Near-Field Optics for Materials Characterization on the Nanoscale

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Measurement paradigms – materials analysis:

1) Serial:

- throughput (significantly) enhanced by automation/scanning.

  e.g., mass spec, chromatography screening.

2) Parallel:

- 2D array-based detection “views” entire library.

  e.g., IR thermography, hyperspectral imaging, anode-array REMPI.

⇒ ***Multitasking:***

- data on two or more distinct system properties using a single integrated measurement platform.
- serial or parallel based techniques.

  e.g., CCD-based detection of selective oxidation of naphthalene:

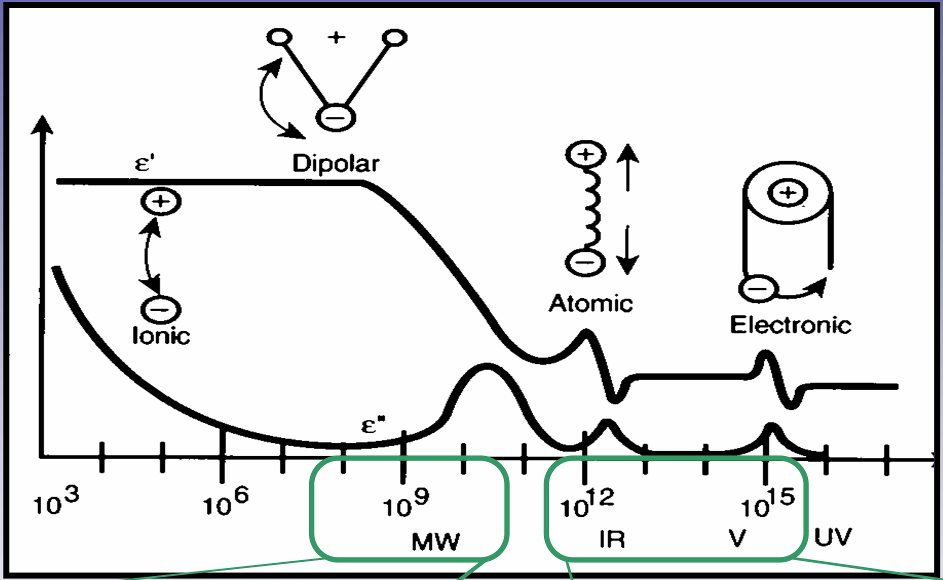
  LIF – reaction product; NIR emission – thermography

  (H. Su and E.S. Yeung; JACS ***122****, 7422, ’00;   H. Su, Y. Hou, R.S. Houk, G.L. Schrader and E.S. Yeung, Anal. Chem.* ***73****, 4434, ’01)*

Multitasking Probe: motivation and systems.

-Single instrument platform: *simultaneous* characterization of materials performance *and* properties.

- Dielectric thin films.



Targeted performance frequency range:

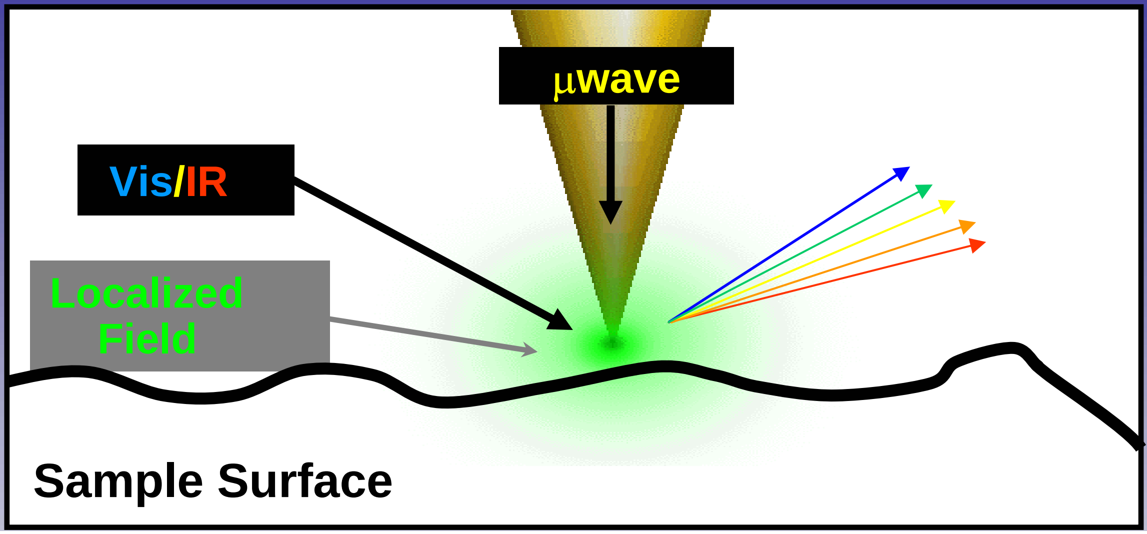
- High-ε mat'l: DRAM, capacitors, …
- Low-ε mat'l: next-generation Si, …

Probes of key materials properties:

- Structural: phase, stress, …
- Chemical: composition, impurities …

Integrated Multitasking/Multispectral Probe:

⇒ evanescent probe in the near-field; sharpened metal tip ≈10 nm from surface



1) Part of μwave cavity: materials performance by NSμM (Near-field Scanning Microwave Microscopy)

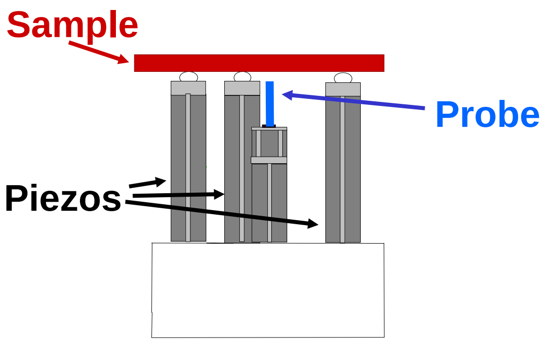
- dielectric loss spectroscopy.
- probes local complex dielectric constant, ε*.

2) External Vis/IR illumination: materials properties by aNSOM (apertureless Near-field Scanning Optical Microscopy)

- local field enhanced IR absorption/Raman scattering.
- probes local chemical functionality/structure.

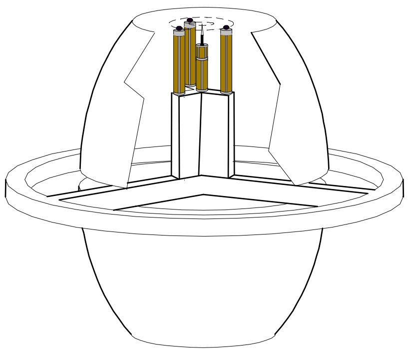
Instrumentation: fully-integrated system (not yet realized)

Probe Positioning/Scanning:

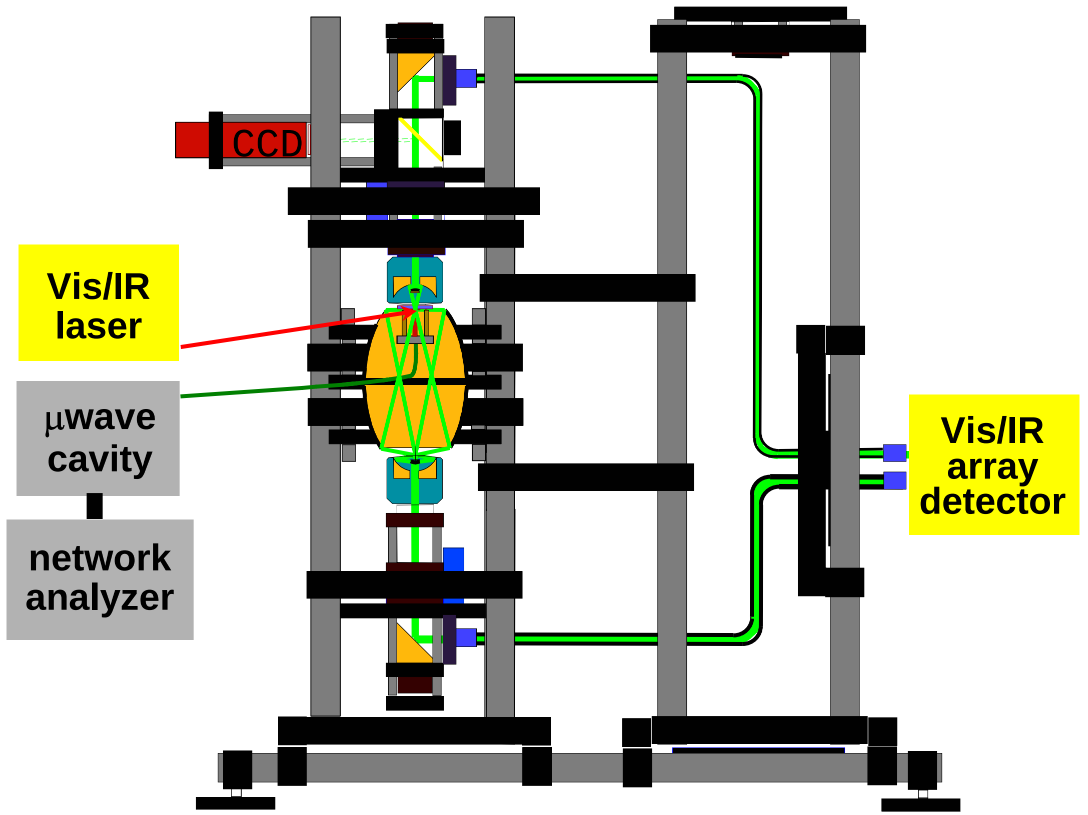


Shear Force Microscopy

Gold-coated ellipsoidal cavity for light collection:



Multitasking aNSOM/NSμM:

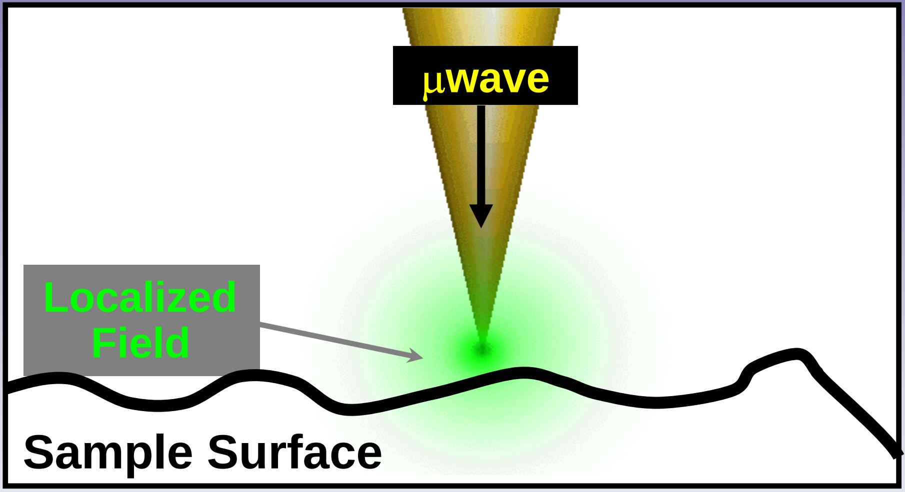


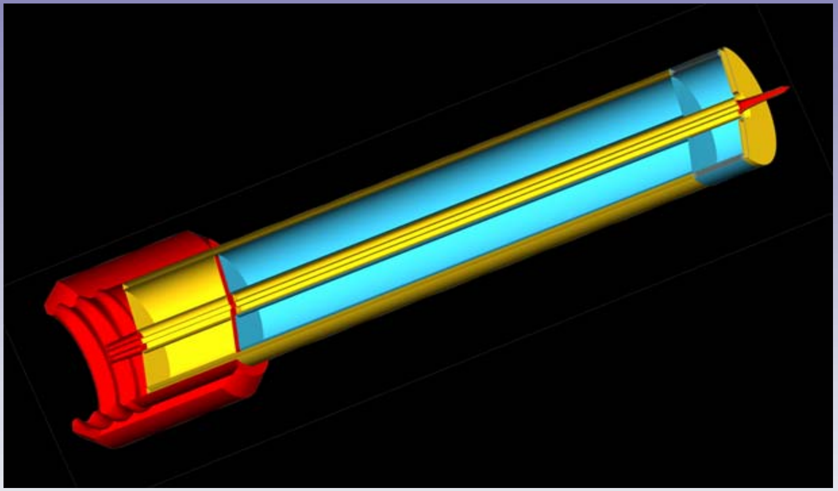
1) NSμM – Near-field Scanning Microwave Microscopy:

Developed in the mid ’90s:

- X.-D. Xiang – LBNL; S.M. Anlage, F.C. Wellstood – U. Maryland
- Used primarily for HTS/HTE of advanced oxide materials:

  e.g., APL **72**, 2185 (’98); Mat.Sci. Eng. B. **56**, 246 (’98); Biotech. Bioeng. **61**, 227 (’99).





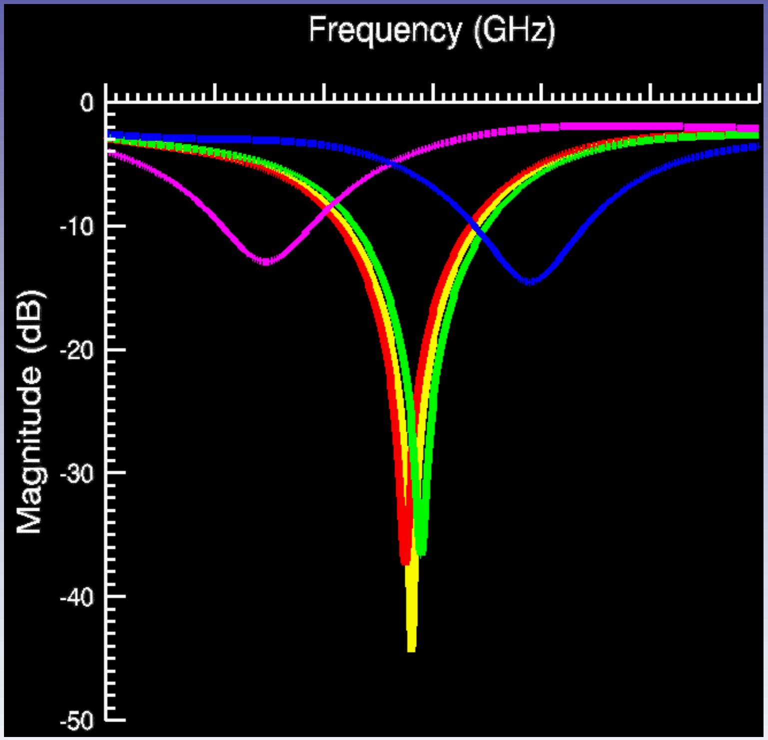
<u>Advantages:</u>

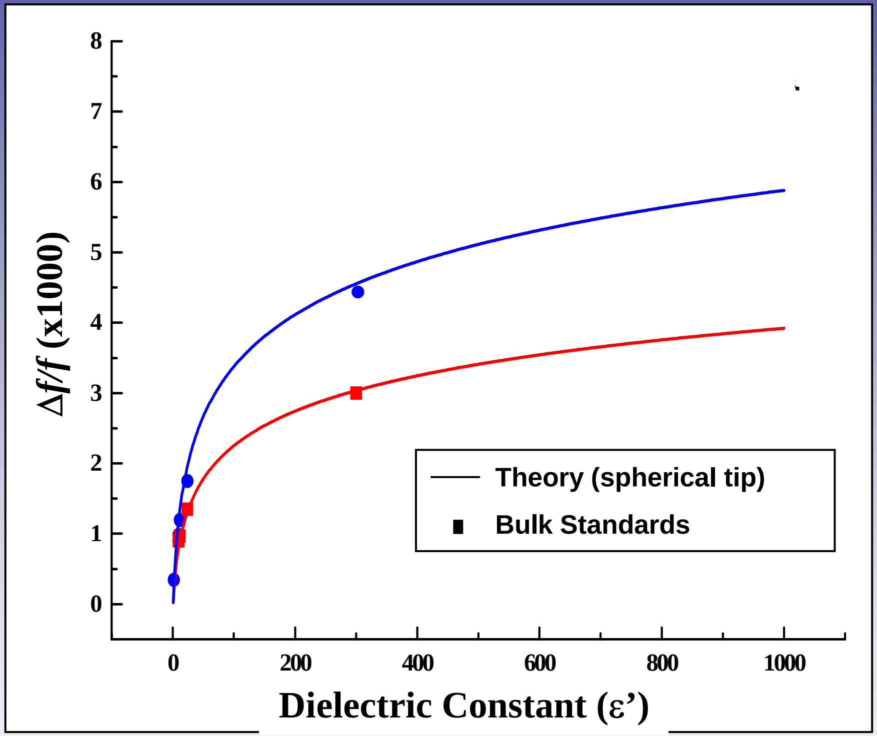
1) Non-contact
2) Sample geometry independent
3) Thin film samples

⇒ Suitable for HTS/HTE.

Dielectric Imaging: NSμM

- By measuring the frequency shift/broadening of the microscope's cavity response, the dielectric constant can be determined.

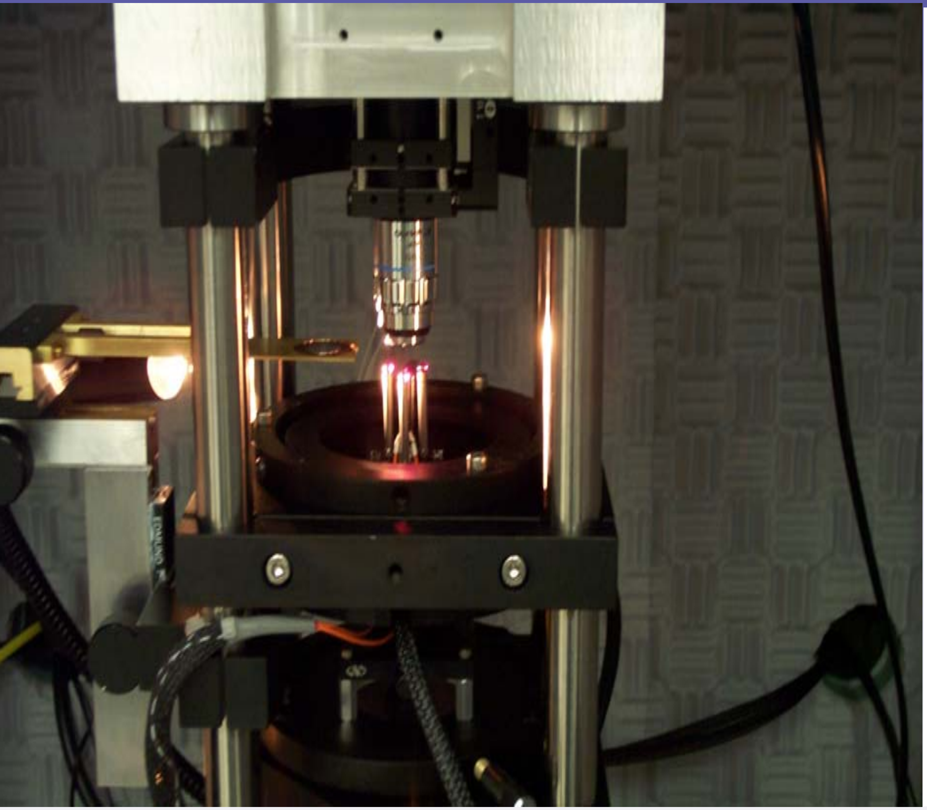




Spatial resolution ⇒ probe shape/radius; height from sample surface.

ε* precision ⇒ Δf/f and cavity Q.

Near-field Scanning Microwave Microscope:



- **Diffraction-limitless resolution.**
  (~ 100 nm in xyz)

- **Shear-force feedback height regulation.**
  (typically 10-50 nm)

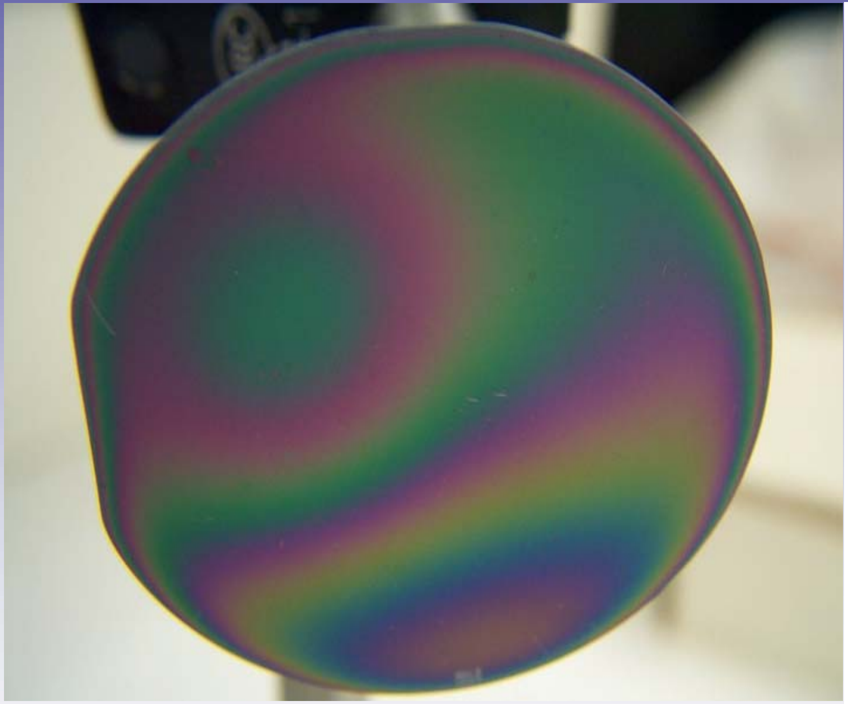
- **Broadband Measurement.**
  (45 MHz to 20 GHz)

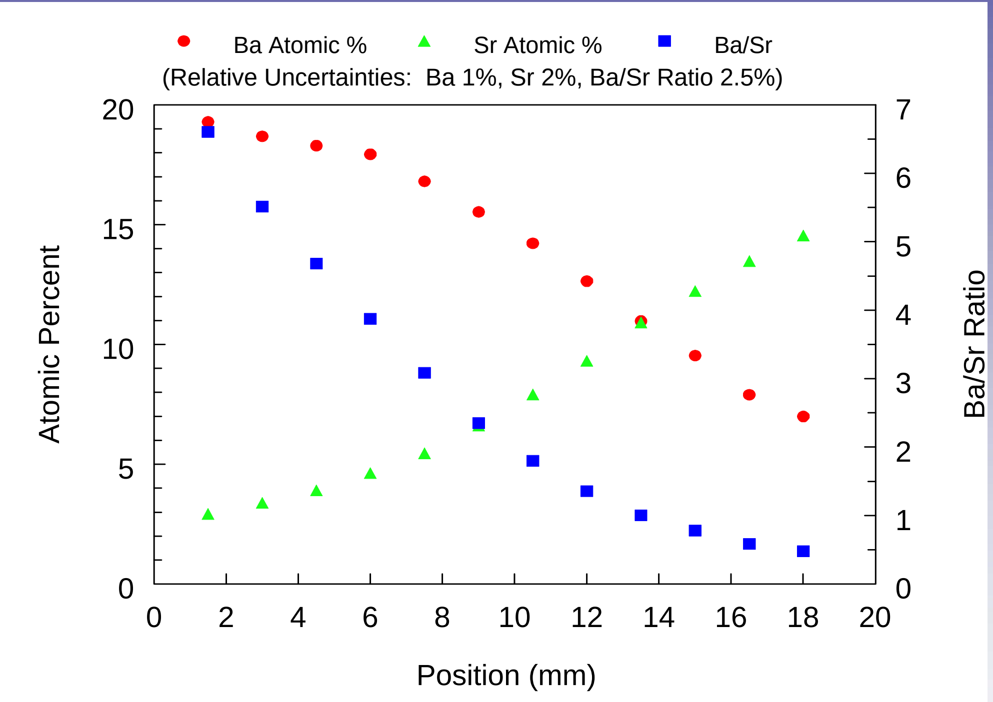
- **Network analyzer: $\Delta f/f \approx 10^{-5}$ to 10^{-6}.**
  (ε to about 1-5 %)

Demonstration of NSμM:

- continuous compositional gradient Barium Strontium Titanate (BST) film.
- prepared by dual-beam pulsed laser deposition:

P.K. Schenck, D.L. Kaiser and B. Hockey of MSEL/NIST

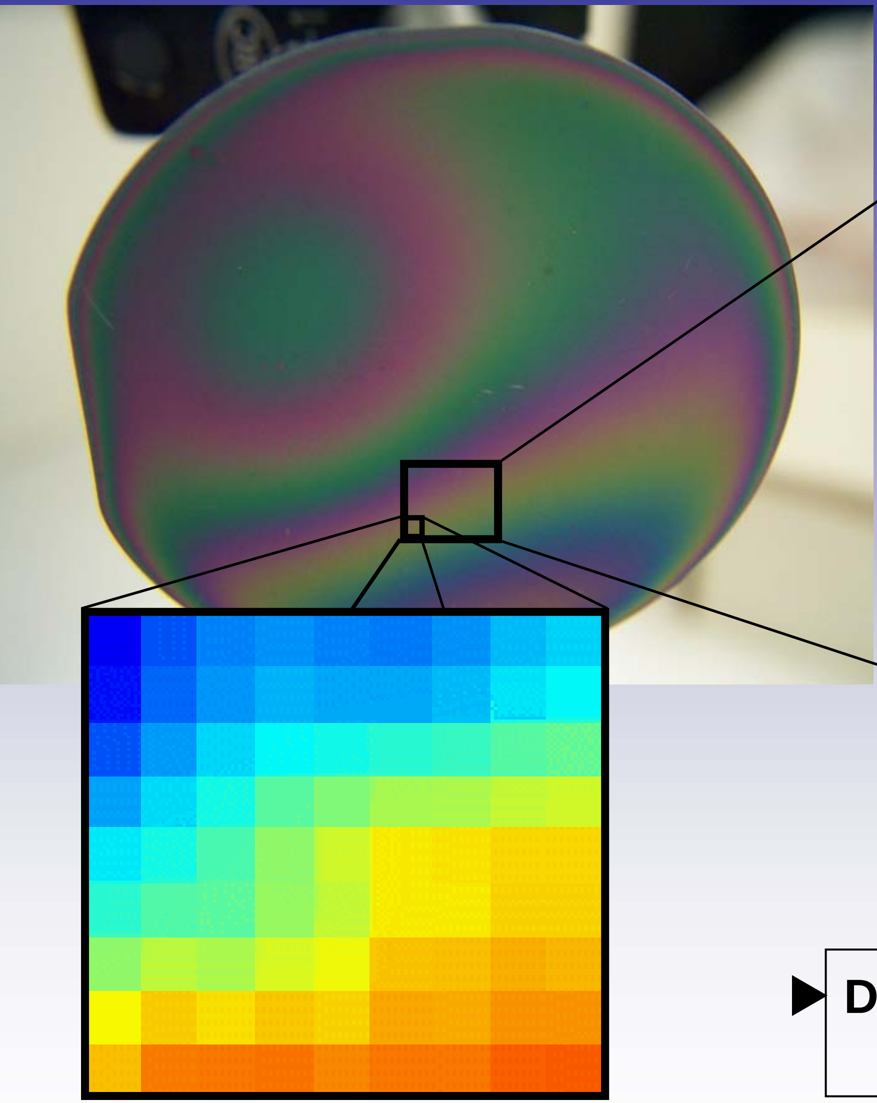


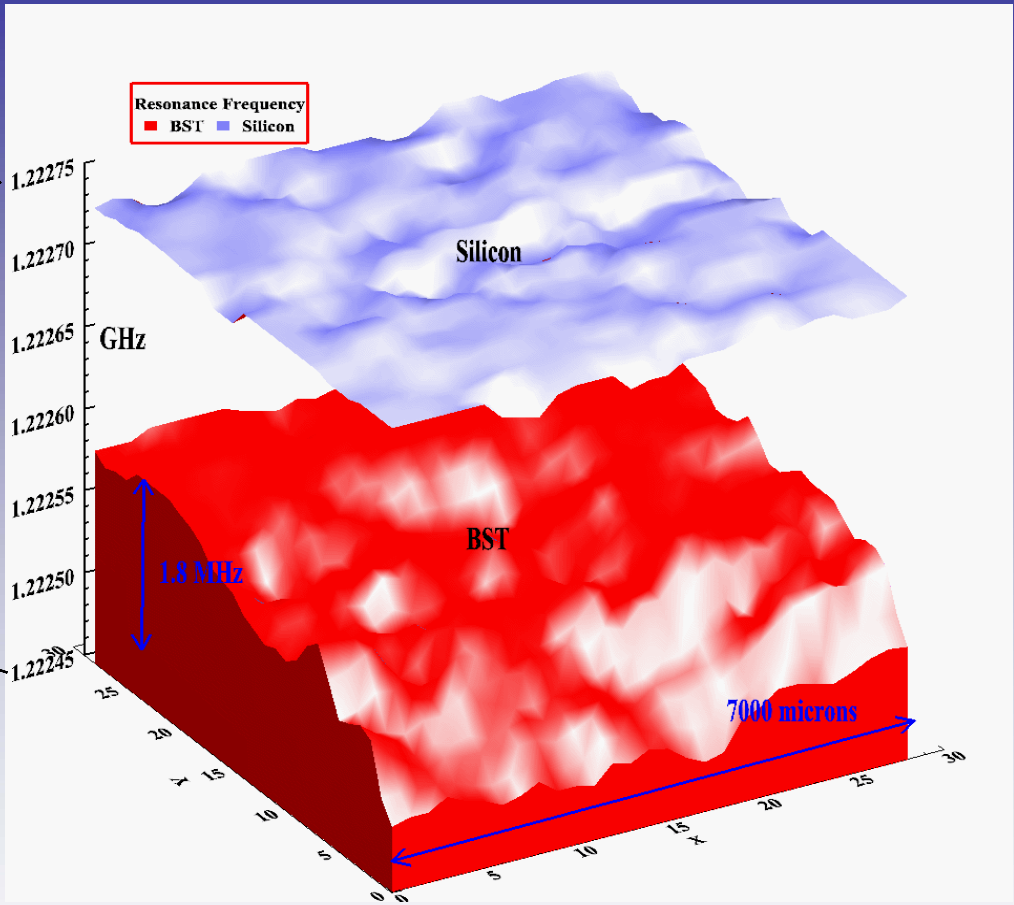


- Film thickness variation is evident.
- Quantitative analysis by spectrometric reflectometry.

- Compositional gradient quantified by wavelength-dispersive electron probe microanalysis: *R.B. Marinenko and J.T. Armstrong of CSTL/NIST.*

Dielectric Response Mapping using NSμM:

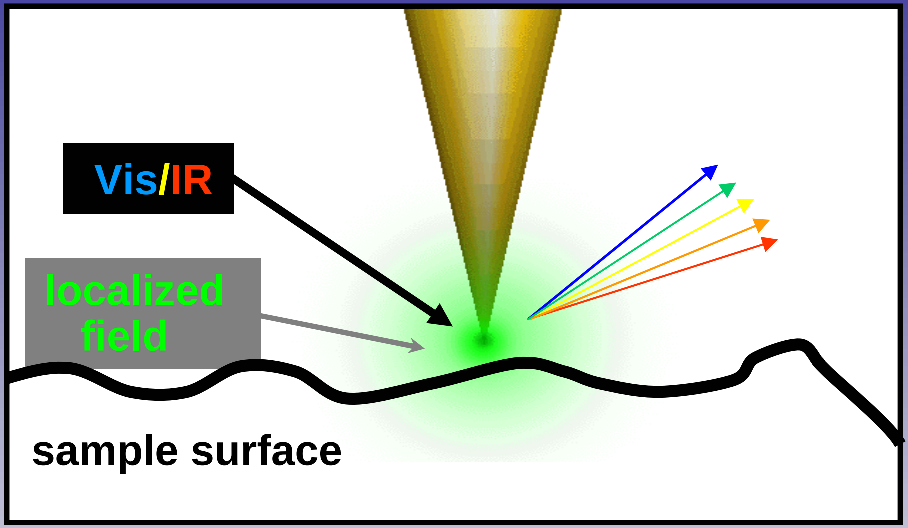




Dielectric response dominated is by film thickness variations.

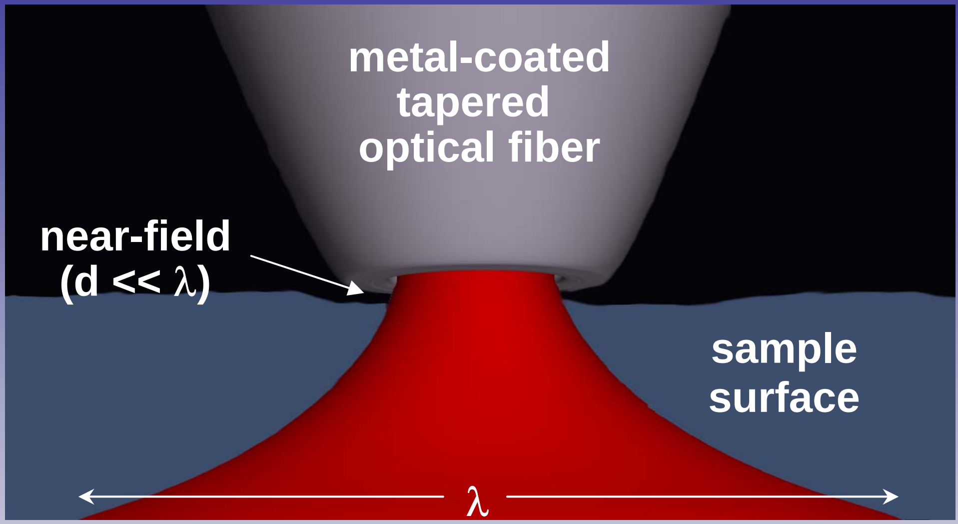
2) aNSOM - apertureless Near-field Scanning Optical Microscopy

aNSOM



Wickramasinghe, IBM '94; Kawata, Osaka U. '94

Fiber-coupled NSOM



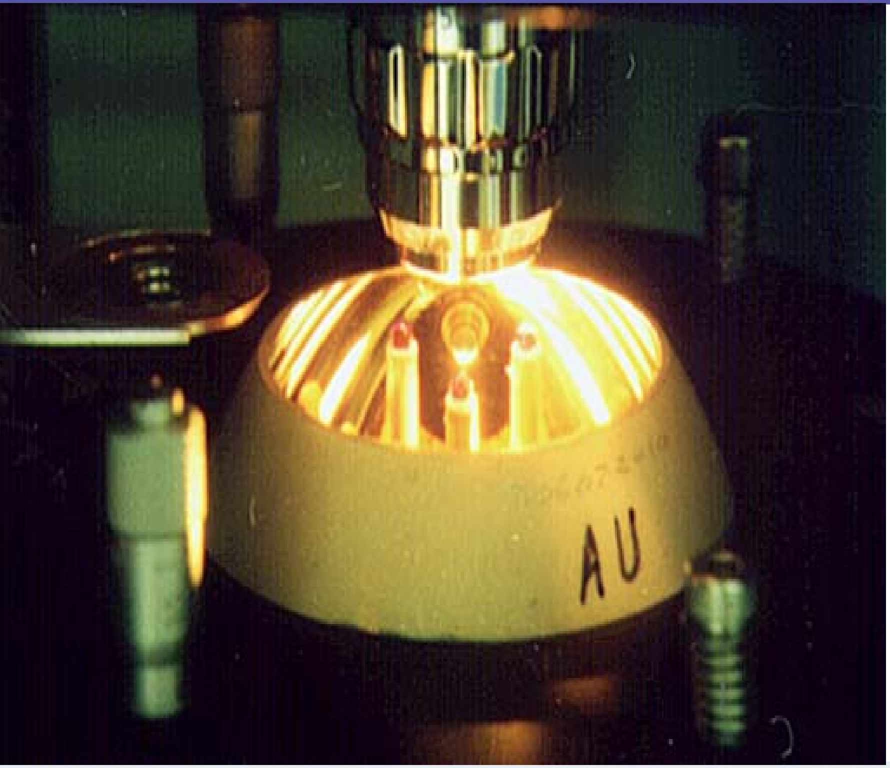
Pohl, IBM '83; Lewis, Cornell U., '83

Similarities:
- near field scanned probe
- subwavelength resolution
- chemical imaging/spectroscopy

Differences:
- radiation coupling
- accessible wavelengths
- resolution: < 10 nm vs < 100 nm

NIST; chemical-imaging using fiber-coupled Raman NSOM:
results illustrate expectations for aNSOM in multitasking application

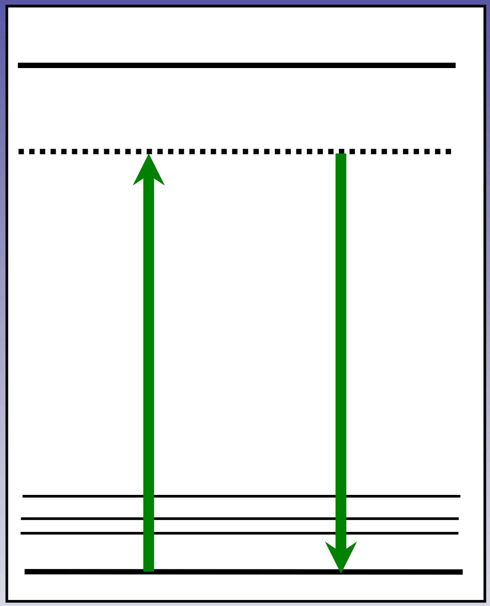
Fiber-coupled NSOM:



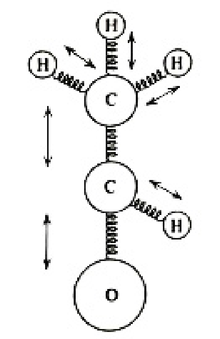
- **Diffraction-limitless resolution.**
  (~ 100 nm lateral)
- **Shear-force feedback height regulation.**
  (typically 10-50 nm)
- **NUV to NIR** ***(0.3 – 1 μm; Raman)***
  IR ***(2.5 – 10 μm; IR absorption)***
- **Hyperspectral imaging.**
  (spectrum at each spatial pixel)

Raman Scattering Spectroscopy/NSOM:

Rayleigh Scattering
(Elastic Process)

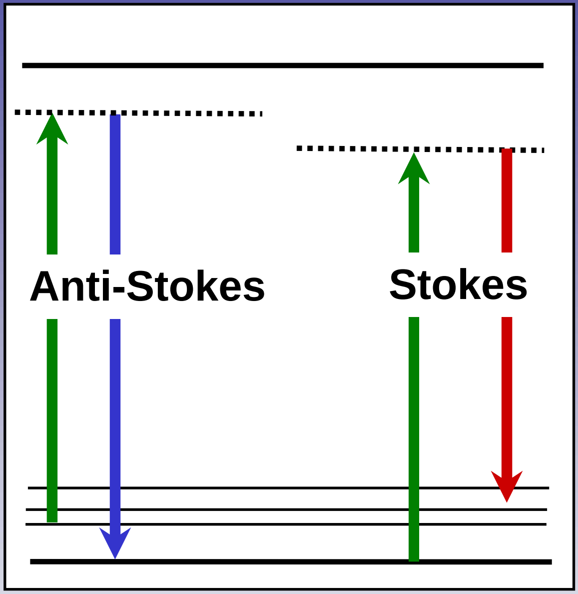


Molecular Excited State
(Virtual Excited State)



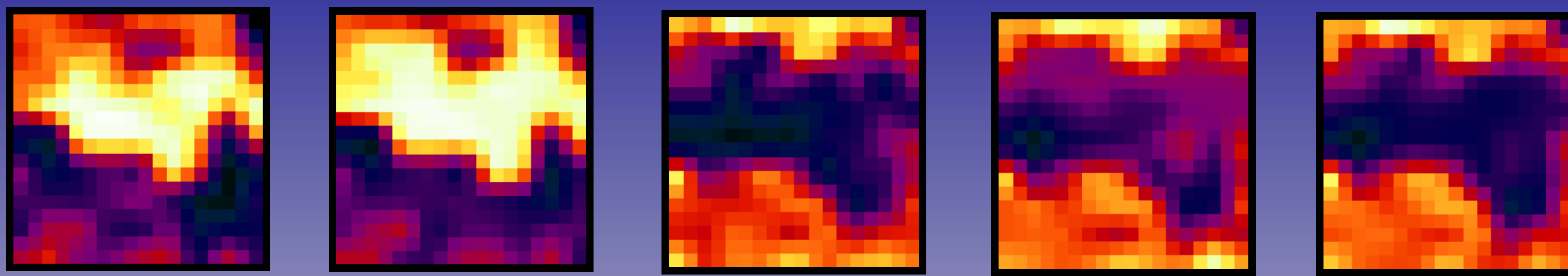
Vibrational Energy Levels
Molecular Ground State

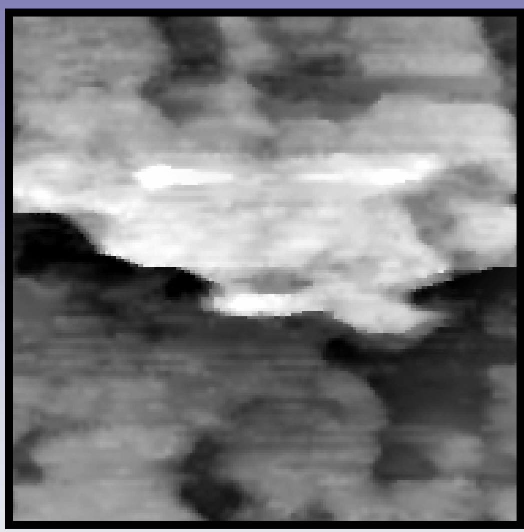
Raman Scattering
(Inelastic Process)



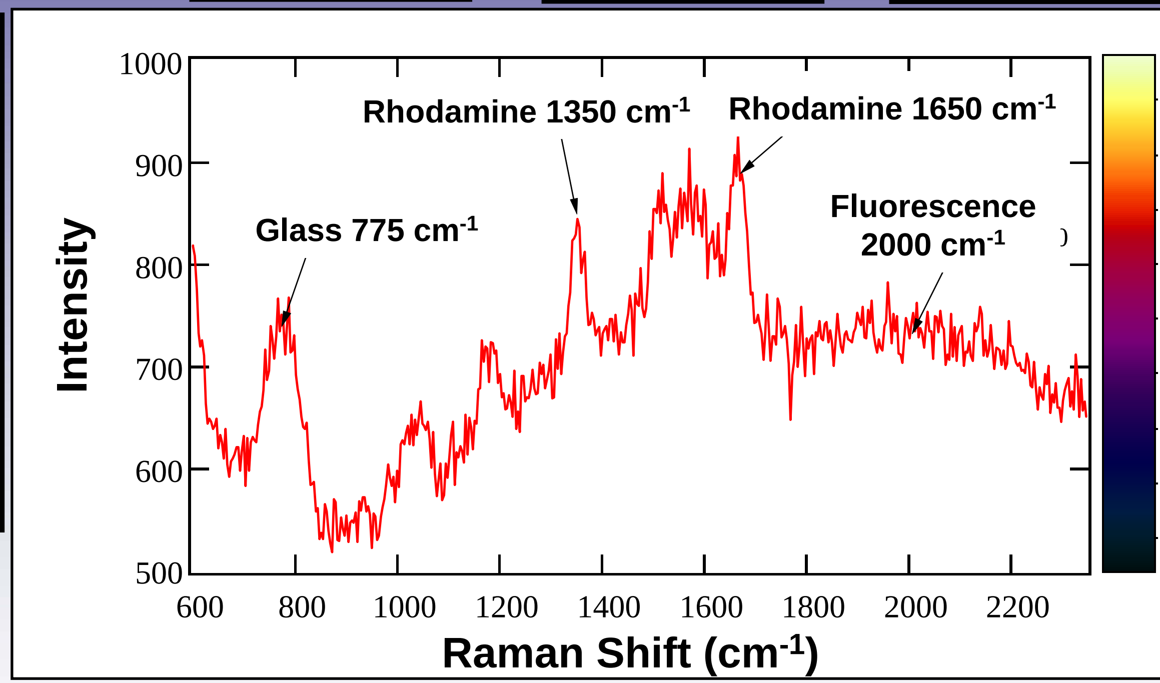
☺
- **Highly specific chemical information/species and structure.**
- **Visible lasers/"standard" fiber optics.**

☹
- **Inefficient process: only one in 10^{13} photons Raman scatter.**
- **NSOM probes have low throughput: ~ 10^{-5} - 10^{-6}.**





Shear- force Image
3 μm x 3 μm



- **50 nm Ag film on glass, 0.7 μMol Rhodamine-B sol.**

Summary:

Program Goal - multitasking scanned probe for HTE/HTS:

- *simultaneously* obtain data for materials **performance** (dielectric constant) *and* **properties** (chemical composition/structure).
- targeting continuous compositional gradient materials libraries with performance/property variation on a sub-μm length scale.

Integrated NSμM/aNSOM platform:

- not yet fully realized.
- have demonstrated independently the workability of Raman/IR fiber-coupled NSOM and NSμM on (nearly) identical platforms.
- work towards demonstrating Raman-based aNSOM and improving NSμM performance.