Microscopic Nano-Characterization of Materials:
The Physics and Methodology of Materials Characterization from Volumes Less than a Cubic Micrometer

Week 9

Scanned Tip Microscopies
a. Scanning Tunneling Microscopy
b. Atomic Force Microscopy
c. Near Field Optical Microscopy
d. Scanning Conductance Microscopy

Outlines/topics due today
lensless microscopes

"scanned-tip" or "scanned-probe" microscopy

generic: SPM

scan a "tip" over a surface.

lateral resolution a convolution of:

1) tip size
2) height of tip above surface
3) interaction process

further away from surface, the poorer the lateral resolution.

In general, SPM is a surface (or near-surface) technique

key technical element: control tip position with

resolution \( \leq \) tip size.

- piezo-electrics

show list

a plethora of methods:

we will discuss some (not all)

show desirable

pxs advantages

- 1st gen. use of this method was the "surface profiler"—
had nm lateral resolution, nm vertical resolution
just drag W tip across a surface.

quit
Established types of scanning probe microscopy

- AFM, atomic force microscopy \[^\text{1}\]
  - Contact AFM
  - Non-contact AFM
  - Dynamic contact AFM
  - Tapping AFM
- BEEM, ballistic electron emission microscopy \[^\text{2}\]
- CFM, chemical force microscopy
- C-AFM, conductive atomic force microscopy \[^\text{3}\]
- EFM, electrostatic force microscopy \[^\text{4}\]
- ESTM, electrochemical scanning tunneling microscope \[^\text{5}\]
- FMM, force modulation microscope \[^\text{6}\]
- KPFM, kelvin probe force microscopy \[^\text{7}\]
- MFM, magnetic force microscopy \[^\text{8}\]
- MRFM, magnetic resonance force microscopy \[^\text{9}\]
- NSOM, near-field scanning optical microscopy (or SNOM, scanning near-field optical microscopy) \[^\text{10}\]
- PFM, Piezoresponse Force Microscopy \[^\text{11}\]
- PSTM, photon scanning tunneling microscopy \[^\text{12}\]
- PTMS, photothermal microspectroscopy/microscopy
- SECM, scanning electrochemical microscopy
- SCM, scanning capacitance microscopy \[^\text{13}\]
- SGM, scanning gate microscopy \[^\text{14}\]
- SICM, scanning ion-conductance microscopy \[^\text{15}\]
- SPSM, spin polarized scanning tunneling microscopy \[^\text{16}\]
- SSRM, scanning spreading resistance microscopy \[^\text{17}\]
- SThm, scanning thermal microscopy \[^\text{18}\]
- STM, scanning tunneling microscopy \[^\text{19}\]
- SVM, scanning voltage microscopy \[^\text{20}\]
- SHPM, scanning Hall probe microscopy \[^\text{21}\]
- SXSTM, synchrotron x-ray scanning tunneling microscopy

*from Wikipedia*
The industry leader in performance, repeatability and application versatility

Dektak 150 Surface Profiler NEW

High performance repeatability, versatility and value in a single system

Industry-leading performance, repeatability, and standard scanning range size are all built into the Dektak 150 Surface Profiler – the culmination of four decades of stylus profiler technology innovations.

The Dektak 150 Surface Profiler offers a variety of configurations and add-on options for superior repeatability, programmability, low-force characterization, and detailed analysis. For power, performance, and reliability, there has never been a more complete profiler at a better price.
Fig. 5. Applications of field emission ultramicrometer; (a) strain gauge, (b) differential thermal expansion cell for small samples (c) mechanical vibration sensor, and (d) surface profile delineator.
the advent of reproducible probe-like stages
led to the scanning tunneling machine by
Binnig and Rohrer in the 1980's and the STM
proliferation

But the principle of using QM tunneling at
the nm scale and below is actually due to
Russell Yunn


→ called "field emission nanomachines"

→ technology kept resolution to 10nm

— NBS killed project

taken up again by Binnig & Rohrer in early 1980's

G.H. Binnig, H. Rohrer, and Ch. Geelhaar
and E. Weible (1982), APL 40, 178-80

(1982), Phy Rev Lett. 40, 118-80

good older STM review:
P.K. Hansma and J. Tersoff (1987)

J. Appl. Phys. 61, R1-23.
Scanning Tunneling Microscopy (STM)

Principles of general SPM

2 modes of operation

1. Use probe to keep tip at constant height, $s$, from surface — probe voltage then is modulated with variation in height due to interaction ($f(s,t)$)

or 2. Keep probe voltage constant; interaction signal changes as tip-sample distance changes.

For STM:

- Monitor probe voltage that moves tip up/down.
- Monitor "tunneling" current between tip-sample.

Consider 1D tunneling between 2 plane electrodes — (between)

$$I(s) \propto e^{-\frac{2Ks}{\hbar}}$$

where $s$ is dist. between

$$K = \frac{2\pi}{\hbar} \sqrt{\frac{2m\Phi}{\hbar}}$$

where $K$ is the decay constant for the electron wave function in the gap and $\Phi$ is local work function (effective)

$\therefore$ for typical $\Phi \approx 4eV$ (like in W)
STM schematic of tunneling
we get \( K = \frac{2\pi}{h} \sqrt{2m\rho} \equiv \frac{1}{n} = \lambda^{-1} / \pi \)

\( \therefore \) for every decrease in gap \( s \) by \( \lambda^2 \)

\[ I \text{ decreases as } e^2 \text{ (almost order of mag.)} \]

---

Thus, in "must be in" mode

one keeps voltage on tip fixed - (should be unit: V mode)

as tip scans in xy, gap dist. changes,

thus I gets modulated by tip surface topography

---

in must current mode, one changes voltage on

probs to keep dist. to sample constant

(re tips move up/down to track samp) so I = constant, then that voltage modulation

related to topography.

---

\( \) NOTE // simple picture not exactly correct at

atomic resolution. ie, if we have an

atomically sharp tip scanning across

a "inert plane" of atomics.

it is not clear what is "s" ---

measures tunneling through states

at Fermi level - so "density of states"

these affect tunneling current

- complex elcr. structure/real 3D problem
Figure 2. Common STM operational modes
So STEM is STEM in that image interpretation at best under no easy — but you need to be careful. Since $V = \frac{2\pi}{12}$, and we can estimate

$$\frac{\text{length m}}{\text{length m}}$$

unambiguously (i.e., $V_{\text{approx}}$), then $V_{\text{approx}}$.

The above implies that the above bounded $\text{length}$. But $\text{length}$ in $\text{length}$.

Thus this is limited to "smooth," surfaces.

I would keep a constant $\text{length}$. I'm assuming a $0.5 \text{mm}$, thus in eventually

without feedback. When $\text{length}$ is unambiguously.

When & $\text{length}$ is unambiguously, $\text{length}$.

For conventional $\text{length}$, we approximately imagine as a "typing" map.

"Tunneling" image.

"So in real world, how do we interpret the
if V between tip and sample << q then tunneling current density

\[ J = \frac{2\pi e^2 kV}{\hbar 4\pi^2} e^{-2ks} \]

where \( k = \frac{2\pi}{\hbar} \sqrt{\frac{2m_e \text{eff}}{\epsilon}} \), \( \rho_{\text{eff}} = \frac{1}{2} (\rho_L + \rho_R) \)

**NOTE:** \( k \approx K(V) \) as long as \( V \gg \rho_{\text{eff}} \)

If that is not the case then exponentional factor is \( V \) dependent.

Re to separate out \( s \) variations from \( q \) variations you need more than 1 measurement.
- get at this by \( \frac{dI}{dV} \) measurements at each pt as well.

**NOTE:** tip is crucial for interpretation.

eg if it looks like this\( \rightleftharpoons \) one gets confusing imaging.

Some can get variation in \( q \) as:

\[ \frac{d[l(q)]}{dV} \propto \frac{d}{ds} (-2ks) \propto \sqrt{q} \]

Oscillate bit of tip and piezo.

Nice tutorial: [http://www.fisp.uni-erlangen.de/methoden/stm/stmtutor/stmpage.html](http://www.fisp.uni-erlangen.de/methoden/stm/stmtutor/stmpage.html)
Si 7x7
Atomic resolution of Au(111)
properties of the "cantilever" and tips for AFM. spring unit

1. want max. defl. for min. min. force
   soft spring, low K

\[ F = -Kx \]

2. want min. sensitivity to bldg. vibrations (20-100 Hz)

3. resonant freq. \( f_0 = \frac{1}{2\pi} \left( \frac{K}{m_0} \right)^{\frac{1}{2}} \)
   should be high.
   \( 10^8 \text{Hz} \approx m_0 \)
   effective mass that
   loads spring
   \( (\text{ie. } \text{He}, \text{H}) \)

\[ \therefore \text{reduce } K \]
\[ \text{reduce } m_0 \text{ further to keep } \left( \frac{K}{m_0} \right) \text{ large.} \\
\quad (\leq 10^{-8} \text{ kg}) \]

limits of AFM on force detection:

thermomechanical noise // bandwidth

free noise, \( F = \left( 4Kk_B T B/Qw_0 \right)^{\frac{1}{2}} \)

\[ \text{spring unit: } \text{thermal energy} \]
\[ \text{qual factor } \text{res. freq. } \]
\[ \text{high } Q \]
\[ \text{low } T \]
\[ \text{high } w_0 \]
Tip is in hard contact with the surface; repulsive regime

Tip is far from the surface; no deflection

Tip is pulled toward the surface - attractive regime

Force

Probe Distance from Sample (z distance)
AFM Cantilevers and Tips

- Microfabricated cantilevers with integrated tips
  - Silicon nitride, silicon oxide, silicon
  - Spring constants: 0.1-1 N/m (contact), 10-100 N/m (non-contact)
  - Resonance frequencies: 1-50 kHz (contact), 100-300 kHz (non-contact)
  - Coatings depend on application: eg. conducting, magnetic, functionalized (specific molecules)
STM (unit):

disadvantages:
- best with "smooth" samples
- best with conducting samples
- if used in an a wales, interpretation gets complicated.

can get around some of those probs with AFM/atomic force microscopy


show pix: // a tip, sharp tip mounted on cantilever
- laser focused on back of cantilever
- back of cantilever reflects light to split photodiode
- optical lever \( \approx 10^{-10} \) to micron tip displacement (Hooke's law)

several modes to look at the forces on the cantilevers:

\[ F = -kS \]

Forces on tip

- repulsive
- attractive

Distance

Load force curve as tip nears sample
AFM (unit)

- different forces
  - mech. uniaxial force
  - van der Waals force
  - capillary forces
  - chem. bonding
  - electrostatic forces
  - magnetic forces (MFM)
  - shear forces
  - etc...

All scanning done piezoelectrically.

Two modes

1. static
   - deflection used as feedback mechanism
   - prob. near surf. attractive forces can be large
   - usual tip vs sample
   - usually done in constant repulsive mode
   - force kept constant by maintaining cont. defl.

2. dynamic
   - tip "oscillates" (rather continuous oscillate)
   - at freq. near fundamental resonance
   - unit
In-situ observation of DNA and histone separation from a single nucleosome molecule due to increased salt concentration using a flow-thru cell.
AFM/

- Nano cantilever cantilever, oscillated just above sample, (<10nm)
- Van der Waals forces predominate (1-10nm above surface)
- They determine sample-surface interaction
- Frequency of cantilever
  → goes to feedback to keep oscillation instant
  thus, measure tip distance (z).
  → best for "soft samples"

One generally uses freq mod under UHV conditions
  (under low temp, thermal fluctuations reduced)

A good reference for applications:
  Bushan and Kawate, eds.
  "Applied Scanning Probe Methods VI,
  Characterization", 2006 (Springer).
AFM

oscillations, amplitude, phase, and freq change
by tip-sample interaction forces.

changes compared to ext. ref. oscillations and give measure of force

In ampl. modulation, changes in osc. ampl., phase used to provide imaginary in feedback.
- phase changes can provide info on material
- whereas ampl. just gives us the topog.

ampl. modulation: contact or non-contact
but in air or fluid to keep tip from striking to surface, one modulates the
distance between tip-infl. by oscillating
chunkles - "tapping" - typical 100 nm

- as tip approaches, force increases,
  ampl. osc. decreases - jury changes hit
to keep same ampl. osc.
  or less destructive than pure "contact"
  dragging over imf. surface
AFM force/regions

(K. Mitchell)
sample and cantilever exchange is performed even at low temperatures. The optimal and reproducible positioning of the optical fiber with respect to a cantilever can be performed with a specially designed three-dimensional micropositioner within 10 min.

As the force sensor, we used a conductive silicon cantilever with a sharpened tip. The spring constant and mechanical resonant frequency were 40–60 N/m and 150–170 kHz, respectively. The nominal radii of curvature for the tip apex were 5–10 nm. The silicon tip was cleaned by sputtering with Ar ions. There are the dangling bonds out of the silicon tip apex. The NC-AFM image was obtained under the constant frequency shift.

18.3 Identification of Subsurface Atom Species

NC-AFM has the capability to identify or recognize atom species on a sample surface, if we can control the atomic species at the tip apex. That is, we succeed in identification of Si and Ge atoms by imaging the Si/Ge intermixing Si(111) surface
Fig. 18.4. NC-AFM image of Si(111) $\sqrt{3} \times \sqrt{3}$-B surface. The bright spots and dim spots correspond to Si-T$_4$ and B-S$_4$ structures, respectively. The scan size is 7.7 nm $\times$ 7.7 nm

the dangling bond orbital and the empty orbital. This suggests that the bright spots correspond to the Si-T$_4$ structure, while dim spots correspond to the B-S$_4$ structure. This experimental result suggests that the contrast of the NC-AFM images changes depending on the atom species under the surface. Thus, we found that NC-AFM has the capability to identify or recognize atom species under a sample surface.

18.4
Tip-Induced Structural Change on a Si(001) Surface at 5 K

The Si(001) surface has attracted much attention because of its practical importance in most large scale integration (LSI) devices that are fabricated on this surface. However, recent scanning tunneling microscopy (STM) studies performed at low temperatures questioned whether the c(4 $\times$ 2) phase is the most stable phase. For instance, the p(2 $\times$ 1) structure was observed in [4, 5]. It was suggested in [4] that the p(2 $\times$ 1) structure is due to the time averaging of the rapid flip-flop motion at 5 K. At the same time, the symmetric p(2 $\times$ 1) structure observed in [2] at 20 K was attributed to static symmetric dimers stabilized by the “antiferromagnetic” dimer-dimer interaction. Thus, up to now, the appearance of the p(2 $\times$ 1) phase in STM images at low temperature remains a controversial issue. Here, we investigate the tip-induced structural change on a Si(001) surface by NC-AFM at 5 K.

Figure 18.5a shows the NC-AFM topographic image of the Si(001) surface taken at $\Delta f = -10$ Hz, where we can assume that the tip-surface interaction is rather weak. The vibration amplitude of the oscillating cantilever was 13.5 nm. Here, the c(4 $\times$ 2) phase with a zigzag pattern is clearly observed. This result is in good agreement with a previous AFM study [6]. In Fig. 18.5b, we show a stable topographic image taken at a larger $\Delta f = -22$ Hz, where the tip-surface interaction is much stronger. We find that a surface phase is observed with bright lines along dimer rows and flicker noise. It is noted that NC-AFM images with flicker noise were observed for the first time, although the same phenomenon has been confirmed by STM studies [4]. The appearance of the flicker noise strongly suggests that surface dimers are frequently tipped by the tip-surface interaction. Notice that the p(2 $\times$ 1) phase was not observed at this frequency shift. Figure 18.5c shows a topographic
EE213 lecture #13

Near Field Scanning Optical Microscopy (NSOM)

“Suggested method for extending microscope resolution into the ultramicroscopic regime”

Another scanned tip technique:

principles // — resolution defined by “opening” within λ from “opening” (near surface)
— evanescent waves

trade-offs: resolution vs signal.

how do we make an optical probe?

marked pipette or fiber //

throughput? fiber > pipette

throughput (d) // Power in / Power out

collimation ~ d, aperture size
AFM mode of operation

**Contact mode**: maintain constant deflection
- Hard contact with surf.
- Lower stiffness < effective force
  holding atoms together (1-10 nN/\(\text{nm}\))
  lower con < 1 nN/\(\text{nm}\)

**VM-contact mode**: oscillating cantilever
  (in attractive regime)
  lower forces between tip-sample (pN)
  change in resonance freq & ampl
  (FM) (QPM)

**"Tapping" mode**: cantilever closer than in NC mode
  - part of tip gets into "repulsive" region
  - very soft cantilever (in tips
  stick in water, strong layers)
  - good for soft samples
  - maxim. lateral forces

**Free oscillation**: tip oscillated at high freq
  into repulsive regime
  - free vs. dist. correlates to elasticity.
  - measure phase shift relative to
    driving freq -
    measure diffusion, viscoelasticity,
NSOM (cont.)

we can look at the probe size we form in NSOM and far-field optics

Far Field: \( I(r) = \text{PSF}(r) = \left| \mathcal{F}[A(P)] \right|^2 \)

Near Field: \( \mathcal{F}(r) = \text{PSF}(r) = |A(P)|^2 \)

"effective" aperture depends upon how much "leakage" thru the "slit"

show example/ different far imaging modes/ with different "throughputs"

one can enhance "throughput" using a metal tip to provide local excitation

e.g. field enhancement


"near field optical microscopy" with pointed probes"
with a contrast of the MTF of 9%. On the other hand, the Sparrow criterion (in which the second derivative at the center of the intensity sum from two point objects is zero) [23] gives a resolution of

\[ r = 0.47 \lambda / \text{msin} \theta \]

(2b)

with an MTF contrast of zero. One should note that the resolution criteria given above are somewhat arbitrary and the practical resolution limit is related to a minimum detectable contrast, which is related to the signal to noise ratio of the imaging system. In addition, it should be stressed that in all cases, the MTF of the far-field incoherent imaging case depends upon the wavelength of the radiation used. All we can do to improve resolution is somewhat reduce the proportionality constant in eq. (2), reduce \( \lambda \) or increase the numerical aperture \( n \sin \theta \).

3. Near-field optics

If we relax the far-field condition, and allow ourselves to investigate the spatial distribution of the radiation in the near field, we can use the same treatment as before to obtain a point spread function and a modulation transfer function for near-field imaging. It should be pointed out that to properly deal with the near-field case we must solve the 3D vector diffraction problem. Here we will consider a simplified case assuming the Kirchhoff formulation [24] and will consider the more rigorous case in a later paper.

Consider the schematic shown in fig. 4. Here, plane wave radiation again illuminates an aperture in an opaque screen. Only now we consider the spatial distribution of radiation in the immediate proximity of the exit side of the aperture. The intensity of radiation here is just given as

\[ I_{\text{NP}}(r) = |A(\rho)A(\rho)^*| = \text{PSF}_{\text{NP}}(r) \]  

(3a)

where \( r \) is again the coordinate in the sample plane (which here is at the aperture exit and is the same as \( \rho \)) and \( A(\rho) \) has the same meaning as before. Thus, the intensity distribution in the near field is essentially the geometric projection of the aperture (or more accurately the modulus squared of the aperture function). Note that this is not exactly true, since a more rigorous calculation indicates an increase in the intensity at the aperture edge. This has been shown before for the case of apertures in thin perfectly conducting screens and the result of such a calculation by Harootunian [16] is shown in fig. 5. In fig. 6a we plot a representation of eq. (3a) where \( R \) is the aperture radius.

The modulation transfer function for the point spread function given by eq. (3a) is again the Fourier transform of the PSF.

\[ \text{MTF}(f)_{\text{NP}} = \mathcal{F} \left[ I_{\text{NP}}(r) \right] \]

\[ = \mathcal{F} \left[ A(\rho)A(\rho)^* \right] \]

\[ = \mathcal{F} \left[ A(\rho) \right] \otimes \mathcal{F} \left[ A(\rho)^* \right] \]

(3b)
The diagram illustrates the propagation of light through a system. The light enters through the aperture and is focused by the lens. The sample is placed at the focal point of the lens. The equation $d\alpha \frac{\lambda}{n \sin \theta}$ represents the angular distribution of the light.
FAR-FIELD

(a) $PSF(r) \quad r \cdot (R/\lambda F)$

(b) $MTF(f) \quad f \cdot (\lambda F/R)$
Near Field Scanning Optical Microscopy

Imaging modes:

(a) collection
(b) illumination
(c) collection/illumination

(d) oblique collection
(e) oblique illumination
(f) dark field
\[ l \text{(arb. units)} \]

\[ r/R \]

- Metal-coated glass pipette
- Metal-coated single-mode fibers

\[ 2R \]

\[ 10 \text{nm} \]

Measurement
Shear Force Microscopy

[Betzig et al.  
App Phy Lett. 60(1992) 2484]

feed back to split detector for shear signal.
Near Field Scanning Optical Microscopy (Reflection)
aluminum on silicon

400nm

Shear force  NSOM

Cline and Isaacson, Ultramicroscopy
Fig. 8. Shear force and reflection images of an aluminum-on-aluminum pattern. The images display the effect of the topography on the imaging. The white scale bars are 2-μm bars, and the detector is oriented on the bottom on the image.
ALUMINUM LETTERS fabricated on a silicon nitride substrate imaged with a near field optical microscope. The full horizontal scale is 550 nm, the wavelength of the light being used.

M. Isaacson and E. Betzig, Cornell University
FIELD ENHANCEMENT MICROSCOPY

L. Novotny et al., Ultramicroscopy 71, 21, 1998

metal tip
local field enhancement
RAMAN SCATTERING
Surfaced Enhanced Raman Scattering
Fluorescence is limited by the need to label and photobleaching.

> **Raman spectroscopy** provides molecular information

Raman: inelastic light scattering

\[ E_i = h\nu_i \]

\[ E_s = h\nu_s \]

\[ \Delta E = E_i - E_s \]

Raman spectrum of a single bacterial spore

Raman spectroscopy provides:
- Fingerprint spectra (molecular identity)
- Information about 3d structural changes (orientation, conformation)
- Information about intermolecular interactions
- Dynamics

Raman scattering, however, is extremely inefficient

Only 1 in \(10^8\) incident photons are Raman scattered

Typical scattering cross-sections \(\sim 10^{-30}\) cm\(^2\) (15 orders of magnitude lower than fluorescence excitation)
In 1977, an interesting finding was reported, starting the “age of surface-enhanced Raman spectroscopy”

- **Flat surfaces give Raman enhancements in the range of** $10^3 - 10^6$
- Jeanmaire and Van Duyne, *J. Electroanal. Chem.*, 84, 1 (1977)
Figure 1
(a) Illustration of the localized surface plasmon resonance effect. (b) Extinction efficiency (ratio of cross section to effective area) of a spherical silver nanoparticle of 35-nm radius in vacuum $|E|^2$ contours for a wavelength corresponding to the plasmon extinction maximum. Peak $|E|^2 = 85$. 
FIG. 2. Typical optical spectroscopy measurements of individual silver nanoparticles. The figure shows the spectrum of an individual red, green, and blue particle, and the high-resolution TEM images of the corresponding particle are shown above their respective spectrum. This example is a representative of the principle conclusion that the triangular shaped particles appear mostly red, particles that form a pentagon appear green, and the blue particles are spherical.
The plasmon resonance of metal nanoparticles depends on their size, shape and composition.

Gold/silver nanoparticles
- are polycrystalline and faceted
- support surface plasmons excited with visible light
- leakage radiation has evanescent nature at surface irregularities
- exponential decay leads to highly localized fields

Figure courtesy O.J. F. Martin
Fig. 3. Surface-enhanced Raman spectra of R6G obtained with a linearly polarized confocal laser beam from two Ag nanoparticles. The R6G concentration was $2 \times 10^{-11}$ M, corresponding to an average of 0.1 analyte molecule per particle. The direction of laser polarization and the expected particle orientation are shown schematically for each spectrum. Laser wavelength, 514.5 nm; laser power, 250 nW; laser focal radius, $\sim 250$ nm; integration time, 30 s. All spectra were plotted on the same intensity scale in arbitrary units of the CCD detector readout signal.
Tip enhanced Raman spectroscopy for chemical characterization of nano-structures

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Keywords: Near field microscopy, Raman spectroscopy, scanning probe microscopy, ferroelectrics

Nano-electronics and biotechnology call for analytical methods with nanometer precision. Common techniques that provide such high resolutions are electron microscopy (SEM) and scanning probe microscopy (e.g. STM and AFM). Although some of these techniques can probe the topography of the sample with atomic resolution, the chemical and structural information remains unknown. Chemically-sensitive methods like Raman or IR-spectroscopy are physically limited by the diffraction limit of light and thus do not provide access to the nano-scale. With the goal of making chemical characterization available at nanometer resolution, we are working on tip enhanced Raman spectroscopy (TERS). This aperture-less near-field scanning microscopy is based on an atomic force microscope that uses localized surface plasmons at the apex of the microscopy tip (Figure 1) to generate an optical near-field of a few nanometers in diameter. While scanning the surface of the sample, the plasmons at the tip act as light source for the Raman spectroscopy (Figure 2) and the chemical structure of the sample can be mapped with molecular sensitivity. Our system is specifically designed to allow the characterization of insulating and opaque samples. We are therefore using a tuning fork AFM operated in shear force mode with electro-chemically etched gold tips. The optical access for the confocal Raman measurement is established from the side. We are presenting scans of carbon nanotubes with 15 nm optical resolution and first TERS spectra of PbTiO₃ nano structures.

Figure 1 – SEM image of an electro-chemically etched gold tip for tip enhanced Raman spectroscopy.

Figure 2 – Tip enhanced Raman spectrum of a carbon nanotube (red). The blue curve shows the loss of the G-band when the carbon nanotube is positioned 30 nm away from the tip. This demonstrates the position dependence and thus the high lateral resolution of TERS.