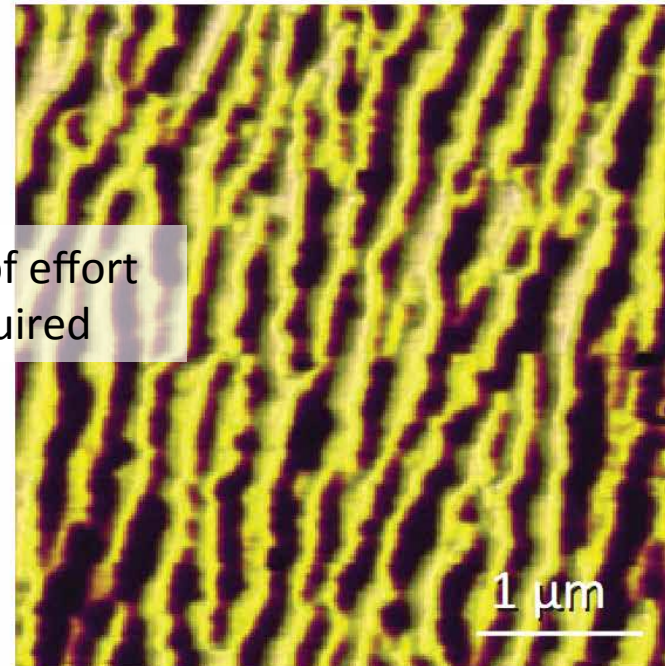
High Temperature AFM and sSNOM on a phase changing material: VO₂

IR sSNOM Reflection

27C



67C

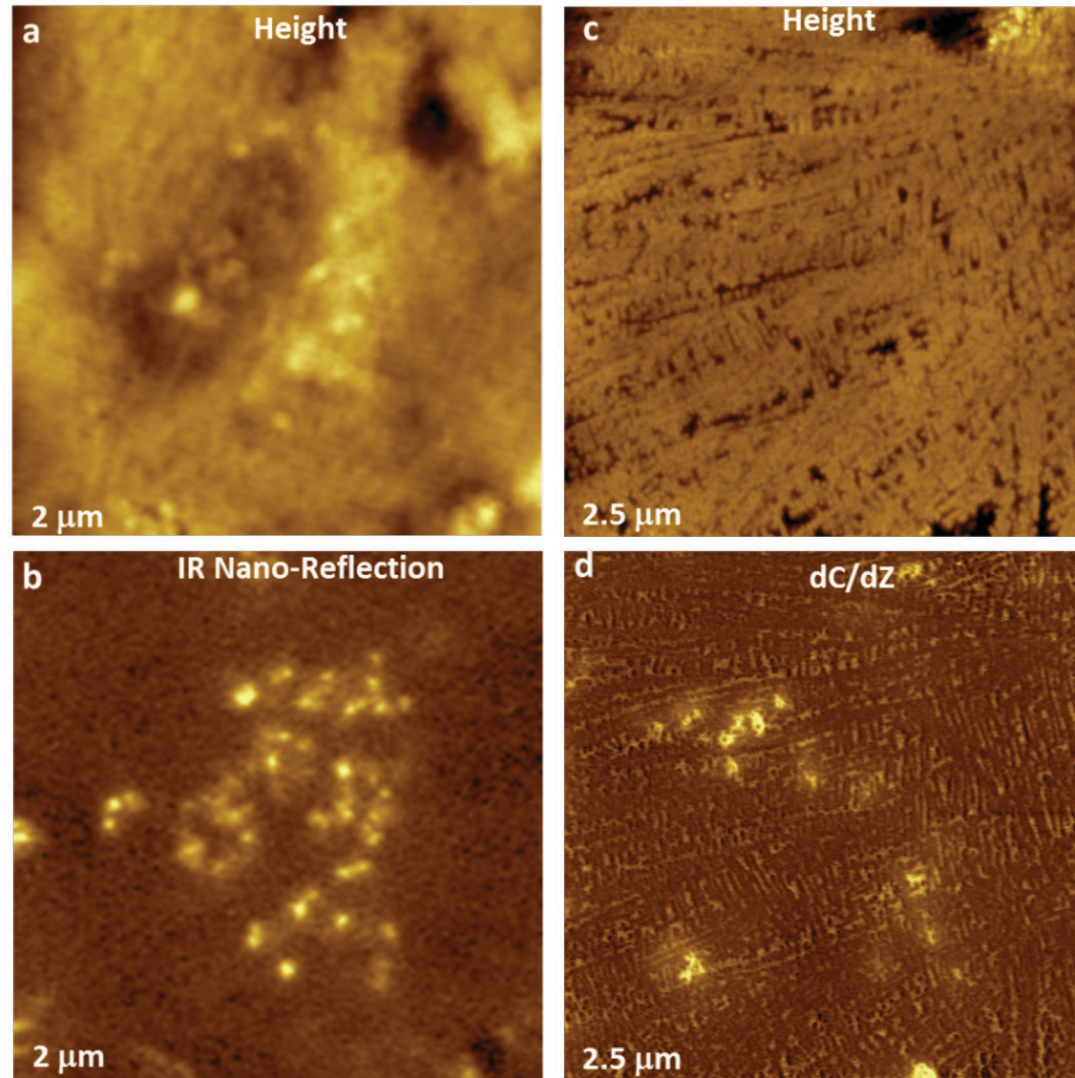


<1hr of effort
required

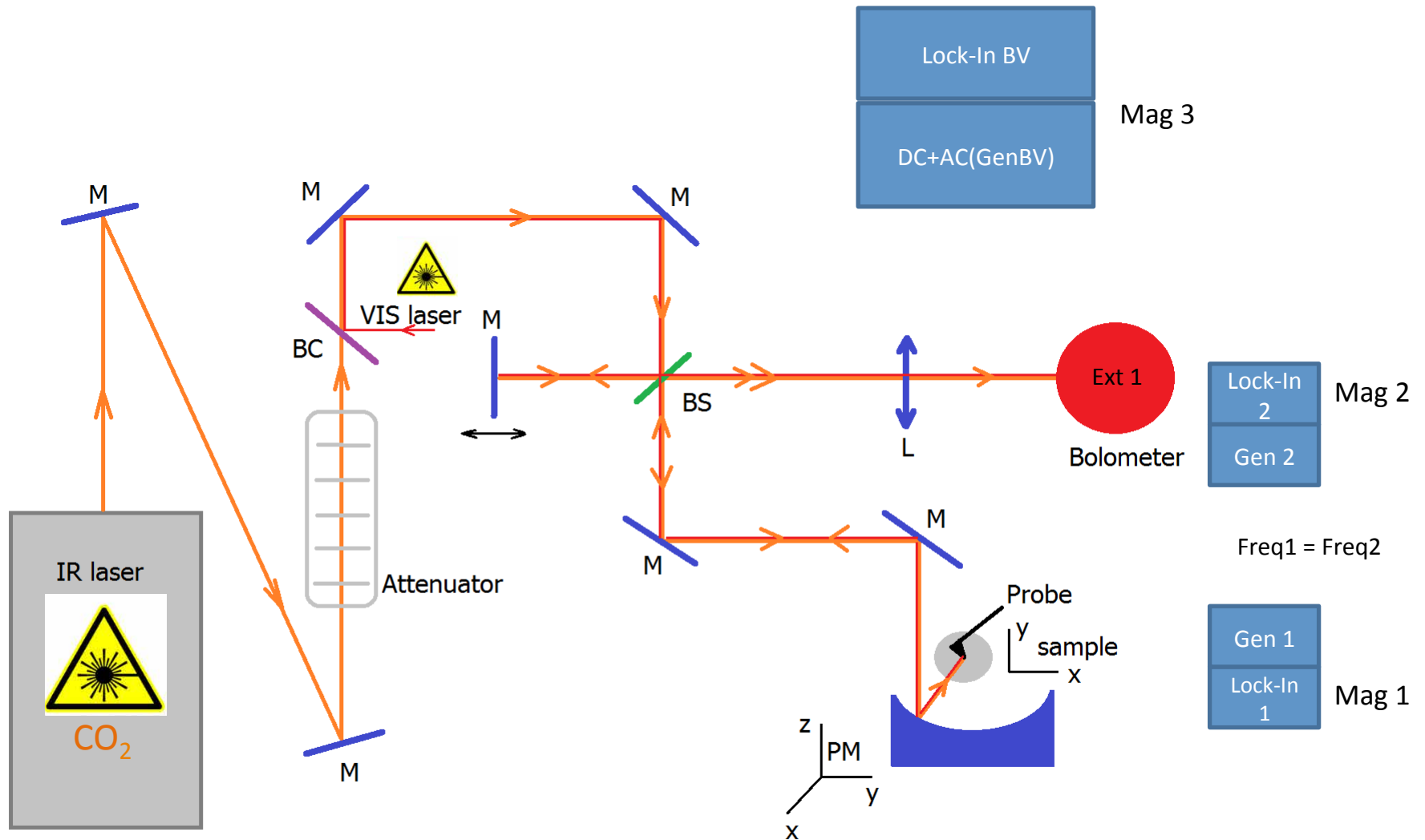
- Superior high temperature performance: under 1 hour needed to acquire images 40C apart. Compare to days on competitor's system
- Low drift and high signal stability: <1μm XY drift from 27 to 67C, no realignment of nanoReflection optics needed

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

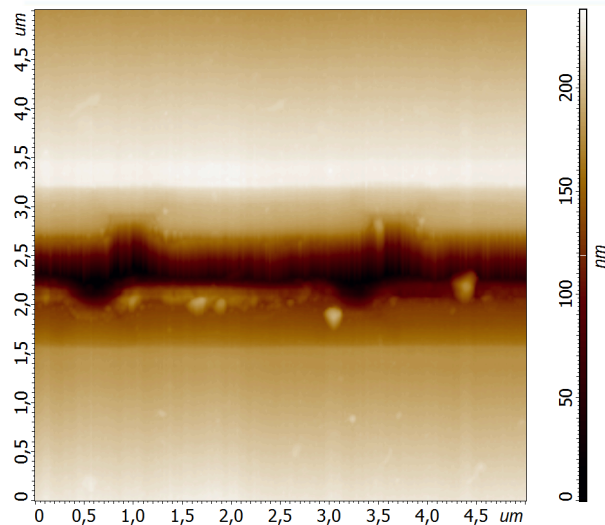
AFM/IR measurements of thermoplastic vulcanizate (TPV)



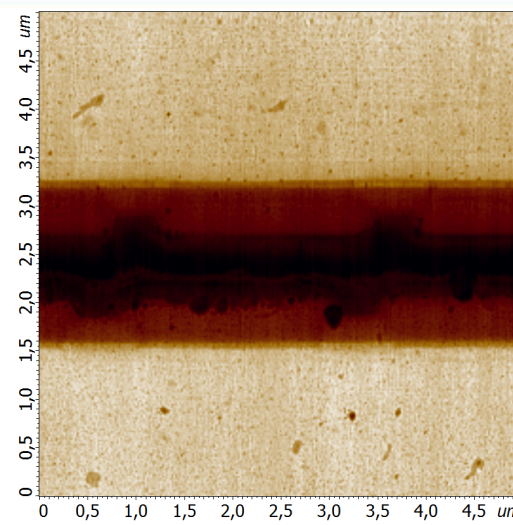
NTEGRA Nano IR: Phase locked homodyne mode



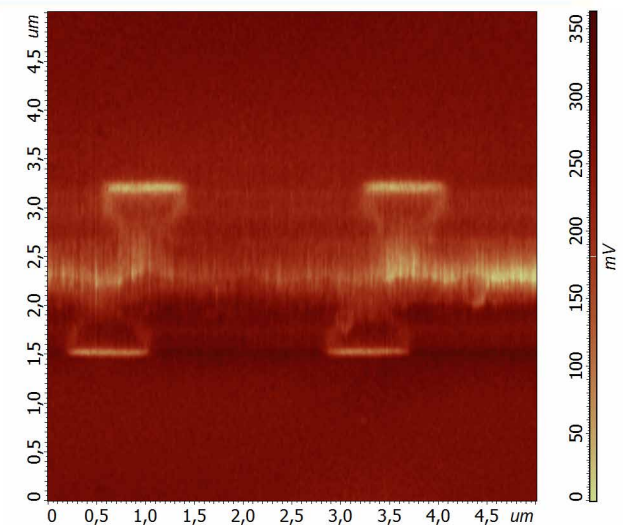
Semiconductor structure mapping



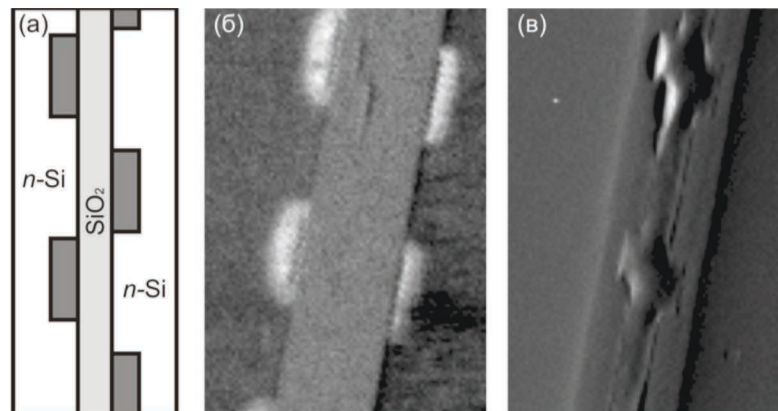
AFM topography



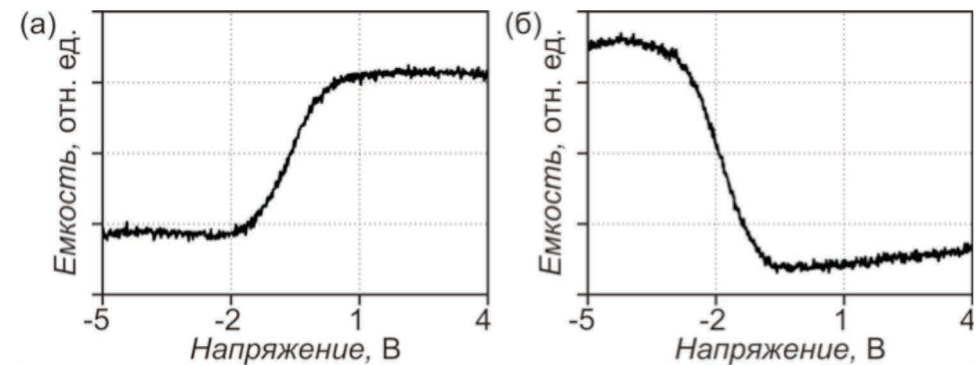
s-SNOM signal, Amplitude



s-SNOM signal, Phase



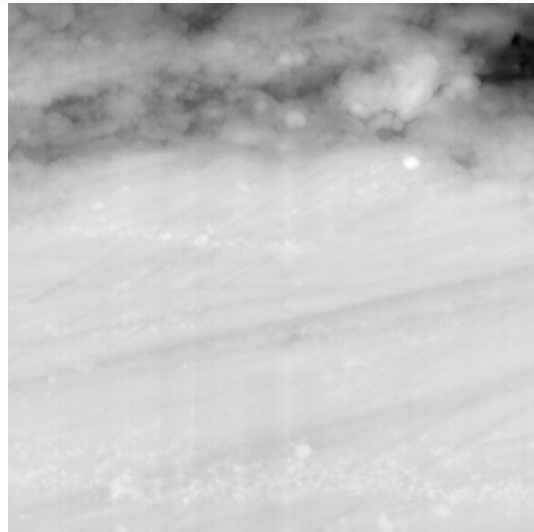
(a) – sample structure, (б) – capacitance contrast dC/dV , (в) – topography (*measured separately*)
Scan size 3.5x5 μm



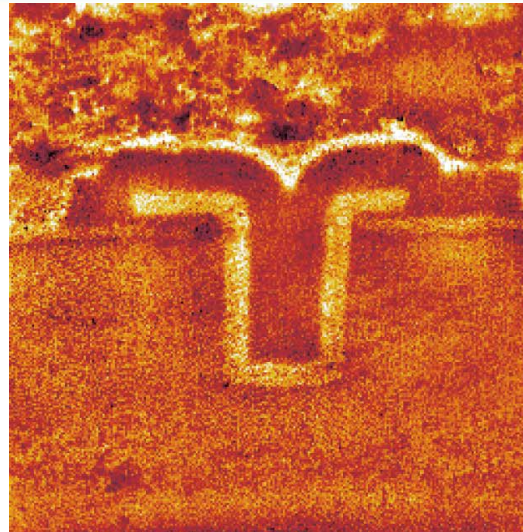
C-V curves measured on the wafer (right) and in the doped region (left)

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

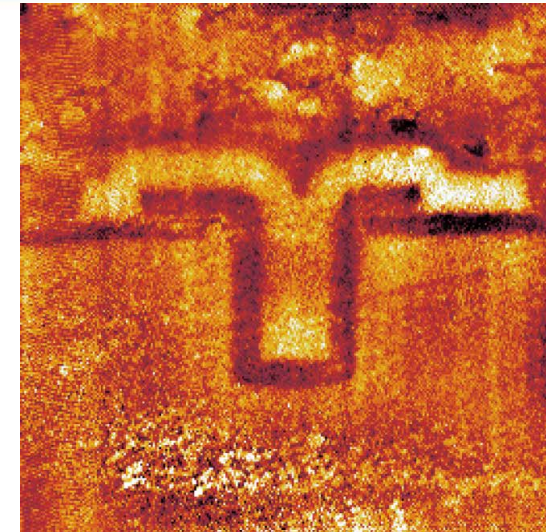
MOS Transistor mapping



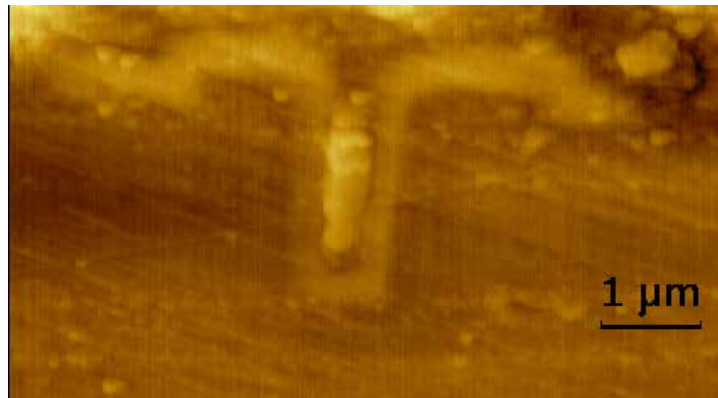
AFM topography



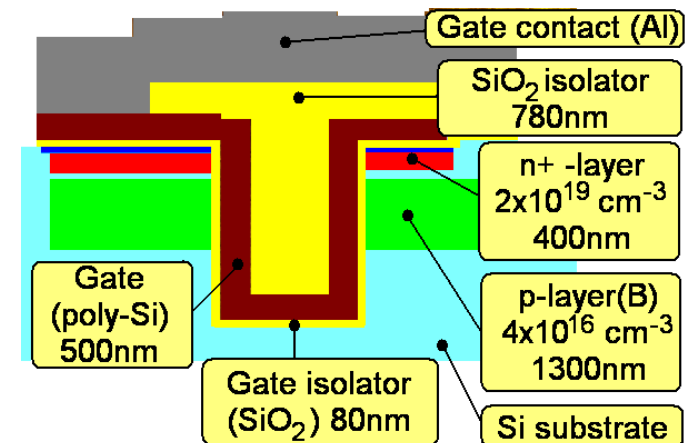
s-SNOM signal, Amplitude



s-SNOM signal, Phase

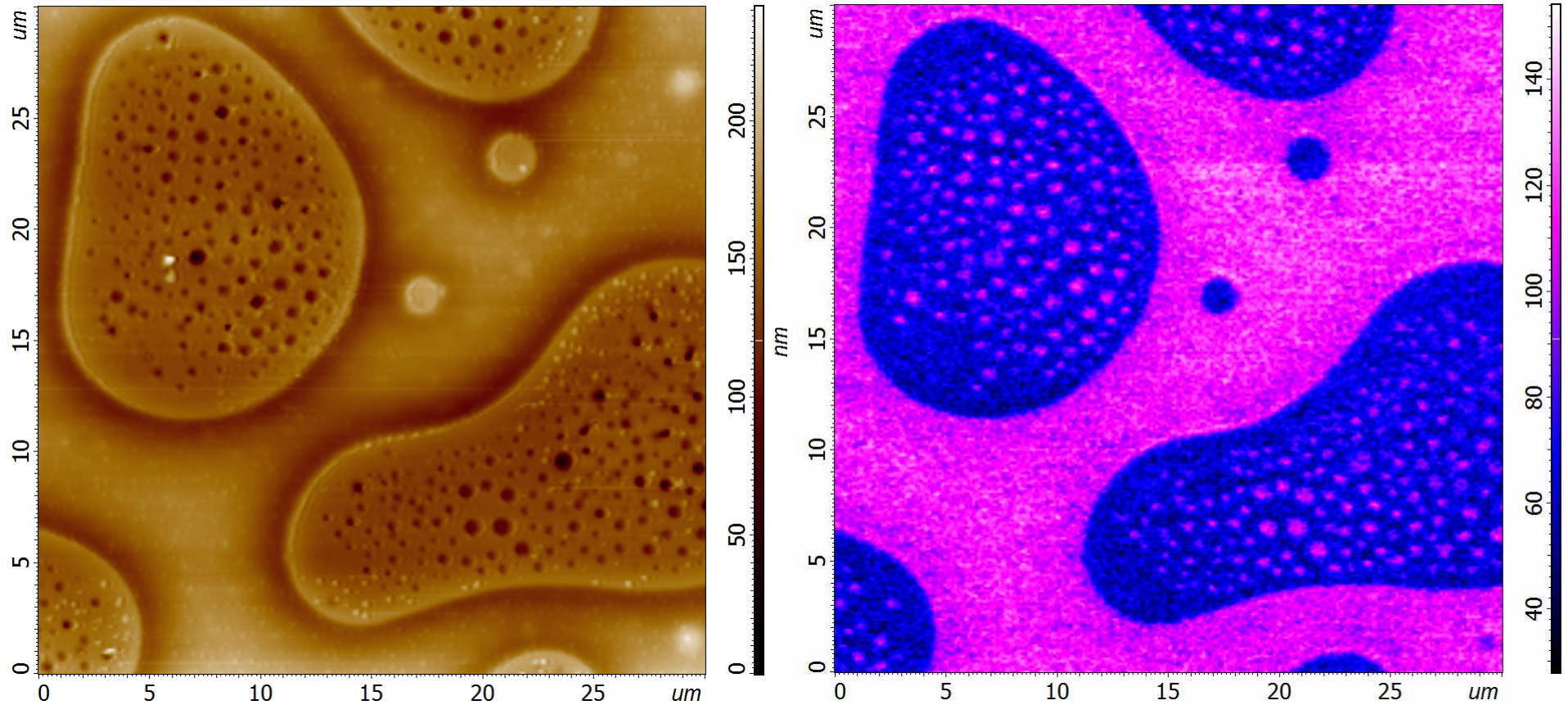


Kelvin probe microscopy, surface potential
(*measured separately*)



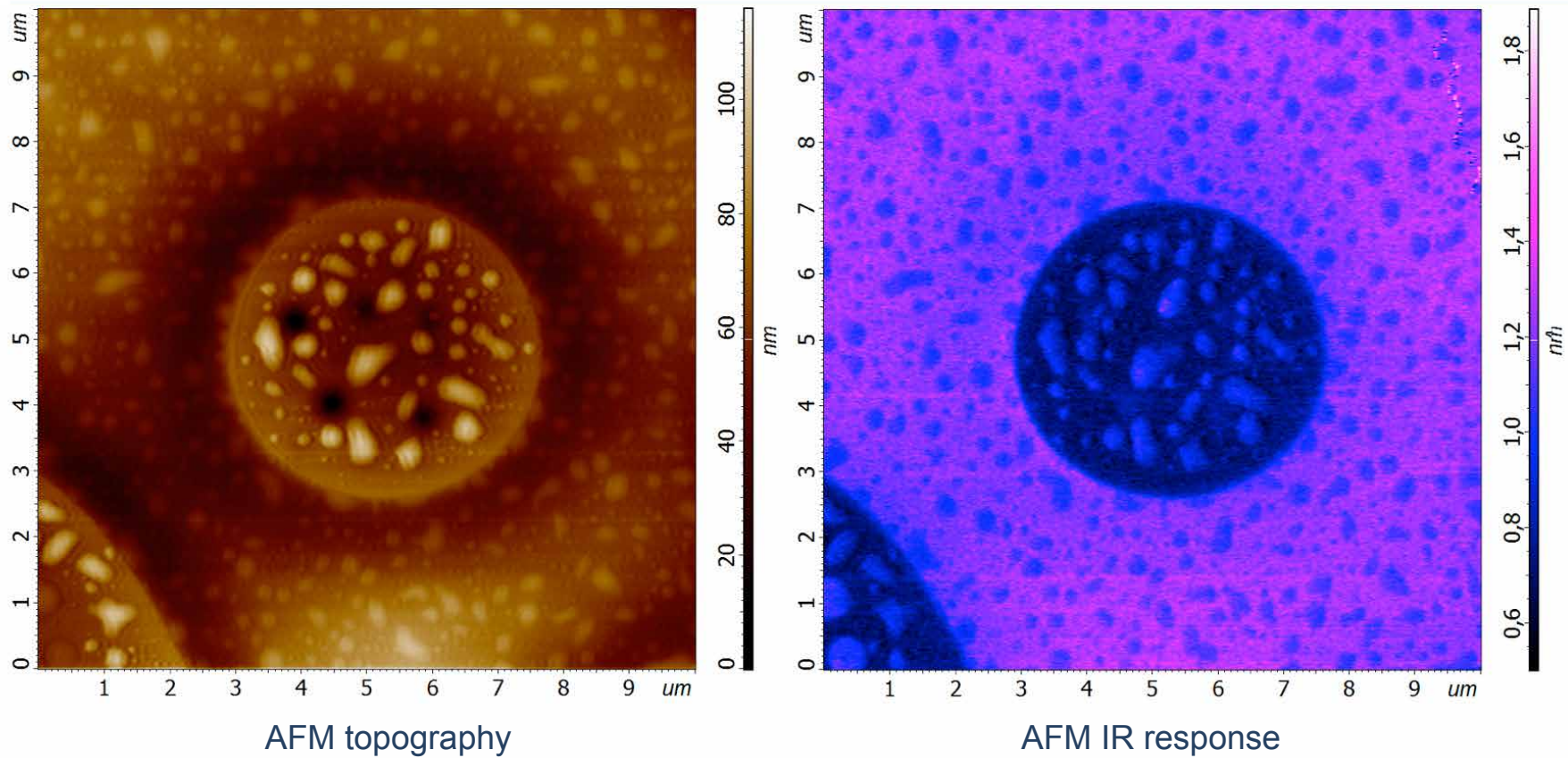
Sample: Si trench defined MOS transistor. Excitation laser: 10.8 μm (923 cm⁻¹). Image size: 10x10 μm
Measurement mode: s-SNOM optical signal (Amplitude and Phase) by interferometric homodyning. Measured by D. Kazantsev

IR thermal expansion response – AFM IR



Sample: PS/PVAC. Excitation laser: $10.8 \mu\text{m}$ (923 cm^{-1}). Image size: $10 \times 10 \mu\text{m}$

IR thermal expansion response – AFM IR



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?

NT-MDT
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