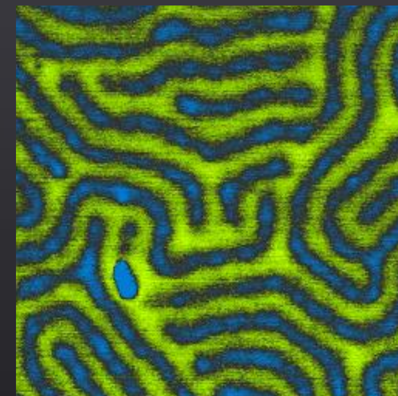
molecular VISTA
www.molecularvista.com



Nanoscale Chemical Imaging with Photo-induced Force Microscopy

Thomas R. Albrecht, Derek Nowak, Will Morrison, Sung Park
Molecular Vista, Inc.

IEEE SF Bay Area Nanotechnology Council
Feb. 16, 2016

Scanning probe microscopy: atomic spatial resolution

STM: Si 7 x 7 atomic resolution

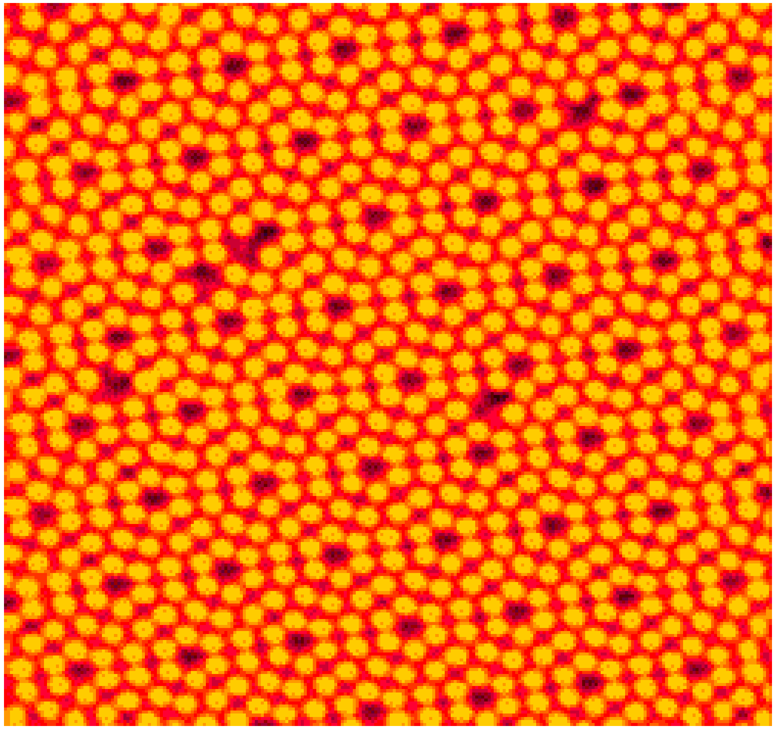


Image credit: Forschungszentrum Julich, Germany

http://www.fz-juelich.de/pgi/pgi-3/EN/Leistungen/themengebiete/Outreach/outreach_node.html

AFM: atomic steps on sapphire

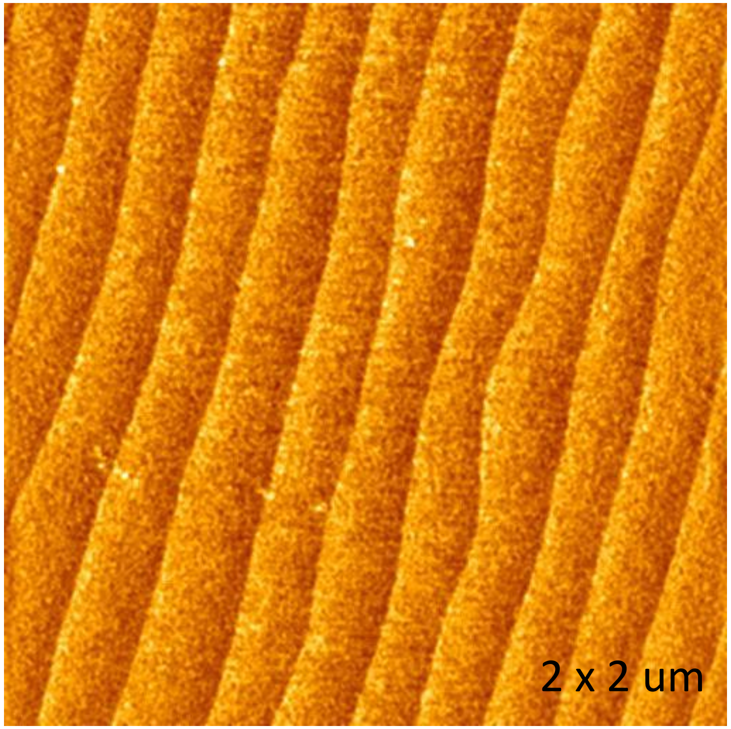


Image credit: Technion, Israel

http://phelafel.technion.ac.il/~pavela/cafm.html

- Limited spectroscopic capability for identification of specific materials (especially AFM)

Electron microscopy: Elemental analysis

Atomic Resolution Elemental Mapping on $SrTiO_3$ crystal by Super X EDS (EDX) system on Titan 80-300 Aberration Corrected Scanning Transmission Electron Microscope

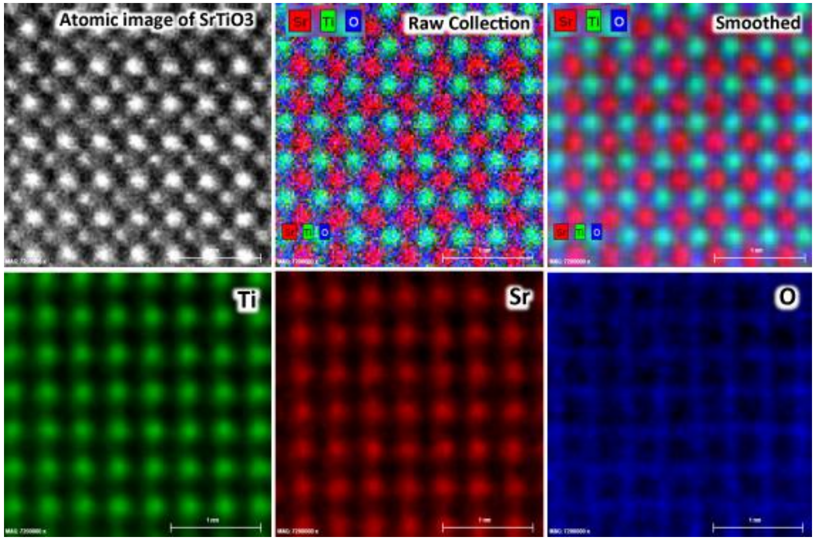


Image credit: North Carolina State Univ. Analytical Instrumentation Facility

https://www.aif.ncsu.edu/tem-lab/

Elemental mapping of a device structure by EDS (EDX)

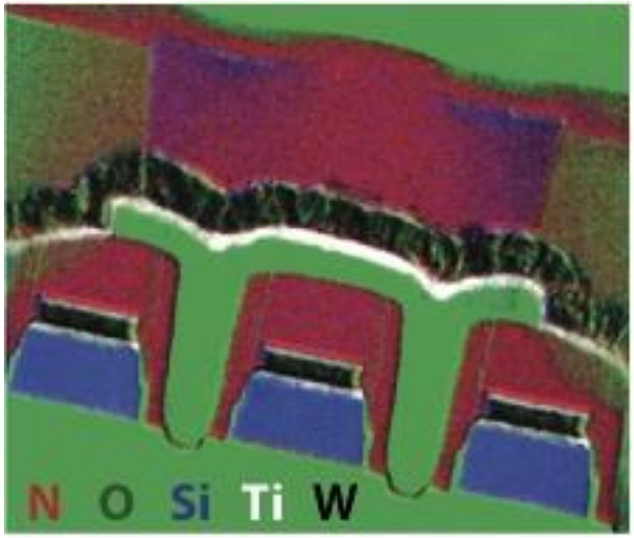


Image credit: Nanolab Techologies

http://www.nanolabtechnologies.com/TEM-STEM-EELS-EDS

- Advanced capability for elemental mapping
- Atomic-scale resolution in certain circumstances

FTIR: Infrared absorption "chemical fingerprint" spectrum

FTIR apparatus

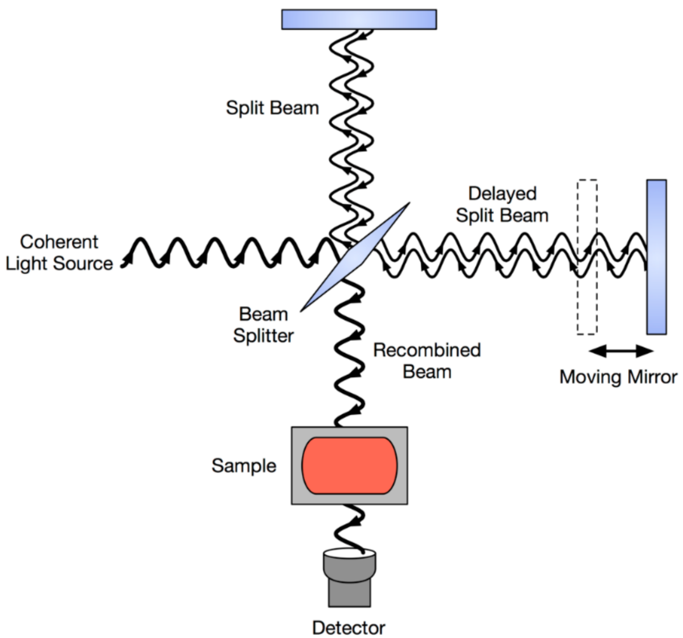


Image credit: Wikipedia

https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#/media/File:FTIR_Interferometer.png

Detailed absorption spectrum – chemical "fingerprint"

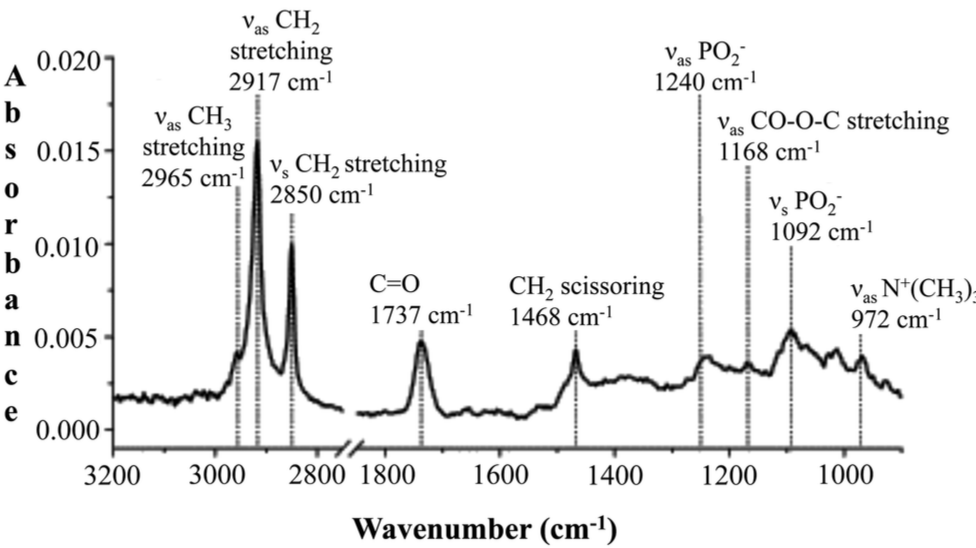
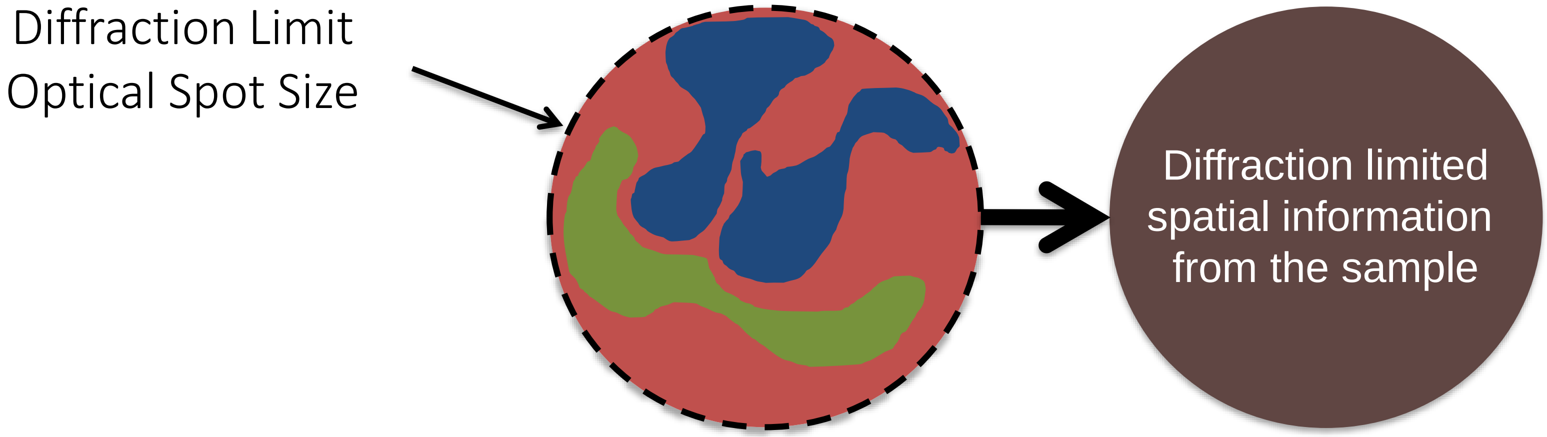


Image credit: Mudunkotuwa et al., Analyst 139, 870-881 (2014).

- Detailed spectra for analysis and identification of molecular materials
- Spatial mapping resolution limited by optical diffraction limit (~ 1 μm)

Problem with conventional optical microscopy λ/2

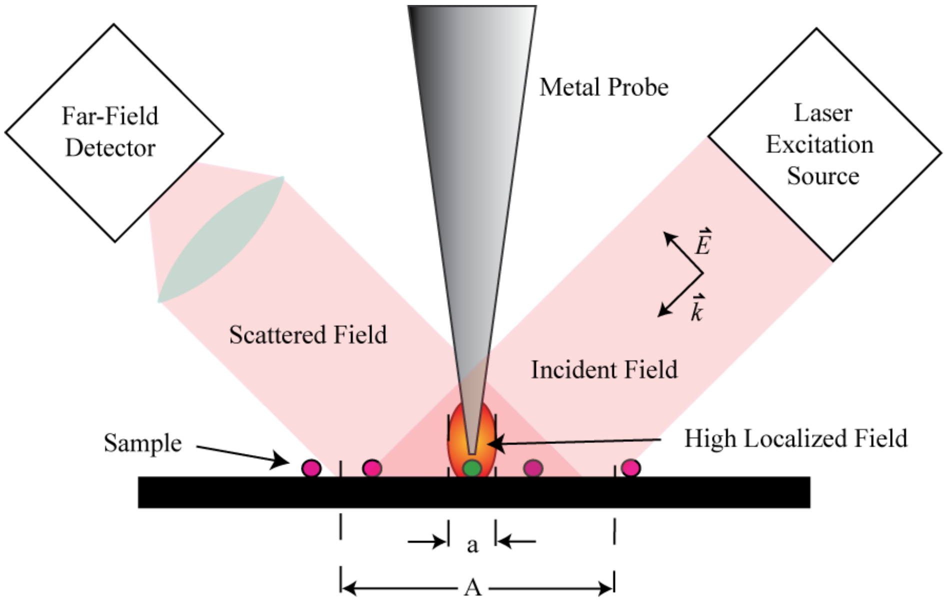
Light provides rich chemical information: electronic states, vibrational states…..



- Cannot resolve dense nanostructures below optical spot size
- Can we combine scanning probe microscopy with optical spectroscopy to achieve nm-scale spatial resolution and detailed chemical analysis?

One approach: Scattering NSOM (optical detection)

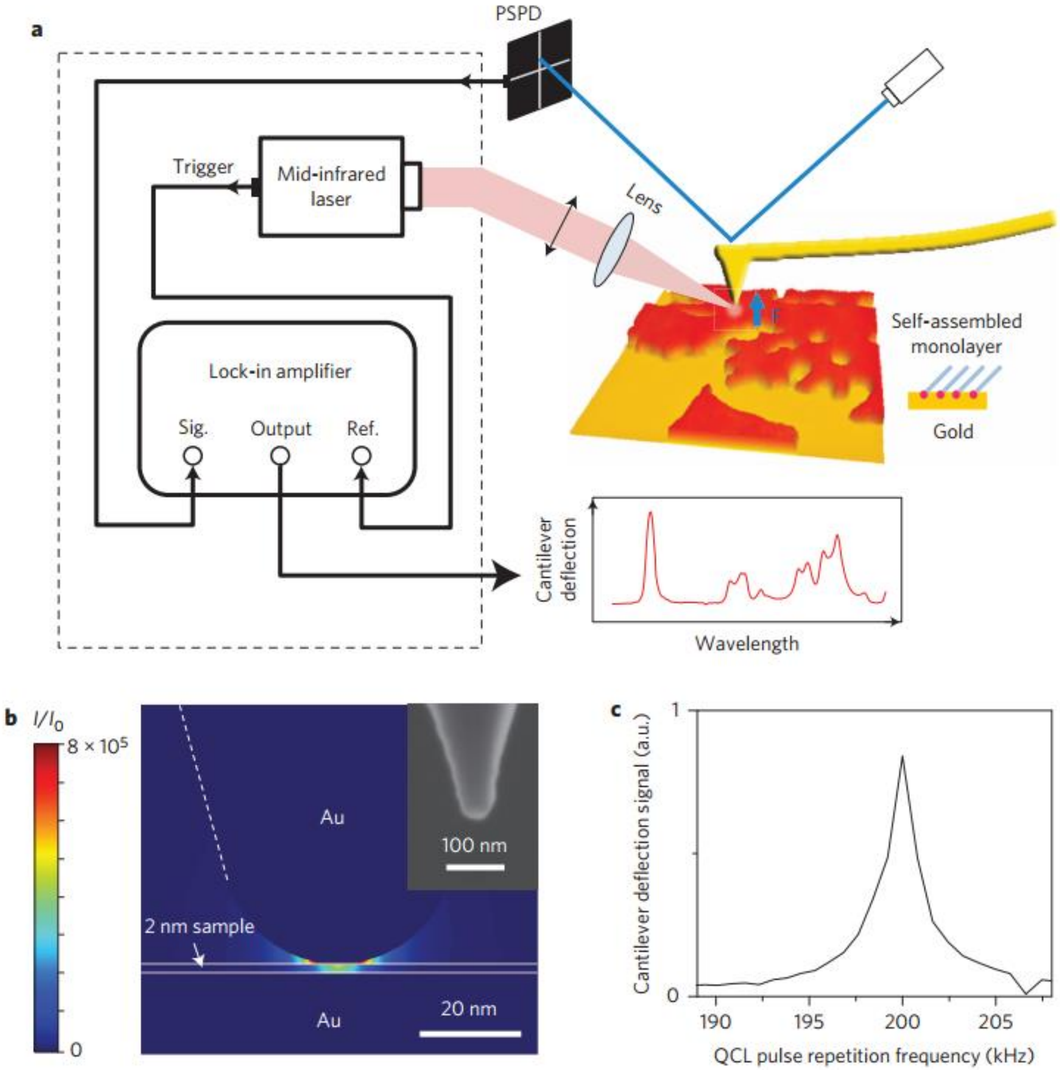
- Interaction region confined by enhanced fields at sharp tip
- Far-field collection of scattered photons (low efficiency)



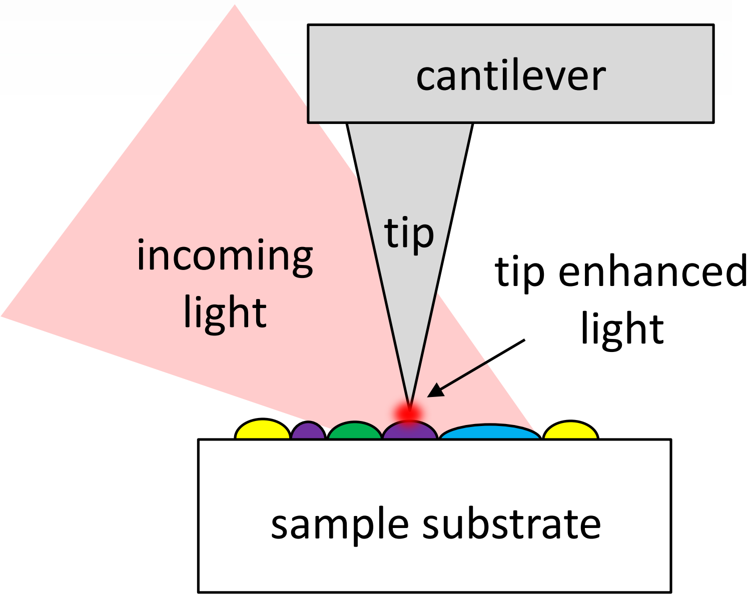
Concept for scattering near-field scanning optical microscope

- sNSOM Probe controlled by AFM
- Scattered light measures the effective polarizability in the near-field
- Near-field signal "a" competes against far-field signal "A".
- Techniques to increase near-field over far-field.
  - Plasmonic enhancement
  - Interferometric methods
  - Higher harmonics methods
- Photon collection is paramount.

Another approach: Photothermal AFM (mechanical detection)



Lu, Jin, and Belkin, Nature Photonics 8, 307-312 (2014)

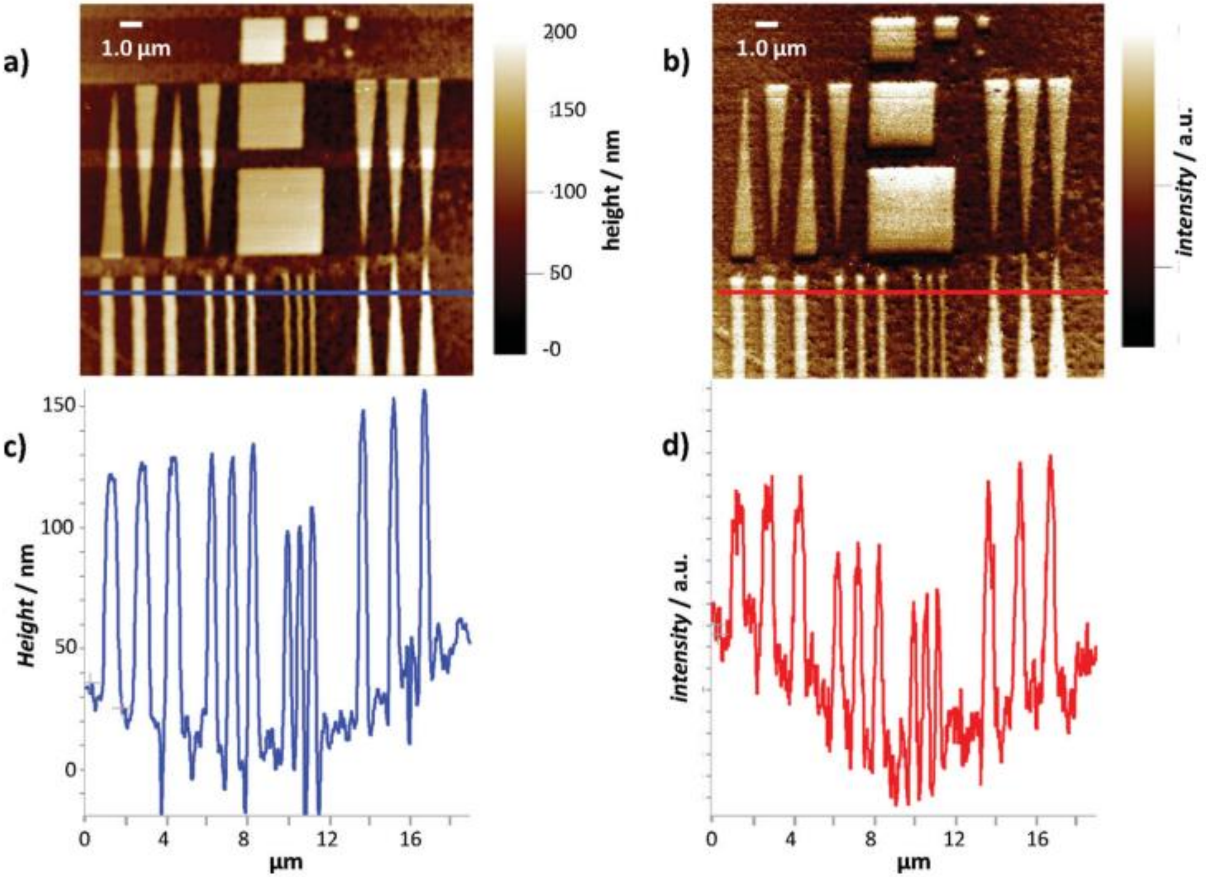


- Material specific wavelength-selective absorption
- Locally enhanced optical field
- Local sensing of thermal expansion
- Tip in hard contact with sample

Patterned PMMA images by photothermal AFM

AFM Topography

Photothermal Expansion



- Spatial resolution around ~100 nm
- Resolution limited by thermal diffusion
- Can we do better?

Lahiri, Holland, and Centrone, *Small* 9, 439-445 (2013)

Photo-induced force microscopy (PiFM)

Photo-induced Force Microscopy (PiFM)

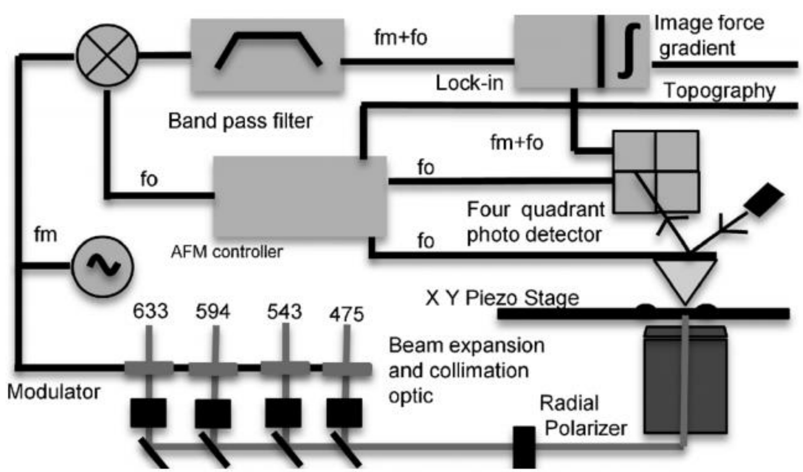
APPLIED PHYSICS LETTERS **97**, 073121 (2010)

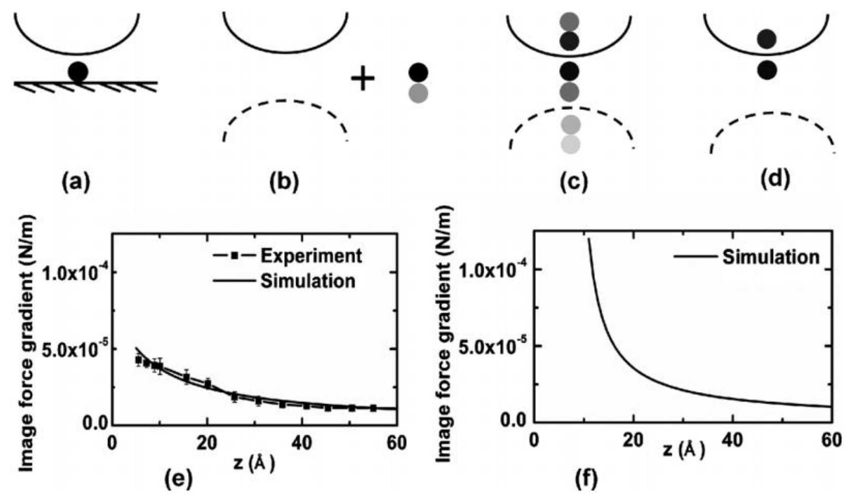
Image force microscopy of molecular resonance: A microscope principle

I. Rajapaksa, K. Uenal, and H. Kumar Wickramasinghe[a)]
Department of Electrical Engineering and Computer Science, University of California, Irvine, California 92697, USA

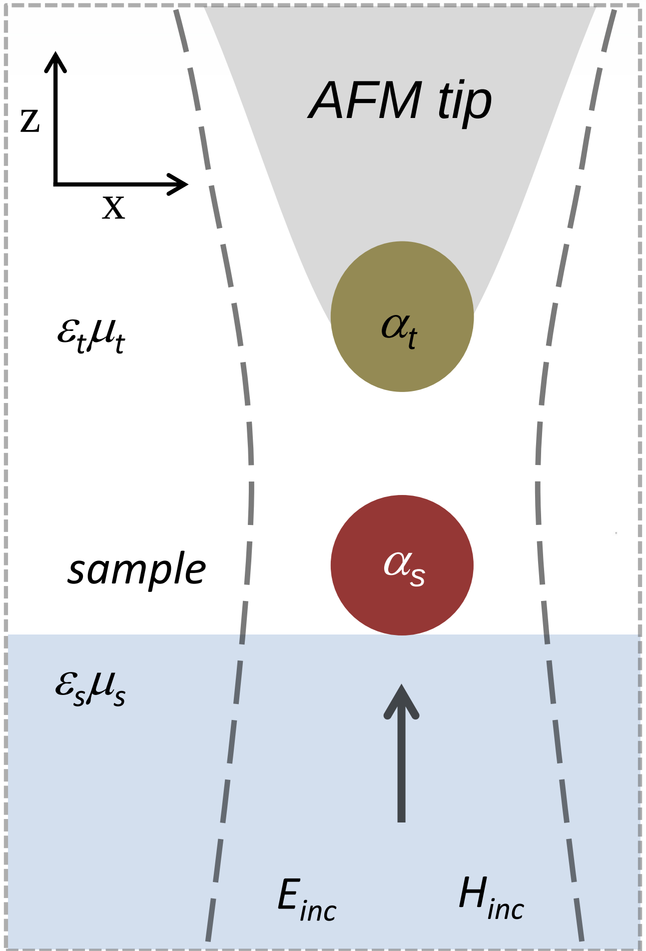
(Received 3 June 2010; accepted 12 July 2010; published online 20 August 2010)

We demonstrate a technique in microscopy which extends the domain of atomic force microscopy to optical spectroscopy at the nanometer scale. We show that molecular resonance of feature sizes down to the single molecular level can be detected and imaged purely by mechanical detection of the force gradient between the interaction of the optically driven molecular dipole and its mirror image in a platinum coated scanning probe tip. This microscopy and spectroscopy technique is extendable to frequencies ranging from radio to infrared and the ultraviolet. © *2010 American Institute of Physics*. [doi:10.1063/1.3480608]





PiFM : Detecting local effective polarizability (via force)



Incident light polarizes sample

$$polarizabilty = a = a' + ia''$$

$$realpart = a' \qquad imaginarypart = a''$$

$$local\ force \propto -\frac{1}{z^4} Re\{\alpha_s \alpha_t^*\} |E_z|^2$$

$$\alpha'_s \alpha'_t + \alpha''_s \alpha''_t$$

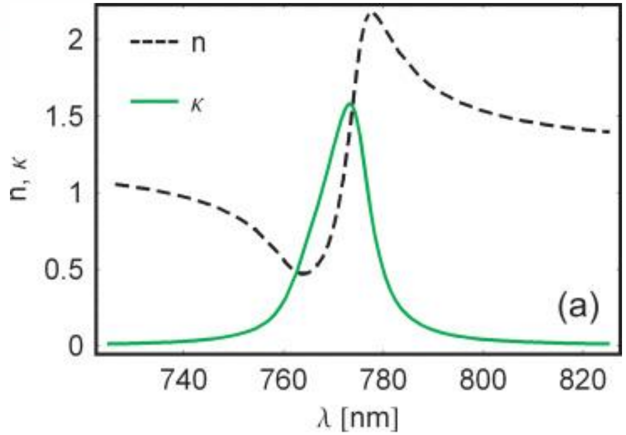
PiFM in the mid-IR, where the imaginary part of the tip dominates the real part, the force will follow the imaginary part (absorption) of the tip and sample.

- Tip limited resolution (like AFM)
- No thermal diffusion effects

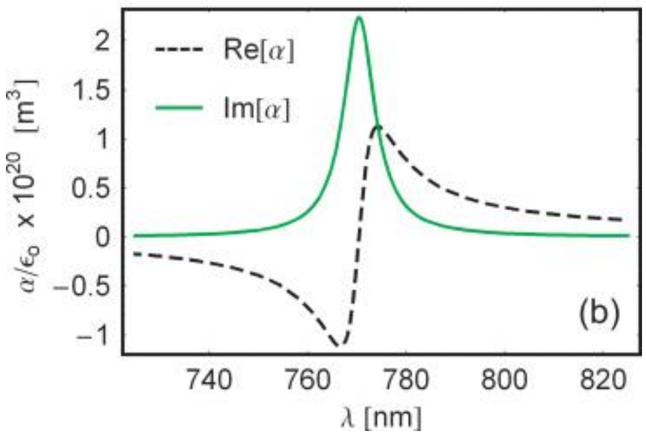
Jahng et al., Acc. Chem. Res. 48, 2671-2679 (2015)

Optical properties near absorption resonance

Sample: Complex Index of Refraction

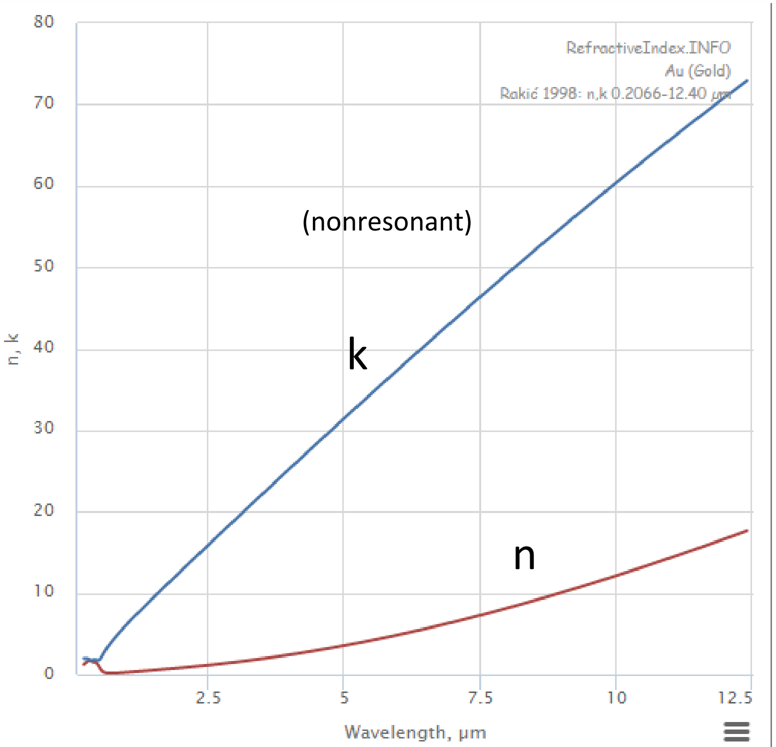


Sample: Complex Polarizability



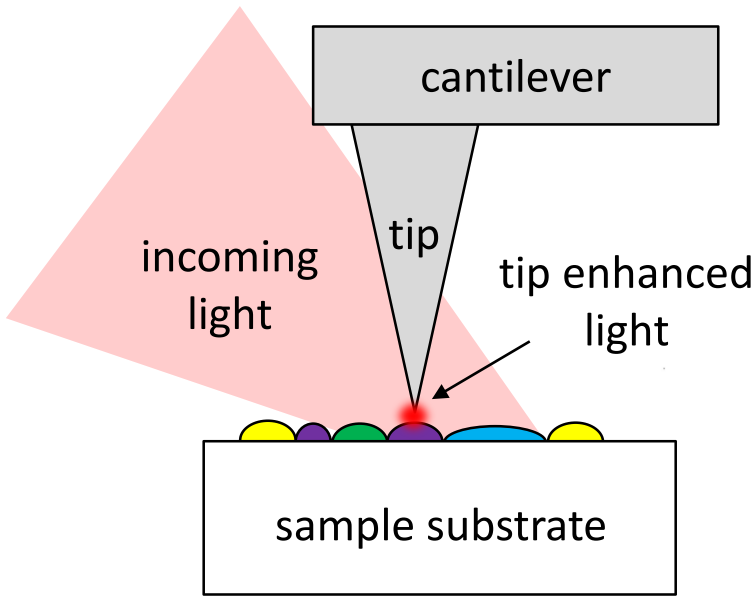
Graphic: M. J. Kendrick et al., J. Opt. Soc. Am. B 26, 2189-2198 (2009)
(simply used as an example of resonant absorption)

Gold Tip: Complex Index of Refraction



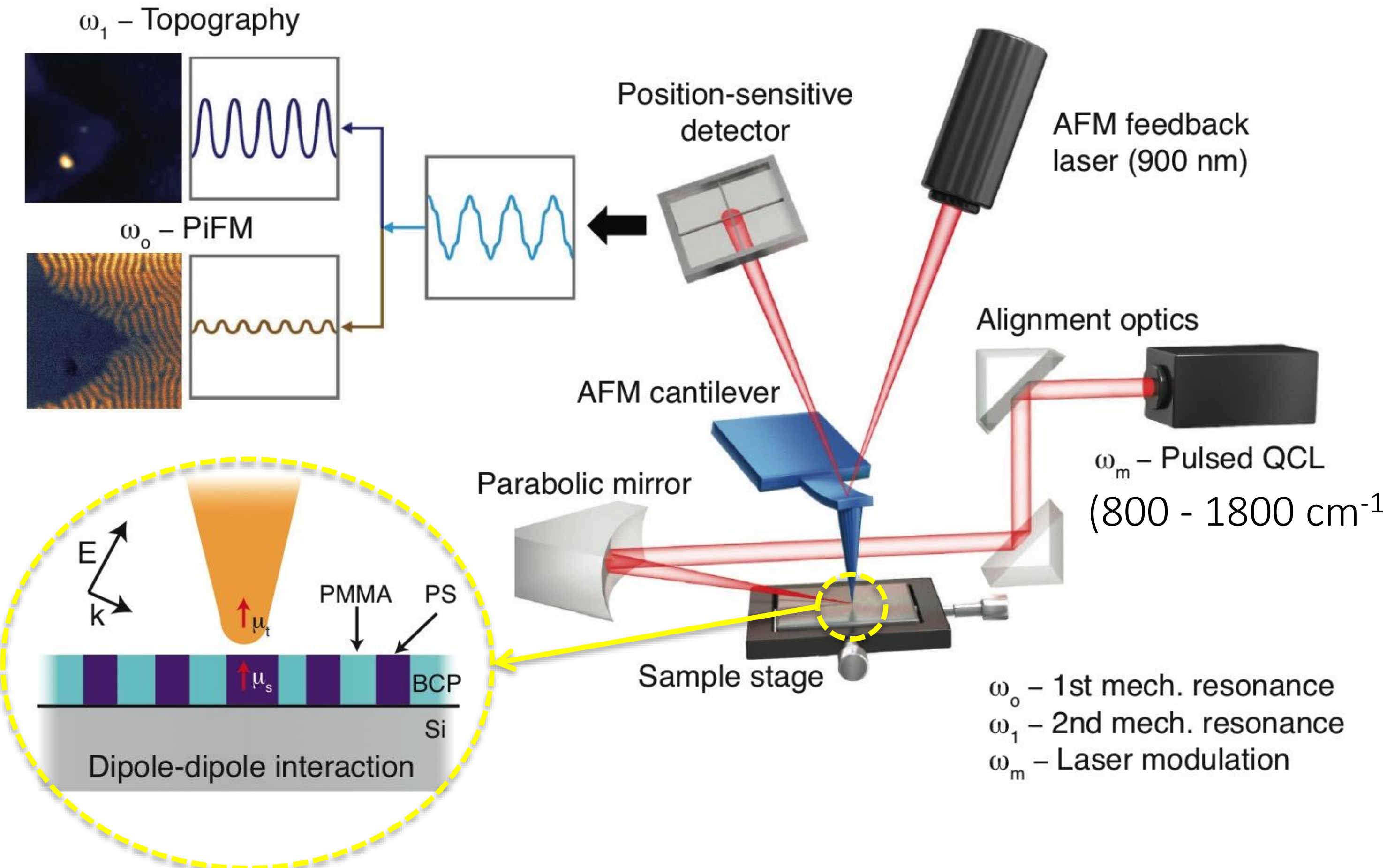
- Sharp peaks in imaginary (quadrature phase) component of sample polarizability
- Broad strong k value for gold tip in infrared
- Sharp peaks in PiFM signal at sample absorption peaks

PiFM properties



- Material specific wavelength-selective absorption
- Locally enhanced optical field
- Local sensing of attractive dipole forces between tip and sample
- Noncontact or gentle tapping of tip on sample
- Resolution not affected by thermal diffusion
- z^{-4} force dependence provides very high spatial resolution

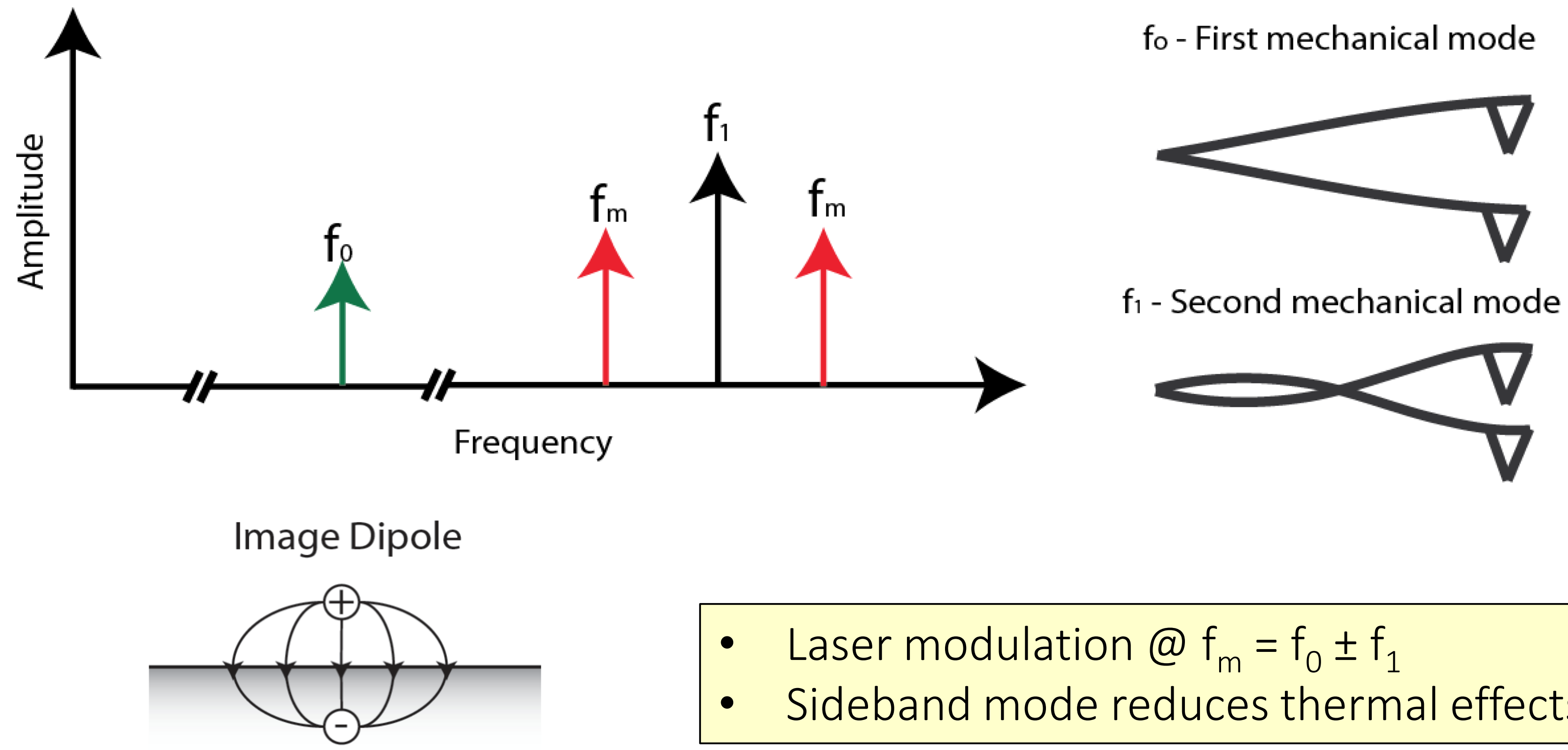
PiFM apparatus – mid infrared



Mid-IR allow access to “molecular fingerprint region”

AFM dipole-dipole force detection

Measure optical dipole-dipole forces using multi modal dynamic mode AFM



- Laser modulation @ $f_m = f_0 \pm f_1$
- Sideband mode reduces thermal effects

I. Rajapaksa, K. Uenal, and H. K. Wickramasinghe, Appl. Phys. Lett. 97,073121 (2010).

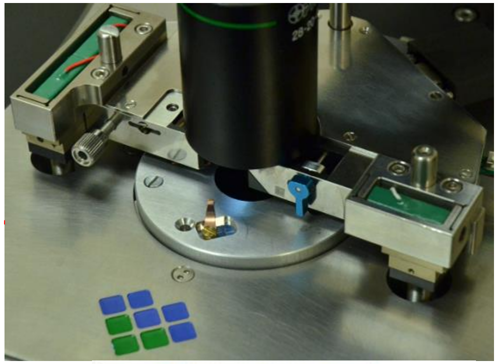
AFM system for PiFM and other modes

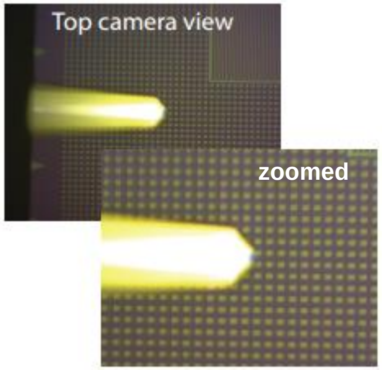
XYZ Sample Flexure Scanner

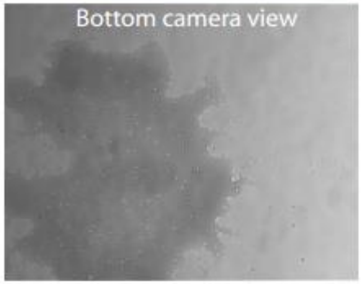
Motorized Focus

Motorized Sample Stage

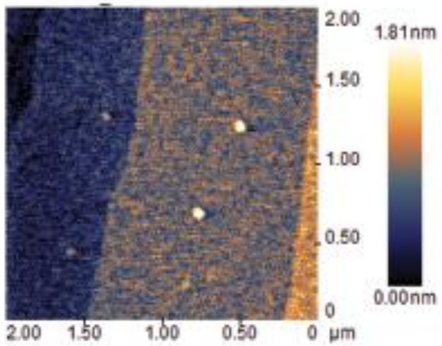
Motorized Approach



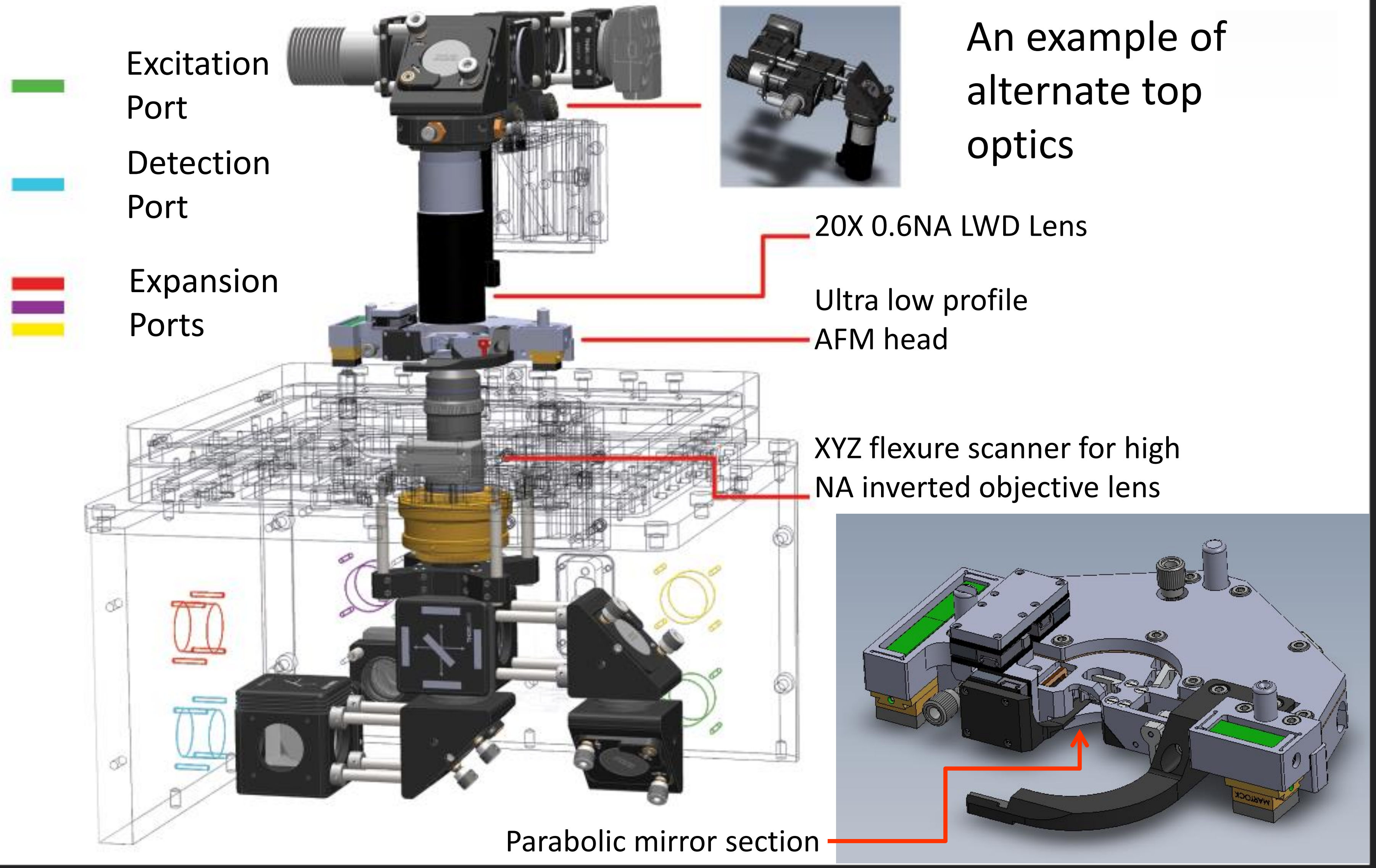




Raw AFM image of silicon atomic steps (0.314 nm per step)

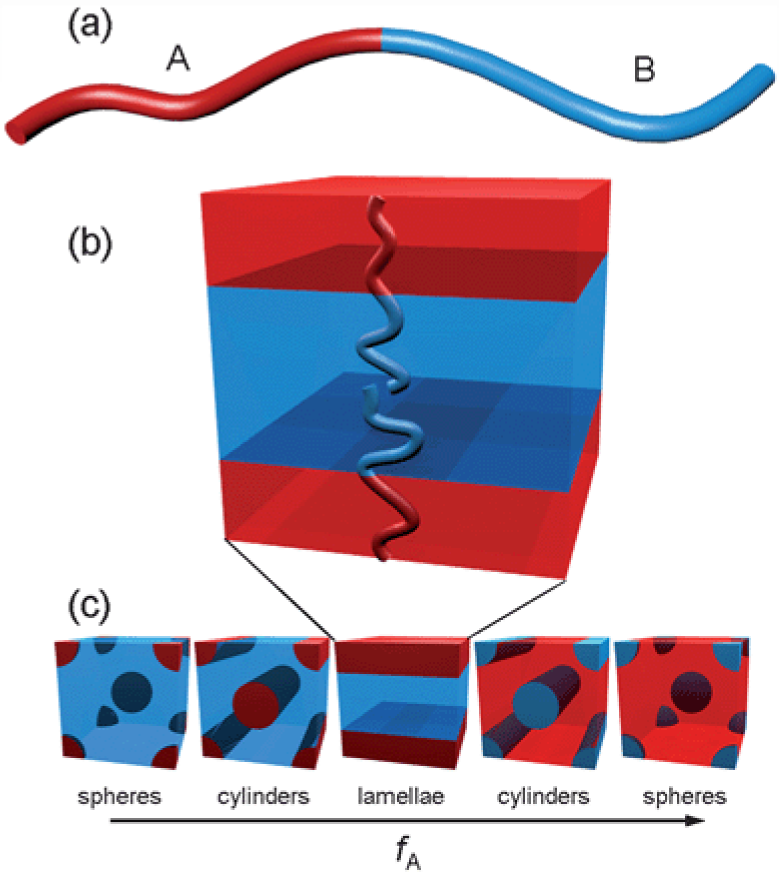


Optical system



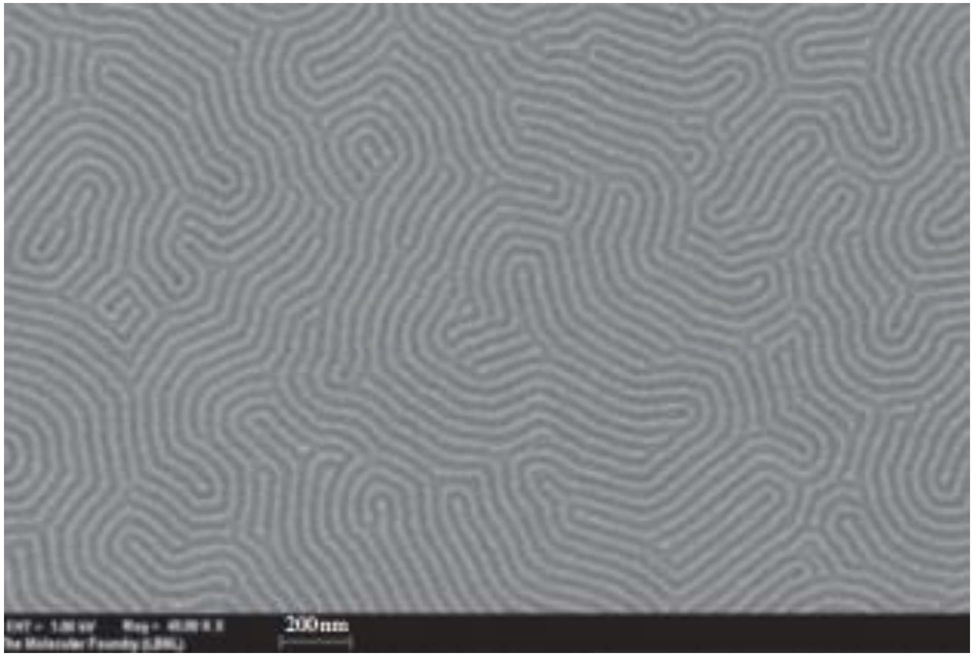
PiFM Applications and Results

Demo sample: Block copolymer patterns



S. Darling, ***Energy Environ. Sci.***, 2009,**2**, 1266-1273

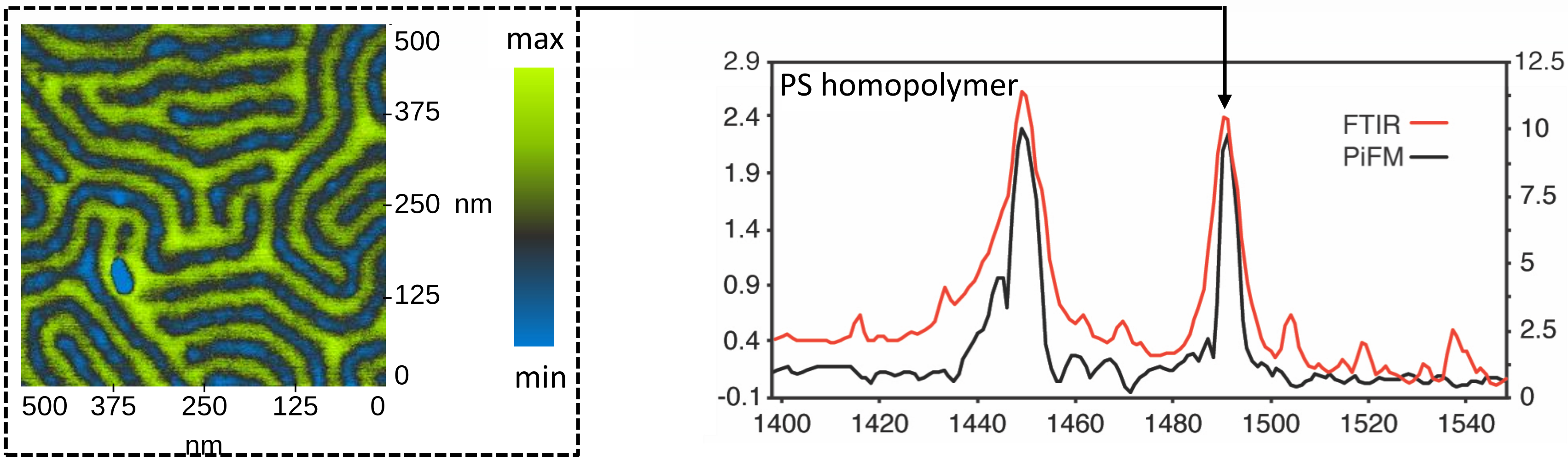
“Fingerprint” pattern of annealed thin film of lamellar block copolymer on Si substrate



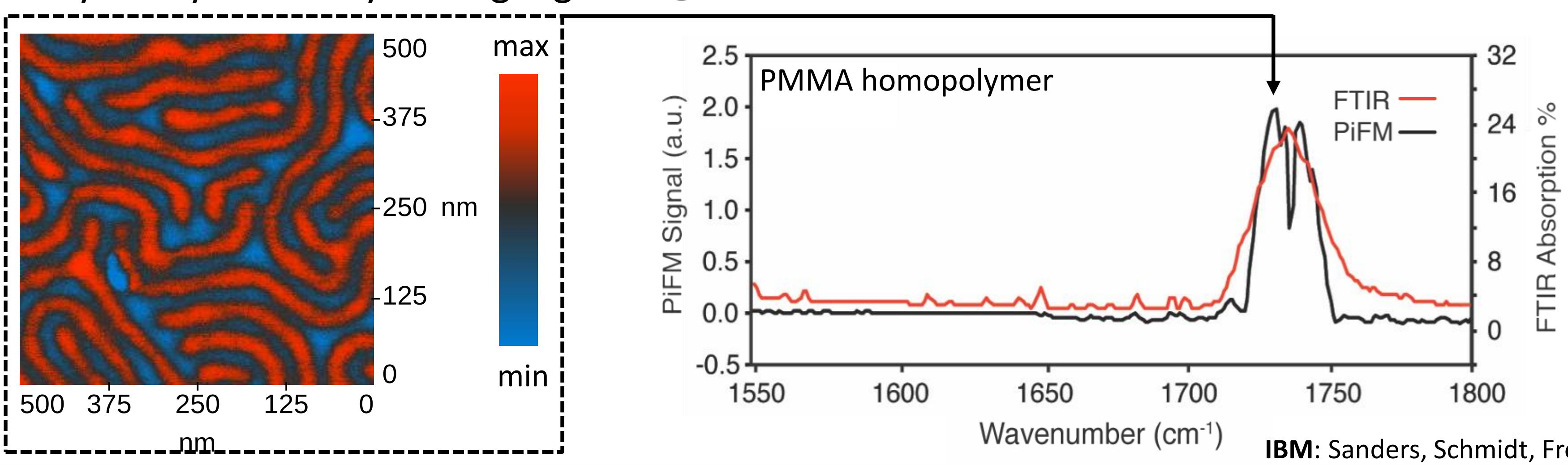
Gu et al., ***Adv. Mater.*** 24, 5505–5511

PiFM of PS-*b*-PMMA Block Copolymer (note image reversal)

Polystyrene highlighted @ 1490 cm^{-1}

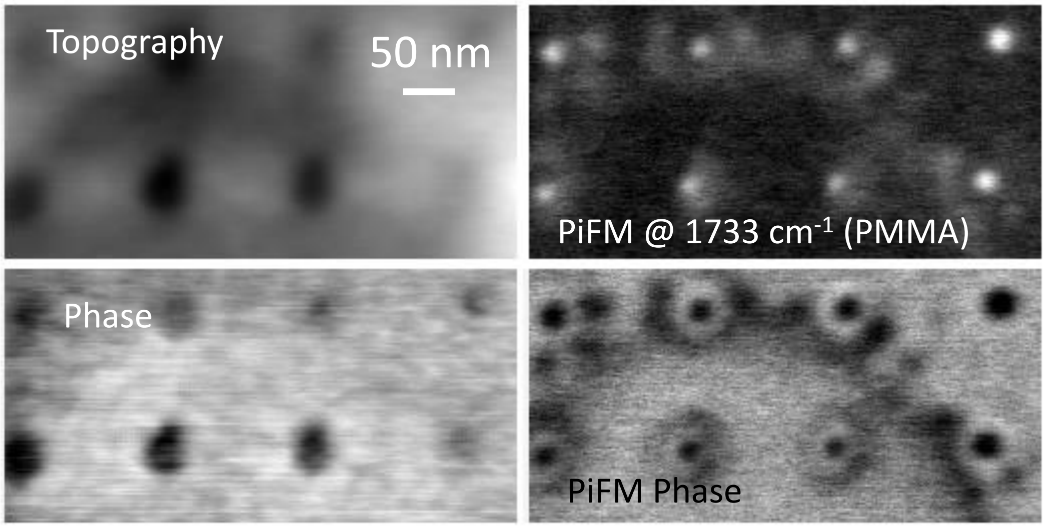


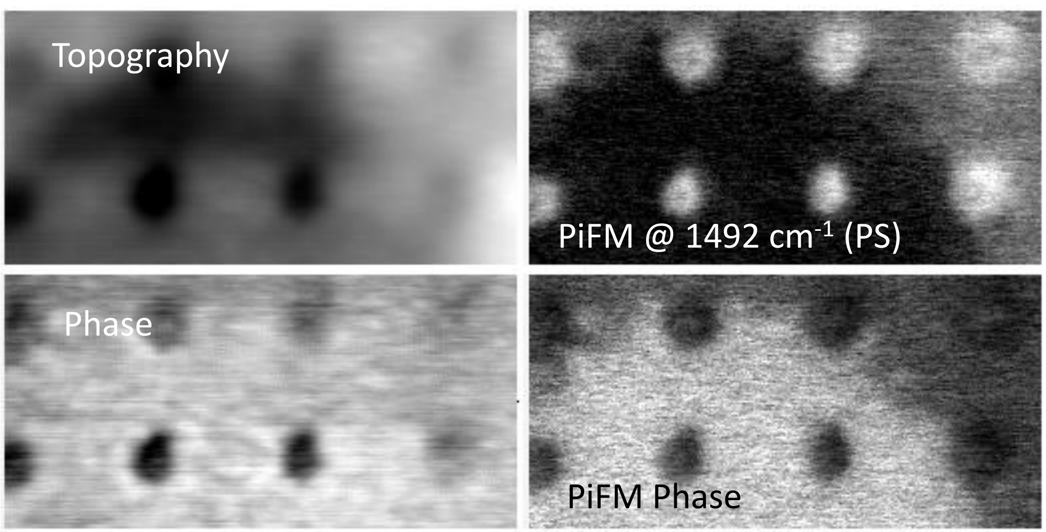
Polymethylmethacrylate highlighted @ 1733 cm^{-1}



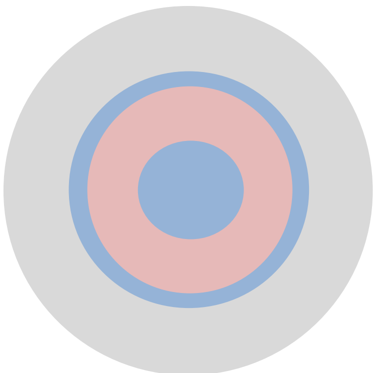
IBM: Sanders, Schmidt, Frommer

Spectral imaging PS-*b*-PMMA via structure

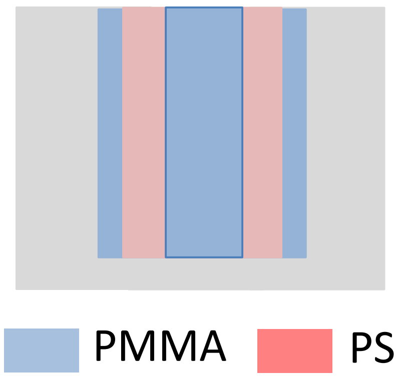




Via structure (top view)

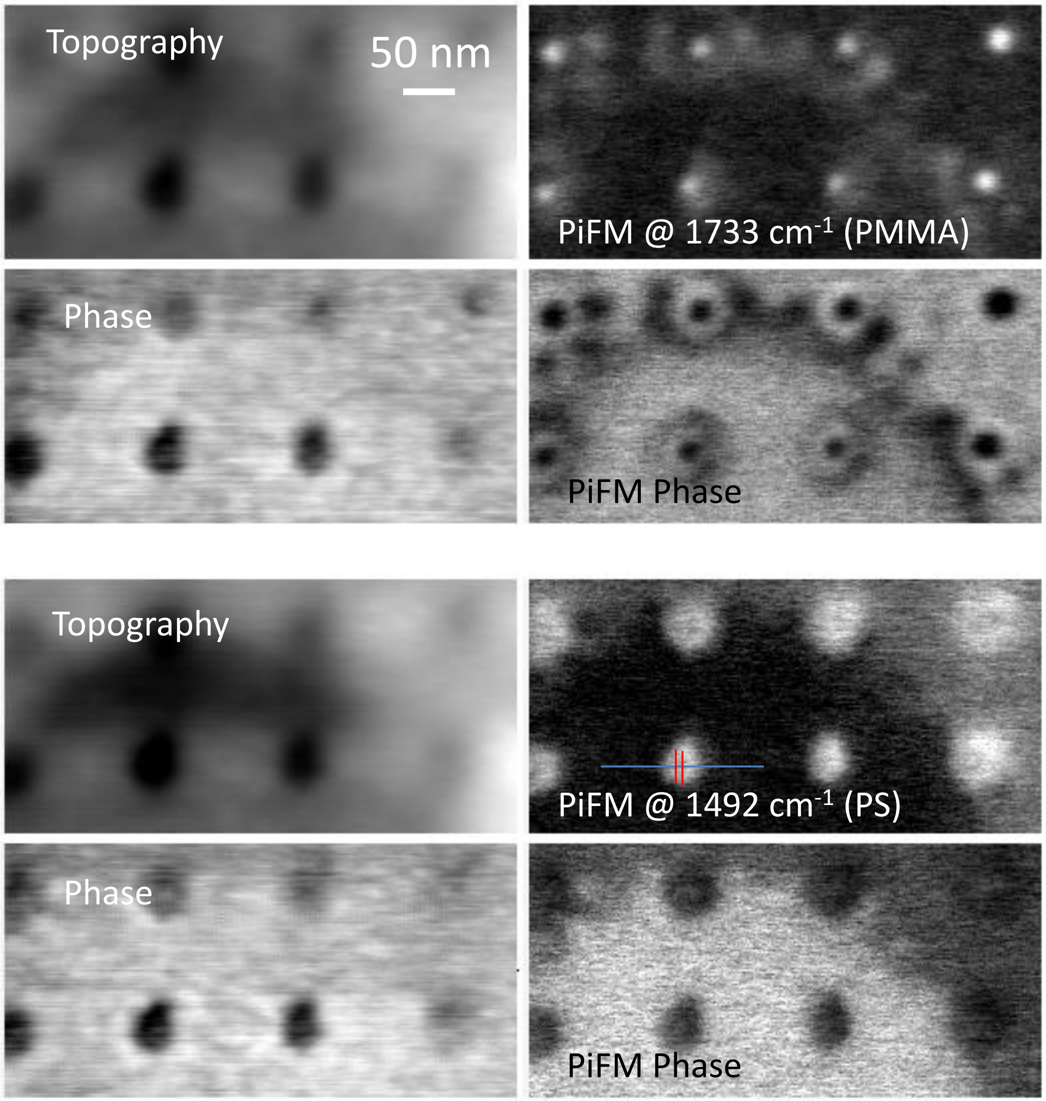


Via structure (side cutout view)

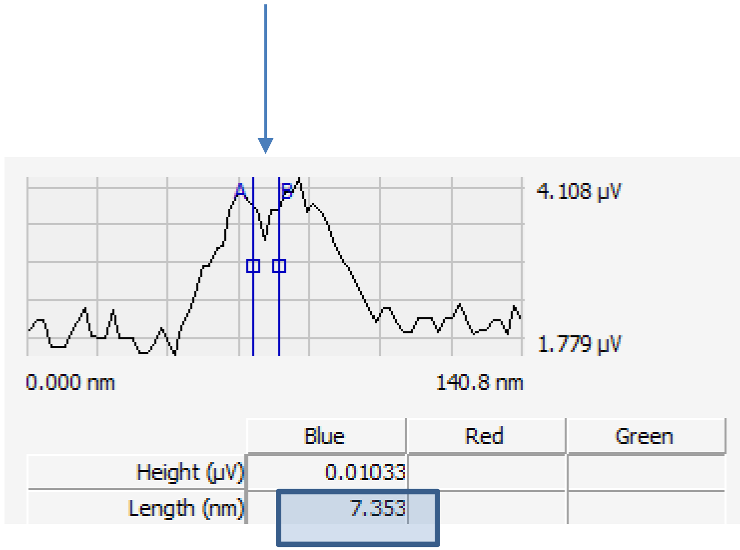


IBM: Dan Sanders, Kristin Schmidt, and Jane Frommer

Spectral imaging PS-*b*-PMMA via structure

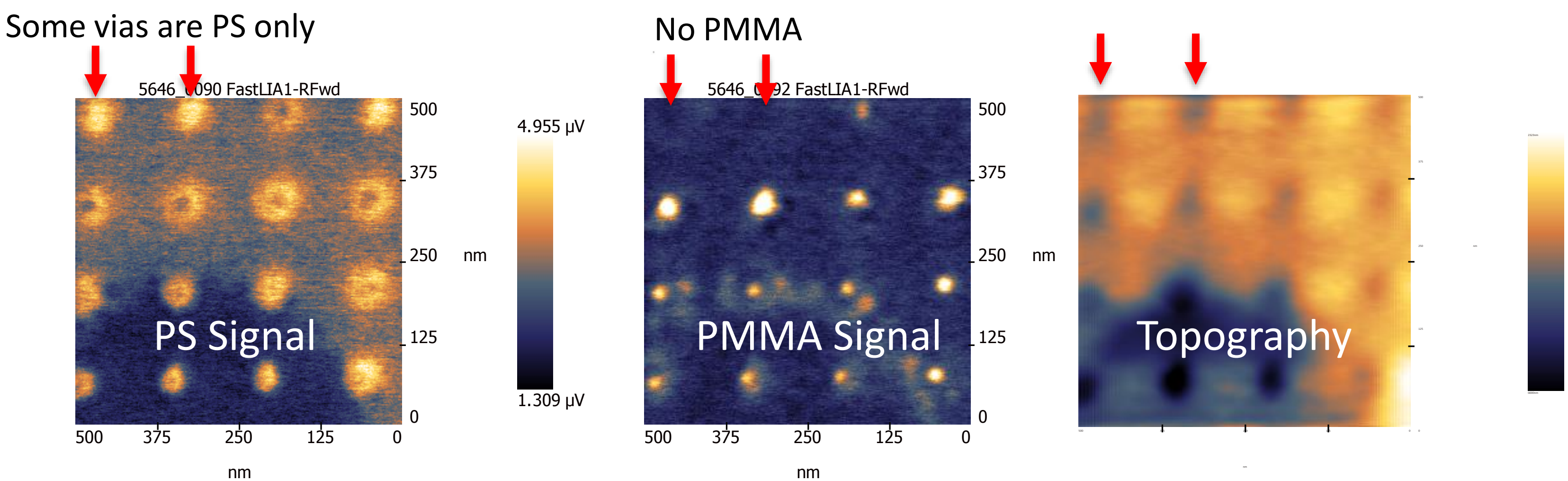


Resolving ~ 7nm PMMA Structure, which shows up as no signal since we are imaging at PS absorption band. On the PMMA image, it shows up as a ~12 nm feature.



Spectral imaging PS-*b*-PMMA via structure

Some of the features cannot be detected via topography at all as shown by the images below. In the top row, three of the four vias have no PMMA section, and it is only confirmed by chemical images since the topography looks the same for all the vias.

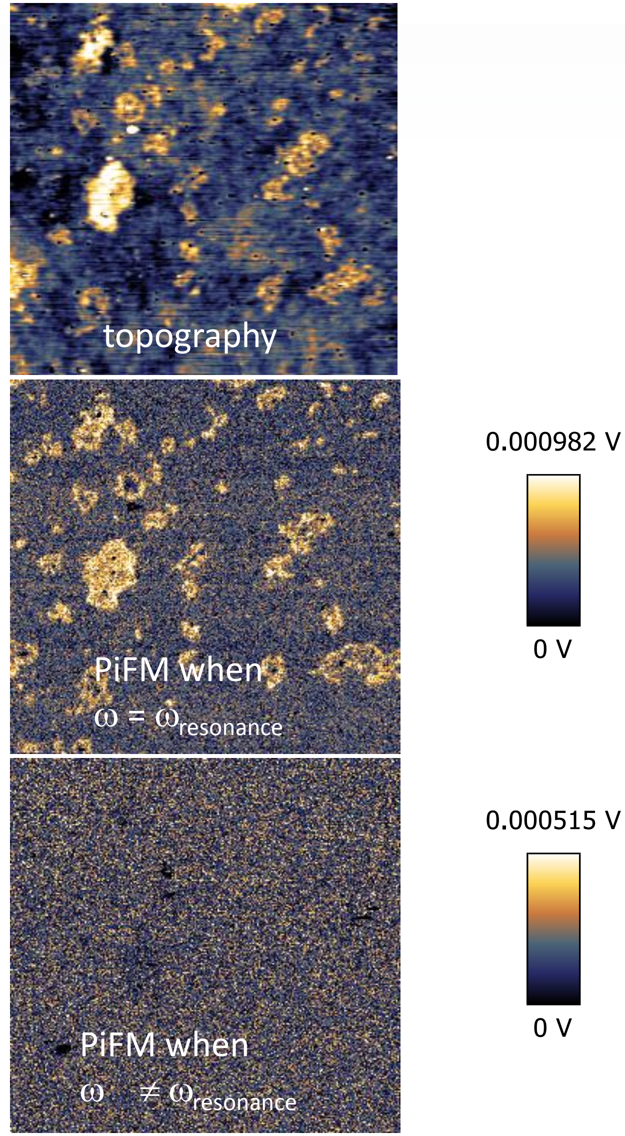


Visible PiFM (absorption band)

2 x 2 μm image of dye molecules (AF750)

764 nm

835 nm



Additional Applications of PiFM

We were not able to include all of the slides shown in the presentation here since some are part of pending publications. Please contact us for more detailed information about applications and results for PiFM.

tom@molecular-vista.com
sung@molecular-vista.com

PiFM Summary

- PiFM - directly measures polarizability via force
- Generates detailed optical absorption spectrum with nm-scale spatial resolution
- Non-contact method
- Works in visible and mid-IR spectrum
- Simplified optical setup with no far-field background signal
- Tip-to-tip reproducibility
- Not affected by thermal diffusion
- Can be combined with far-field (Raman, PL, etc.), near-field photon collection techniques (TERS, sSNOM), and scanning probe techniques (SKPM, Conductive AFM, etc.)