Multispectral Imaging for Materials Analysis

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1901 - 2001
NIST CENTENNIAL

Measurement paradigms – materials analysis:

1) Serial:

- throughput (significantly) enhanced by automation/scanning.
- e.g., mass spec, chromatography screening.

2) Parallel:

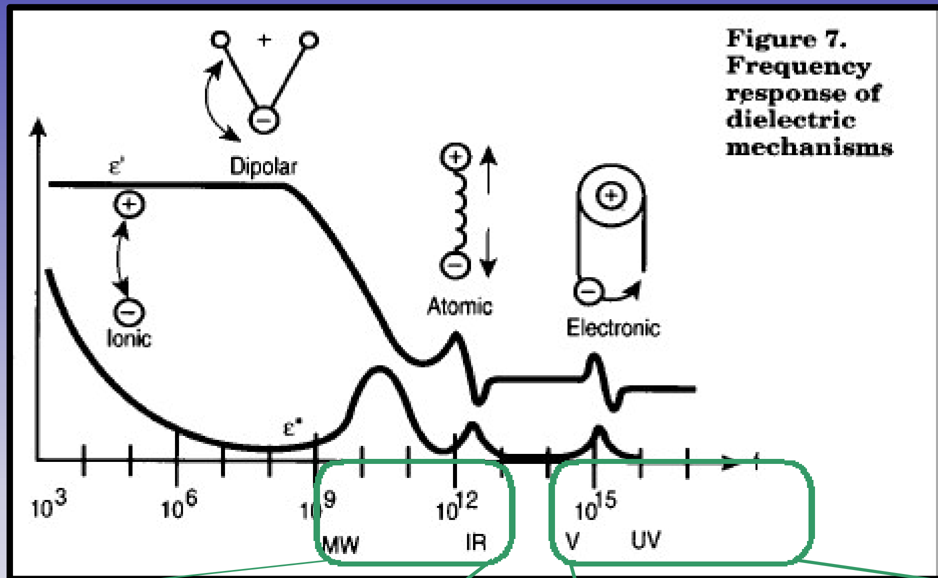
- 2D array-based detection "views" entire library.
- e.g., IR thermography, hyperspectral imaging, anode-array REMPI.

• **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: materials performance and properties.
- Dielectric thin films.



Targeted performance frequency range:

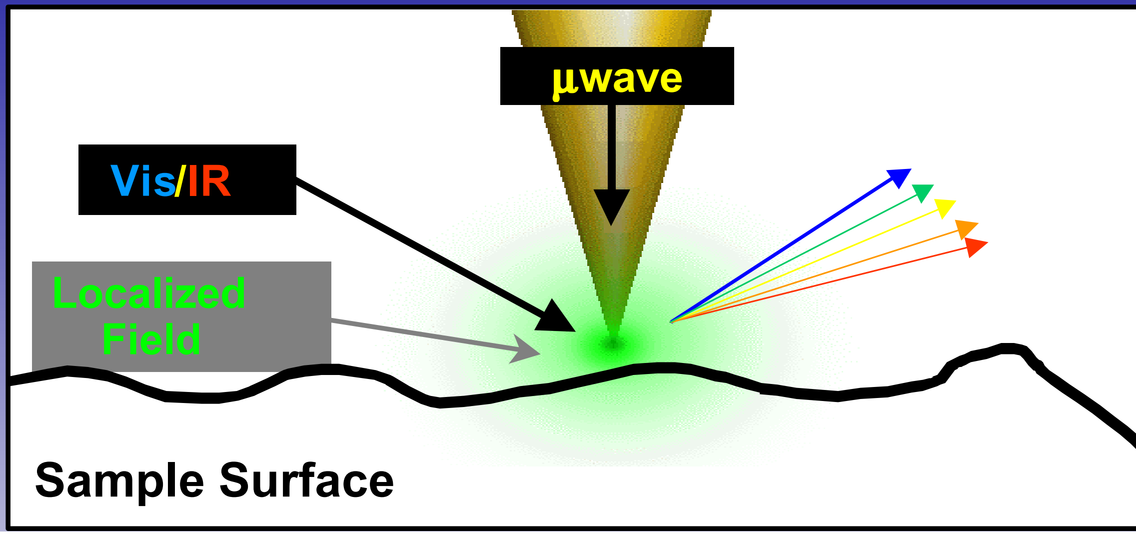
- ➢High-ε mat'l: DRAM, capacitors, …
- ➢Low-ε mat'l: next-generation Si, …

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

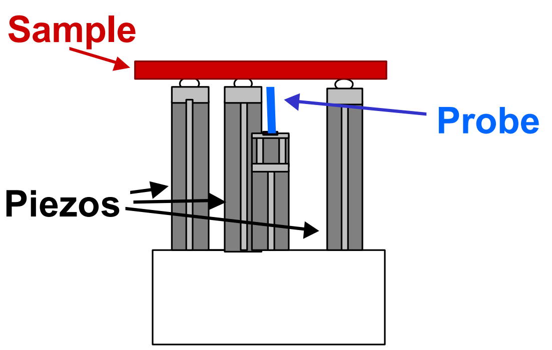


1) **Part of µwave cavity: materials performance by NSµM (Near-field Scanning Microwave Microscopy)**
   - dielectric loss spectroscopy.
   - probes local complex dielectric constant.

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.

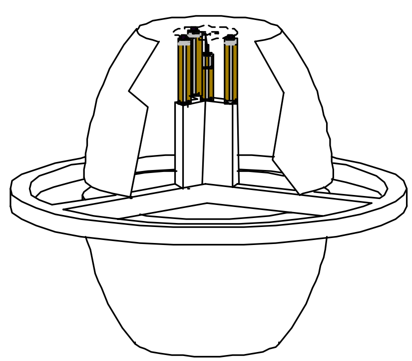
Instrumentation: fully-integrated system (not yet realized !)

Probe Positioning/Scanning:

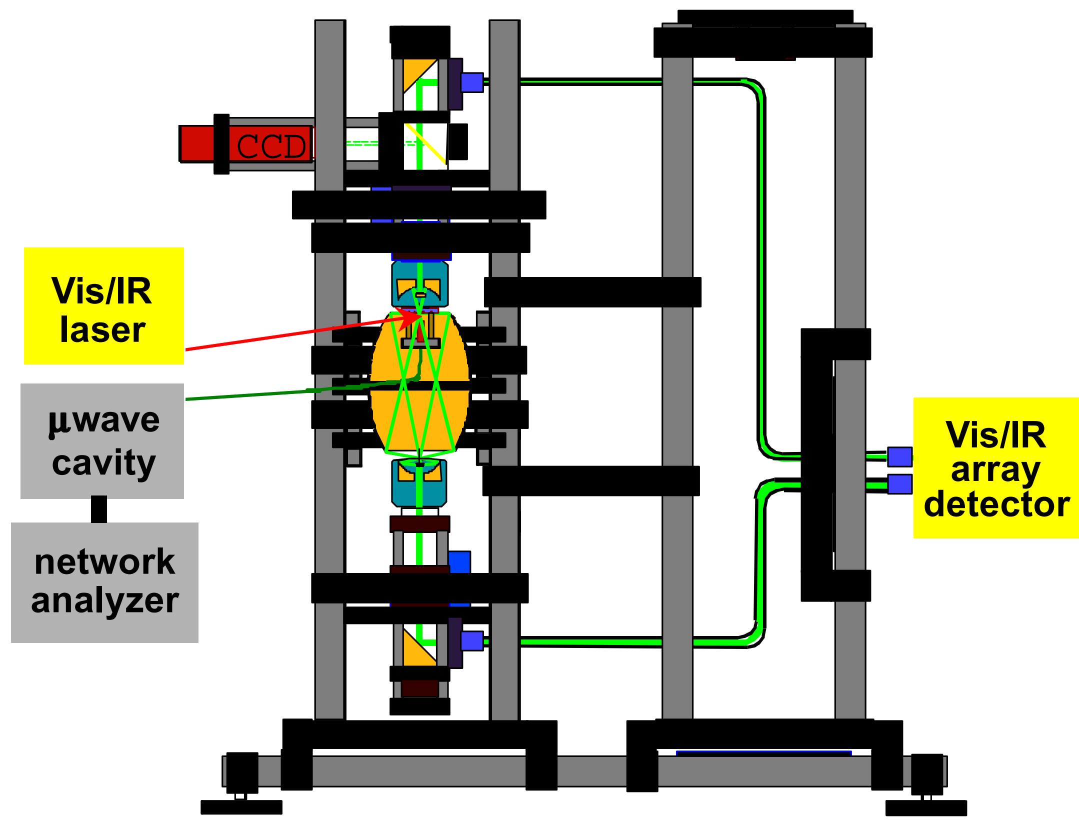


Shear Force Microscopy

Gold-coated ellipsoidal cavity for light collection:



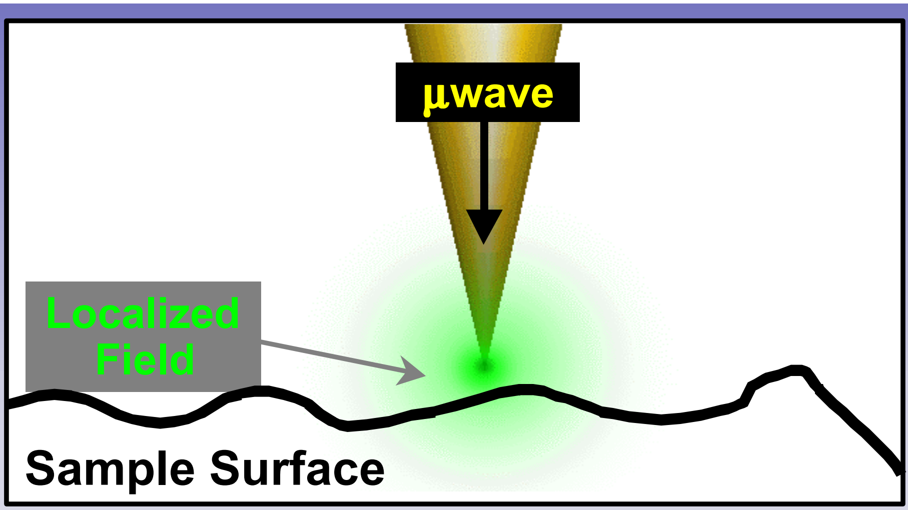
Multitasking aNSOM/NSµM:

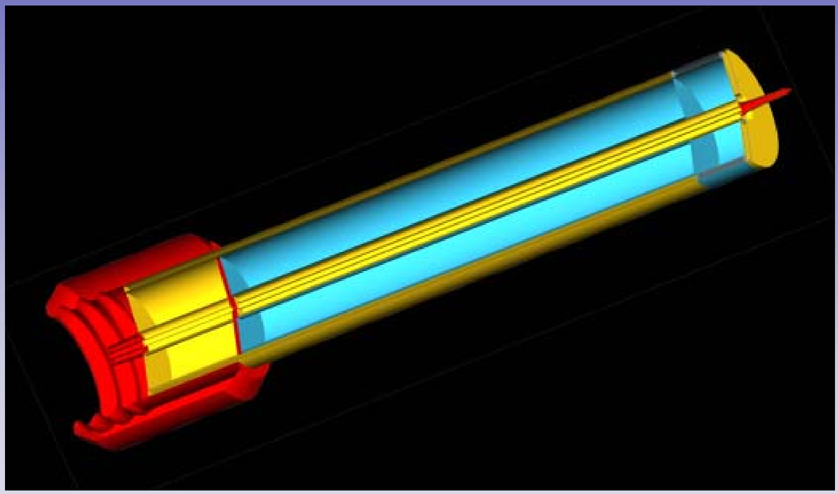


1) NSµM – Near-field Scanning Microwave Microscopy:

Developed in the mid '90s:

- X.-D. Xiang – LBNL; S.M. Anlage, F.C. Wellstood – U. Maryland
- Used by Xiang *et al.* for HTS/HTE of advanced oxide materials:
  APL **72**, 2185 ('98); Mat.Sci. Eng. B. – Sol. **56**, 246 ('98); Biotech. Bioeng. **61**, 227 ('99).





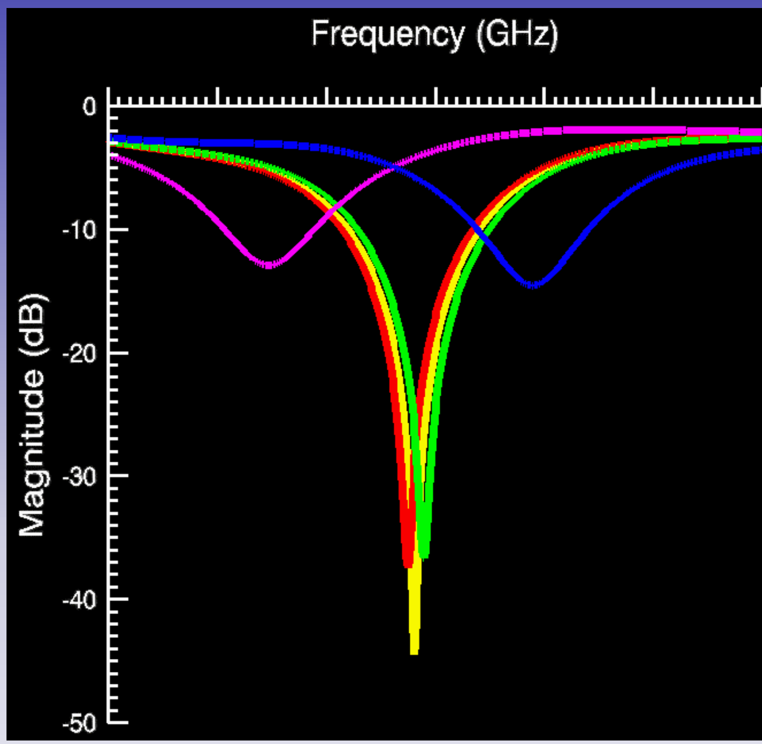
Advantages:

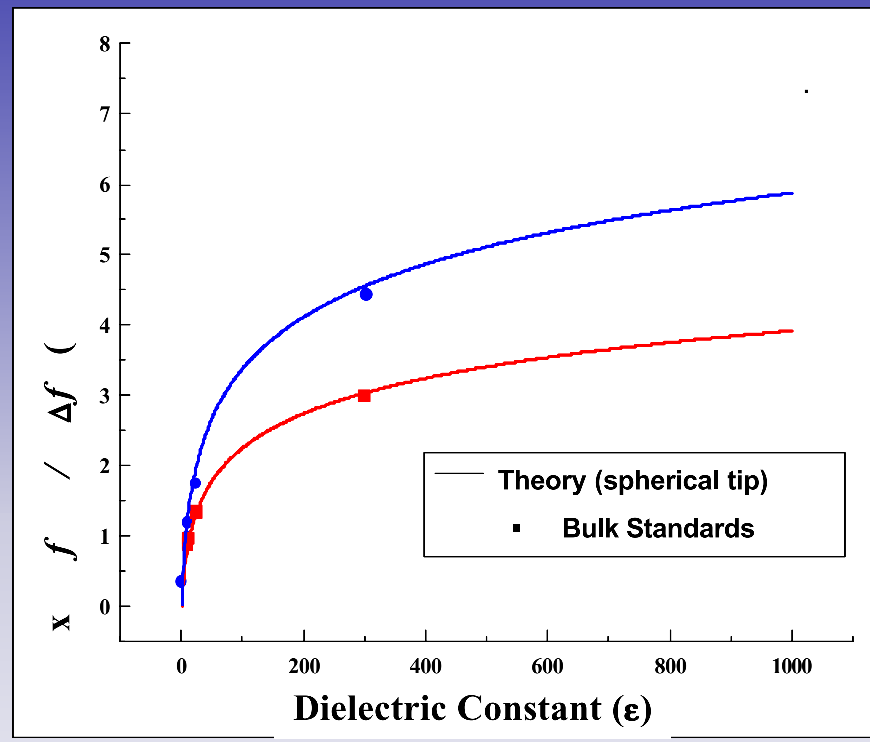
1) **Non-contact**
2) **Sample geometry independent**
3) **Thin film samples**

⇒ Suitable for HTS/HTE.

Dielectric Imaging: NSμM

- By measuring the frequency shift of the microscope's resonant cavity, a dielectric response can be determined.

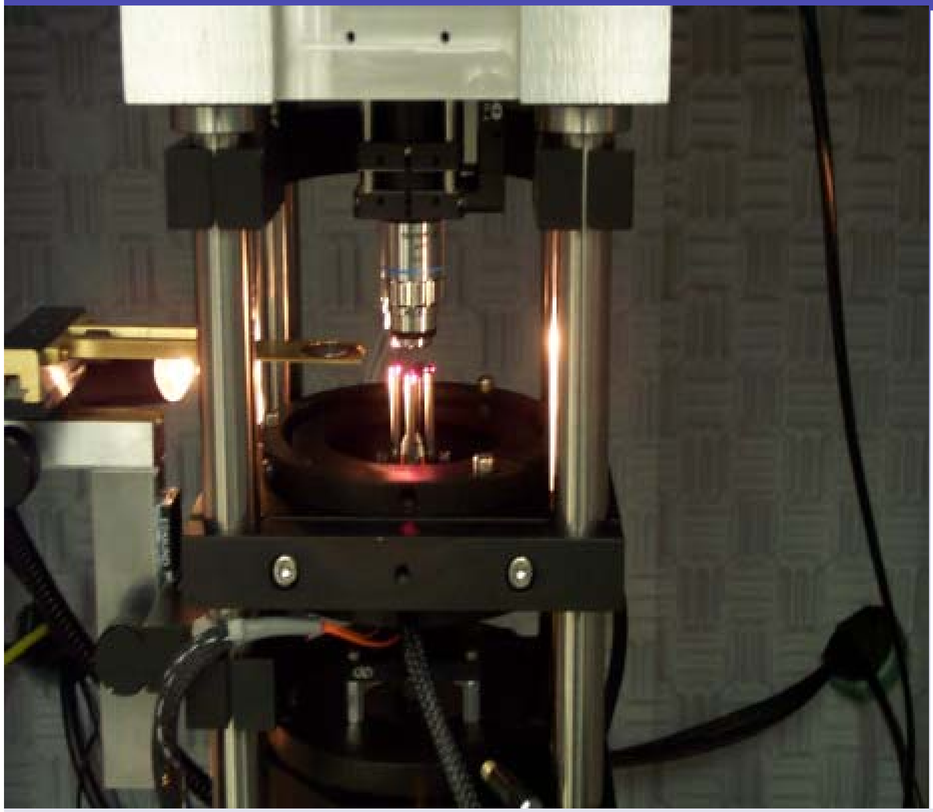




Spatial resolution ⇒ probe shape/radius; height from sample surface.

ε precision ⇒ Δf/f and cavity Q.

Near-field Scanning Microwave Microscope:



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

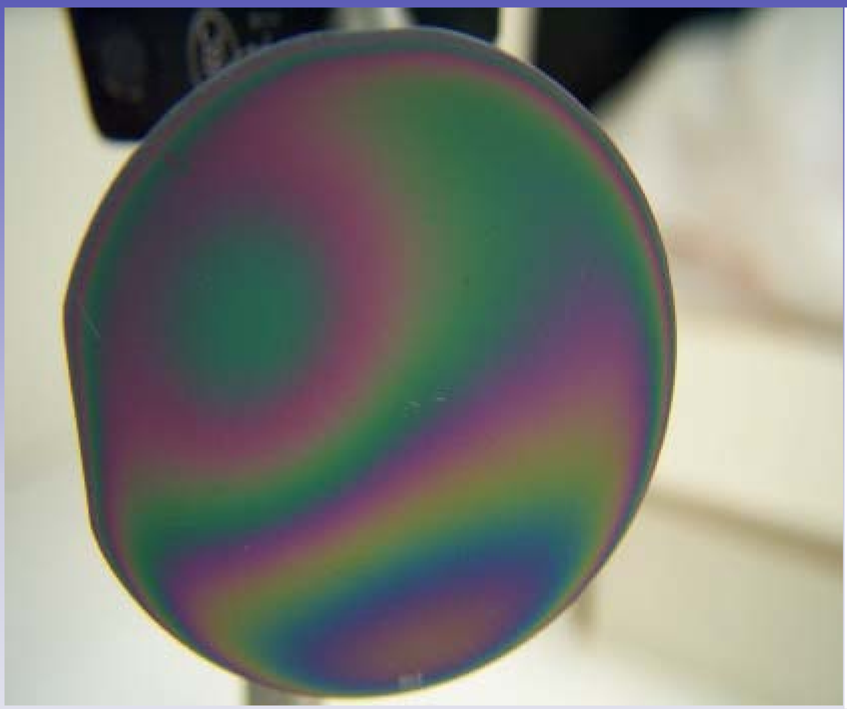
- **Shear-force feedback height regulation.**
  (typically 10-50 nm)

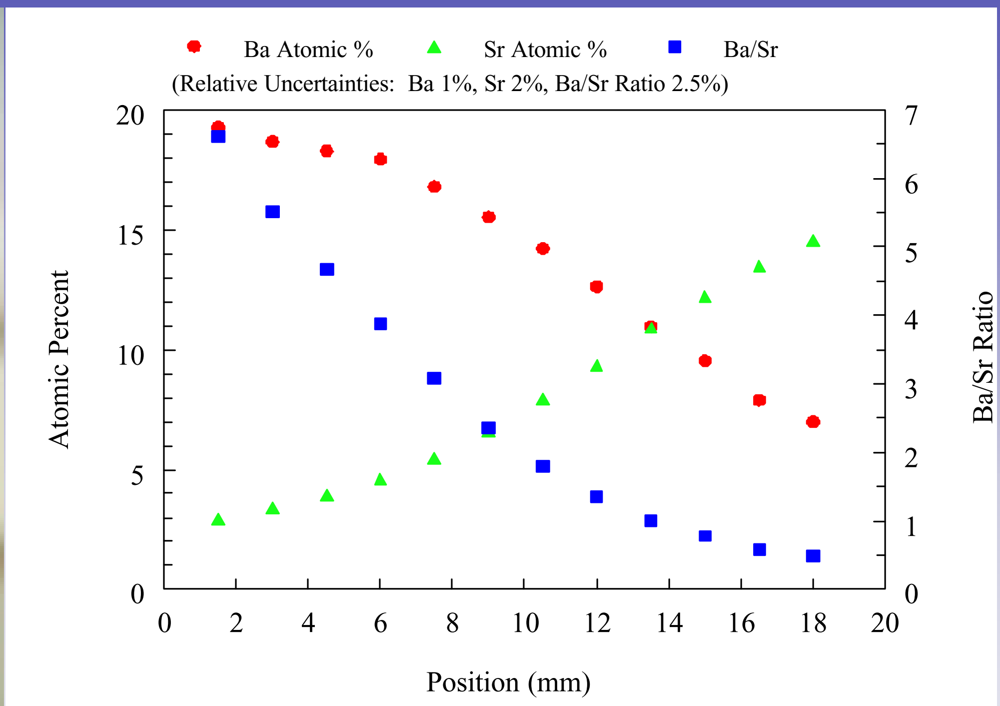
- **Broadband Measurement.**
  (45 MHz to 20 GHz)

- **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.

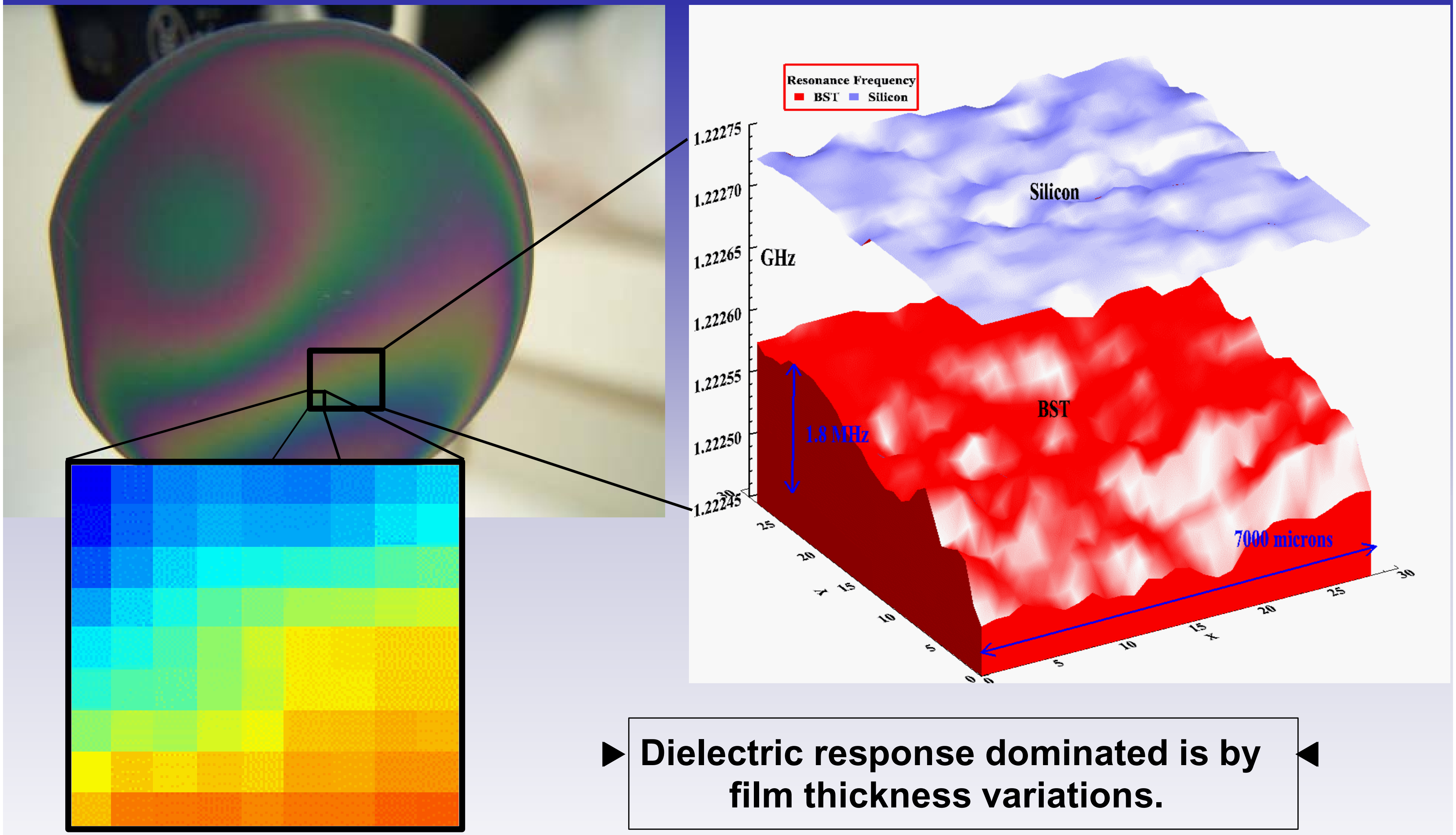




– Film thickness variation is evident.
– Quantitative analysis by spectrometric reflectometry.

– Compositional gradient quantified by wavelength-dispersive electron probe microanalysis.

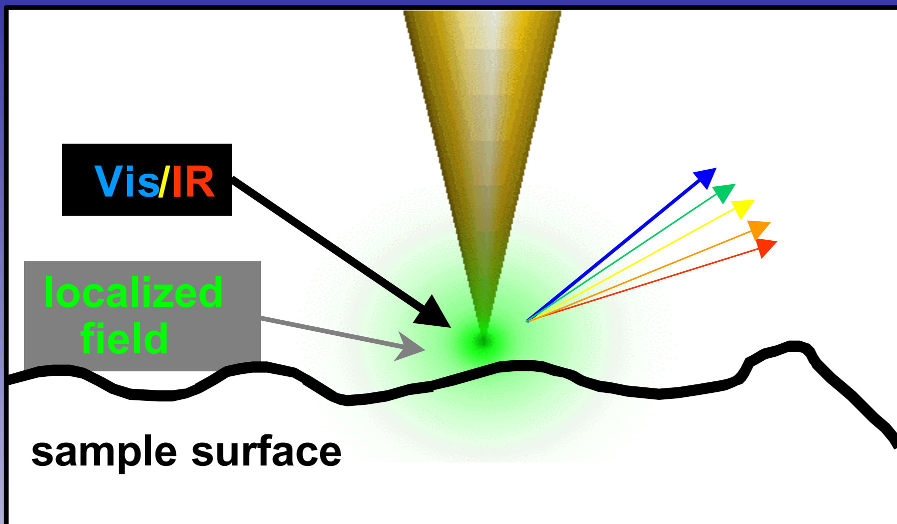
Dielectric Response Mapping using NSμM:



Dielectric response dominated is by film thickness variations.

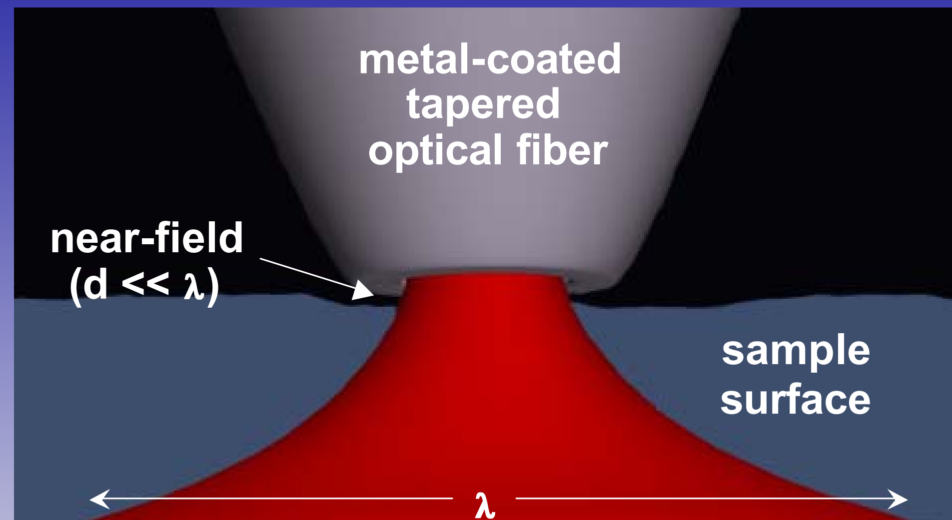
2) aNSOM - apertureless Near-field Scanning Optical Microscopy

aNSOM



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

Fiber-coupled NSOM



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

Similarities:

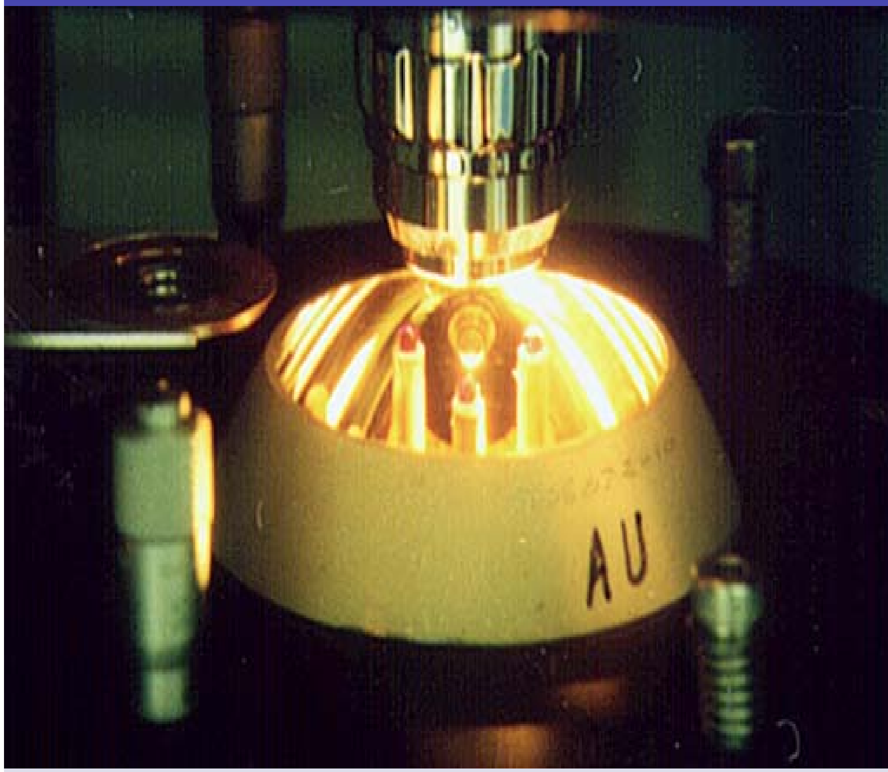
- near field scanned probe
- subwavelength resolution
- chemical imaging/spectroscopy

Differences:

- radiation coupling
- accessible wavelengths
- resolution: 1-2 nm vs ≈ 50 nm

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

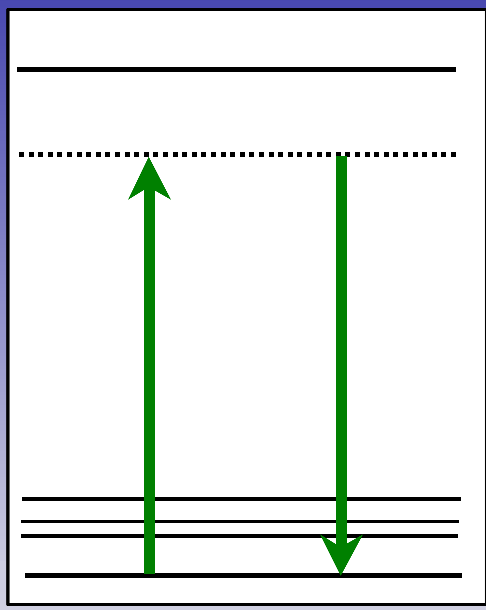
Fiber-coupled NSOM:



- **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)

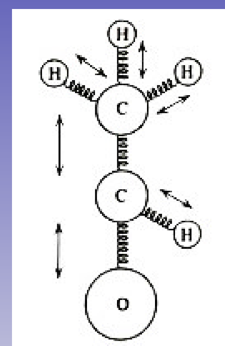
Raman Scattering Spectroscopy/NSOM:

Rayleigh Scattering (Elastic Process)



Molecular Excited State

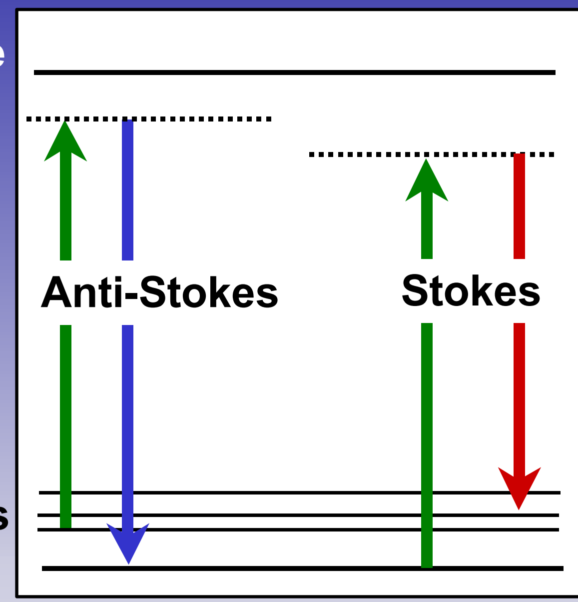
(Virtual Excited State)



Vibrational Energy Levels

Molecular Ground State

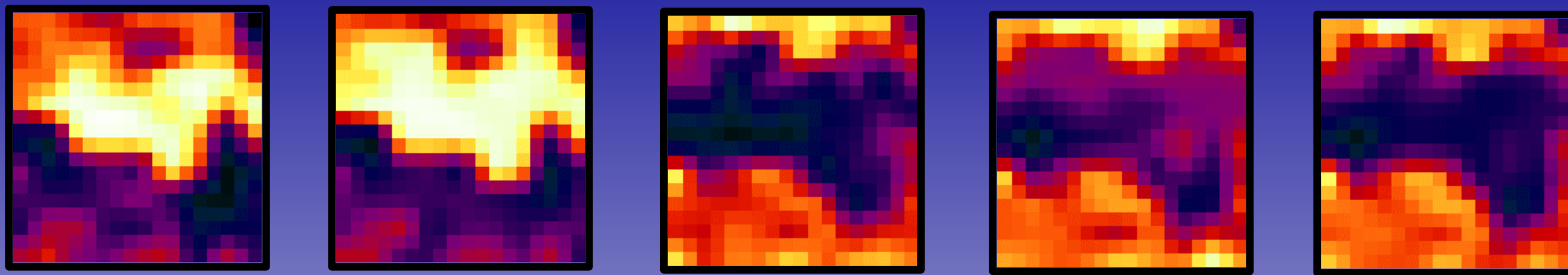
Raman Scattering (Inelastic Process)

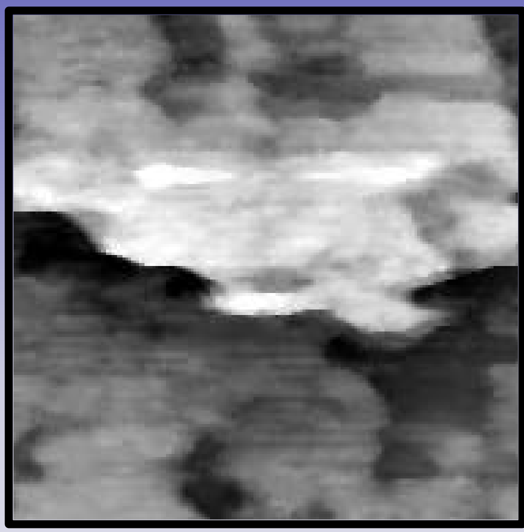


- Highly specific chemical information/species and structure.
- Visible lasers/"standard" fiber optics.

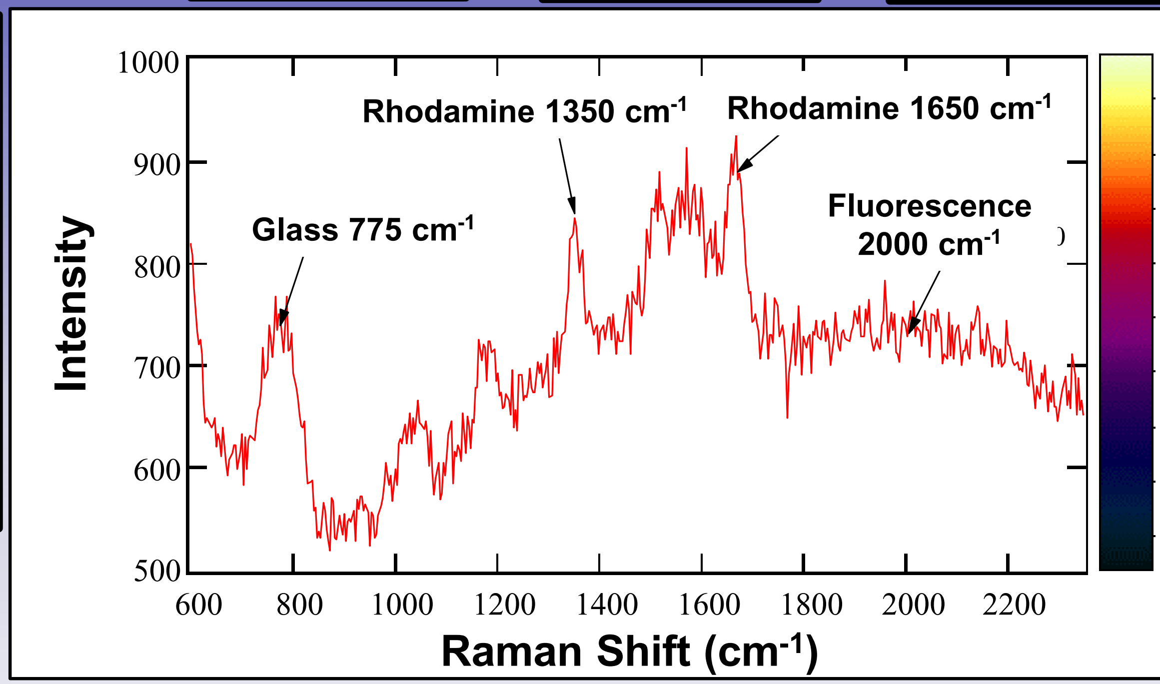
- Inefficient process: only one in 10^{13} photons Raman scatter.
- NSOM probes have low throughput: ~ 10^{-5} - 10^{-6}.

Rayleigh 514 nm | Glass (SiO_x) 775 cm^{-1} | Rhodamine-B 1350 cm^{-1} | Rhodamine-B 1650 cm^{-1} | Fluorescence 2000 cm^{-1}





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* materials properties (chemical composition/structure).
- targeting high-density (μm length scale) discrete samples and/or continuous compositional gradient materials libraries.

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.

Research Team:

S.J. Stranick, C.A. Michaels and S.W. Robey:

NSμM and Raman/IR NSOM.

P.K. Schenck, D.L. Kaiser and B. Hockey:

BST library fabrication.

R.B. Marinenko and J.T. Armstrong:

Electron probe microanalysis.