The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR: 1643/3

WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS IN NANOSCIENCE AND NANOTECHNOLOGY

(7 - 18 February 2005)

“Optical spectroscopy at the nanoscale”

presented by:

Fritz Keilmann
Max-Planck-Institut für Biochemie,
82152 Martinsried (München), Germany

Strada Costiera 11, 34014 Trieste, Italy - Tel. +39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it, www.ictp.it

Optical spectroscopy at the nanoscale
- physical concepts

Fritz Keilmann
Max-Planck-Institut für Biochemie, 82152 Martinsried (München), Germany

motivation: „chemical nanoscope“

microscope principle for attaining 10 nm resolution

microwave, visible and mid-infrared realisations

applications in

- materials sciences
- polymers
- semiconductors
- biology

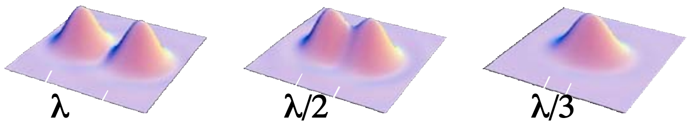
Optical spectroscopy at the nanoscale
- physical concepts

I **overview of SNOM**

II **s-SNOM basics**

III **s-SNOM spectroscopy**

Why near fields?



because **far-field diffraction limits the optical resolution to λ/2**
far fields are propagating waves far away (>> λ) from an object/source

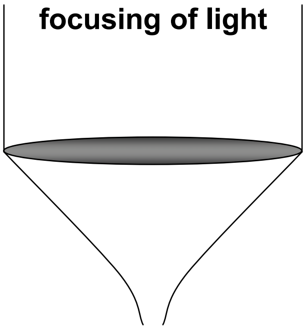
near fields
- decay evanescently, i.e. they are non propagating
- are bound to matter (they „stick“ to the object)
- are strongly localized (<< λ)

exploiting near-fields allows optics at the nanometer scale

Abbe limit (1873)

numerical aperture
$NA = n \cdot \sin\alpha$

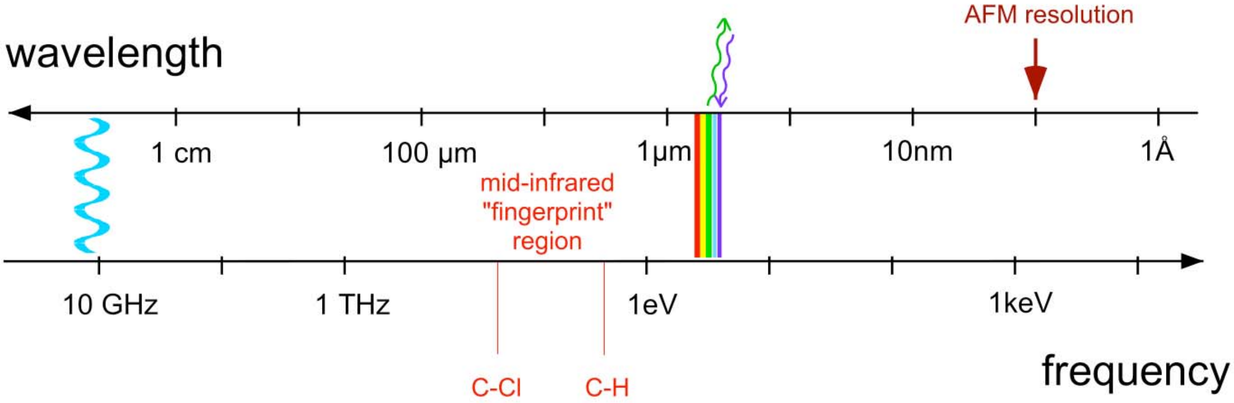
in air: $NA \leq 1$
$d_{\min} \geq \lambda/2$



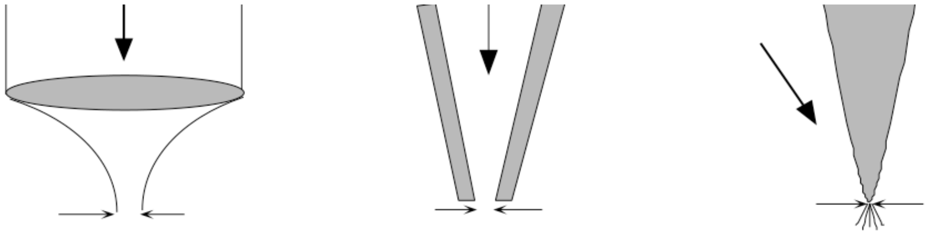
but .... many interesting objects are much smaller than λ:
- nanoparticles
- quantum dots
- single molecules
- biological structures

optical-spectroscopic analysis at the nanoscale should be fascinating

Greatly sub-wavelength resolution?



Photon focusing concepts



λ/2

classical

diffraction-limited

λ/10

aperture SNOM

aperture-limited

< 30 nm

scattering SNOM

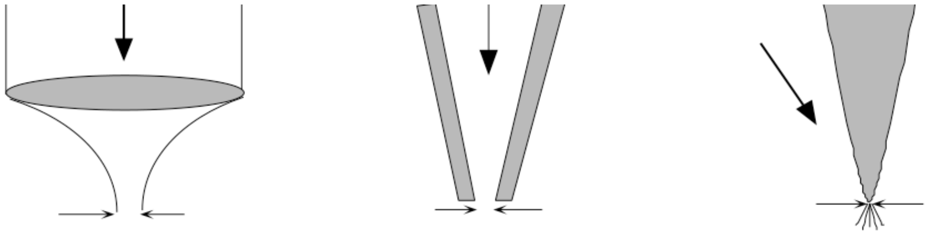
tip-limited

History of SNOM

1928	Proposal by Synge on subwavelength resolution by aperture scanning
1972	First realization of Synge´s idea by Ash and Nicols using microwaves; resolution $\lambda/60$
1982	Scanning Tunneling Microscope (STM) by Binnig and Rohrer
1984	Near-field aperture SNOM, independently by Lewis and Pohl
1985	Scattering probe proposed by Wessel
1986	Atomic Force Microscope (AFM) by Binnig, Quate and Gerber
1991	Betzig et al. metal coated tapered fiber tip aperture
1995	Zenhausern, Martin, Wickramasinghe 7 Angström optical resolution ! ? by light scattering from an AFM tip

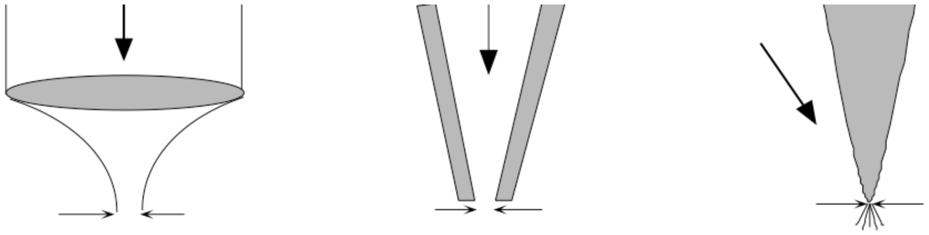
---

Optical microscope concepts



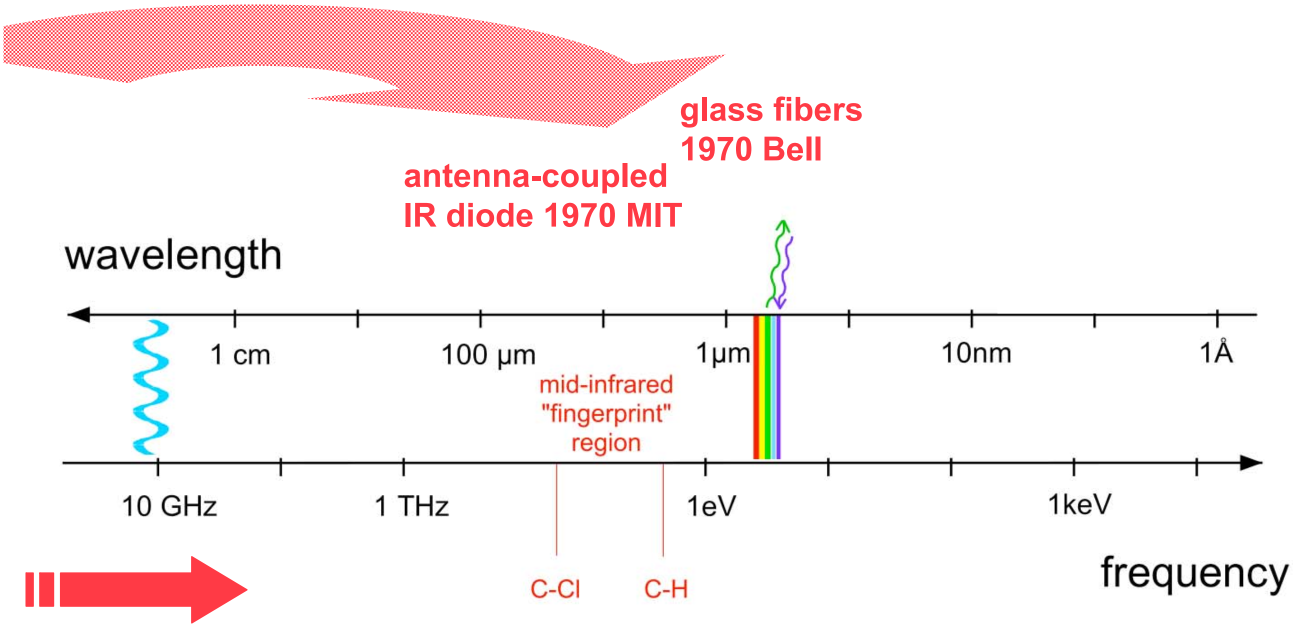
$\lambda/2$	$\lambda/10$	< 30 nm
classical	**aperture SNOM**	**scattering SNOM**
diffraction-limited	aperture-limited	tip-limited
free-space	guided	confined

Historic roots of microscopy concepts



λ/2	λ/10	< 30 nm
classical	**aperture SNOM**	**scattering SNOM**
diffraction-limited	aperture-limited	tip-limited
light	**microwaves**	**electronics**
≈1600? Galileo	≈1940 GB, MIT	≈1950 Bell

Electronics concepts push optics

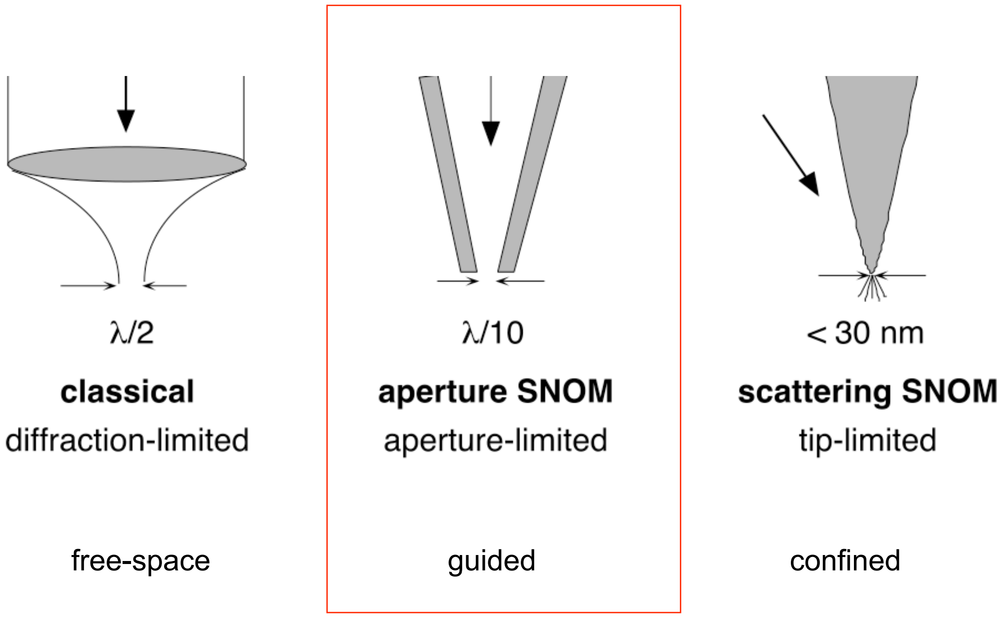


glass fibers
1970 Bell

antenna-coupled
IR diode 1970 MIT

computers
2005

Aperture SNOM basics



λ/2

classical

diffraction-limited

free-space

λ/10

aperture SNOM

aperture-limited

guided

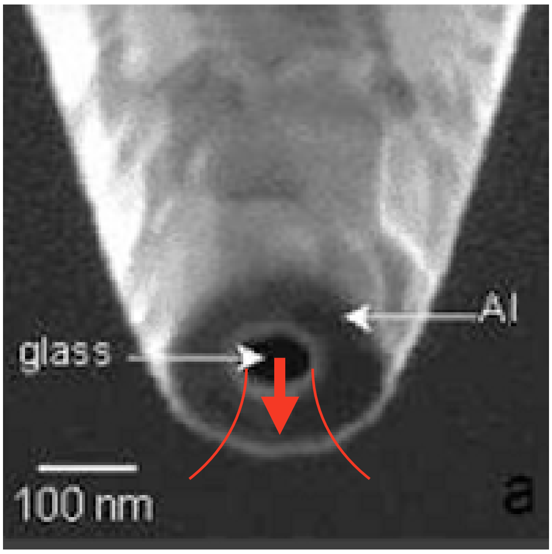
< 30 nm

scattering SNOM

tip-limited

confined

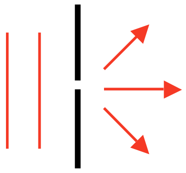
Aperture probe for visible light



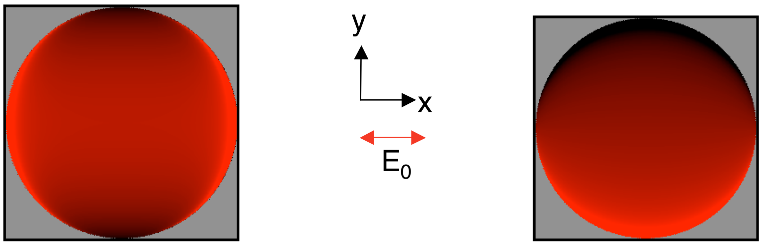
Theory of optical fields in the aperture

infinitely thin screen
with infinite conductivity

hole of diameter 2a<<λ



1944	Bethe
1950/54	Bouwkamp



$$\frac{E_x}{E_0} = -\frac{8ik}{3\pi}\left(\sqrt{a^2-r^2} + \frac{r^2}{2\sqrt{a^2-r^2}}\cos^2\varphi\right)$$

$$\frac{E_y}{E_0} = -\frac{8ik}{3\pi}\left(\frac{r^2}{2\sqrt{a^2-r^2}}\cos\varphi\sin\varphi\right)$$

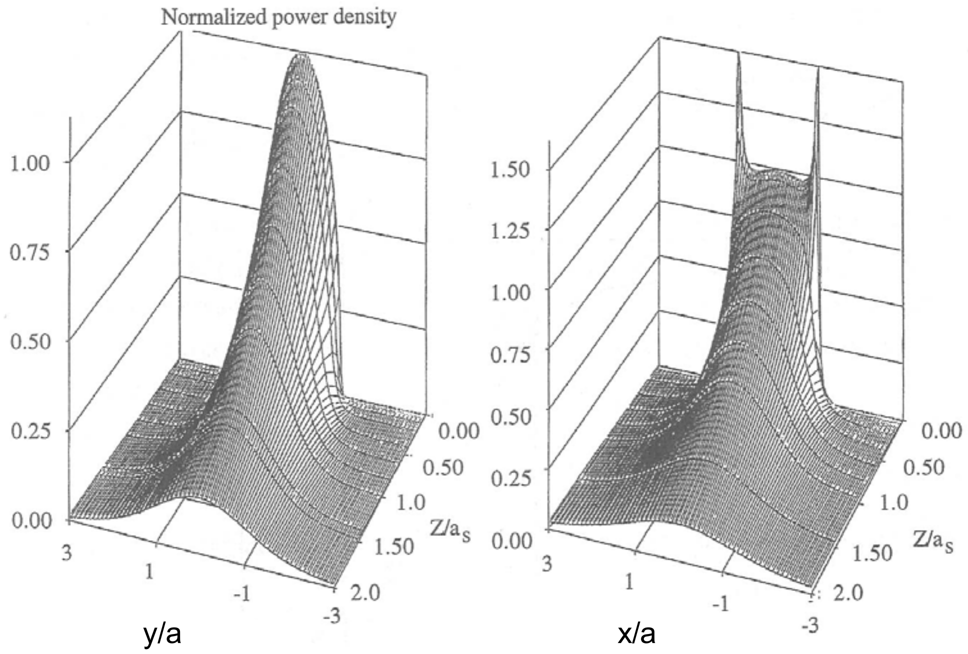
$$\frac{E_z}{E_0} = 0$$

$$\frac{H_x}{H_0} = 0$$

$$\frac{H_y}{H_0} = 1$$

$$\frac{H_z}{H_0} = -\frac{4}{\pi}\frac{r}{\sqrt{a^2-r^2}}\sin\varphi$$

Light intensity decays outside the aperture



Propagation away from aperture

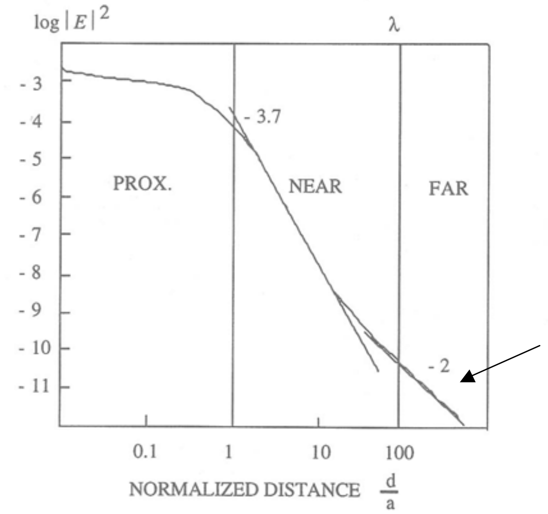
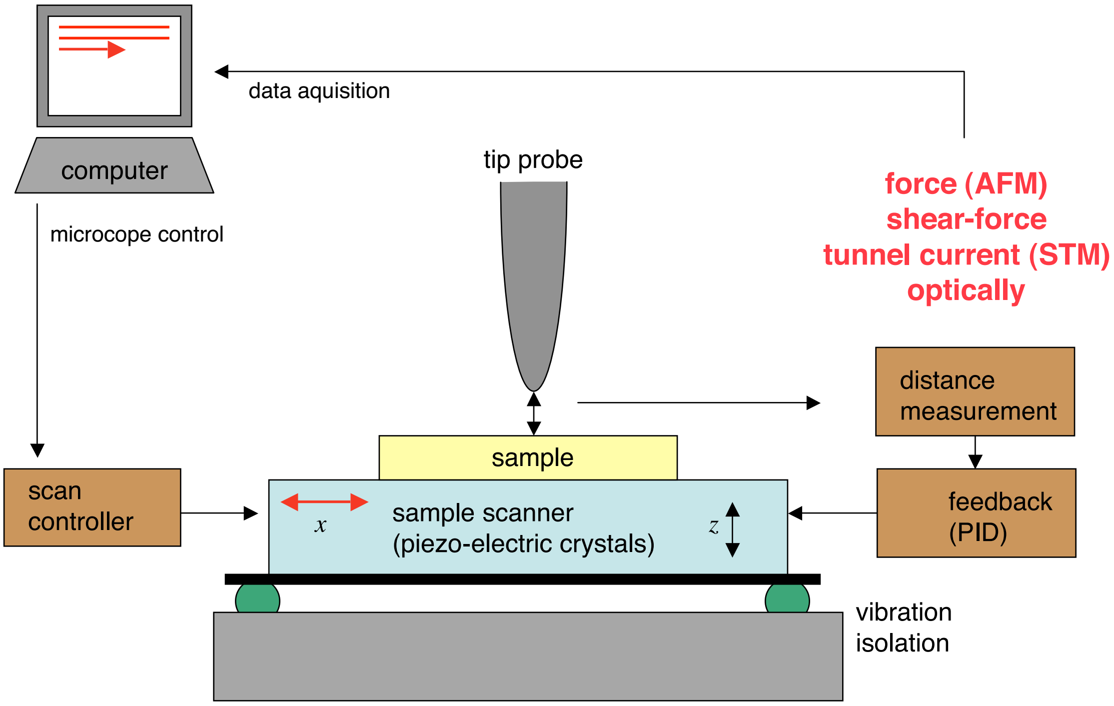


Fig.1.3.10 Calculated on-axis transmitted energy density *vs* normalized distance from the center of the hole of radius taken as a = λ/100. After Dürig[41].

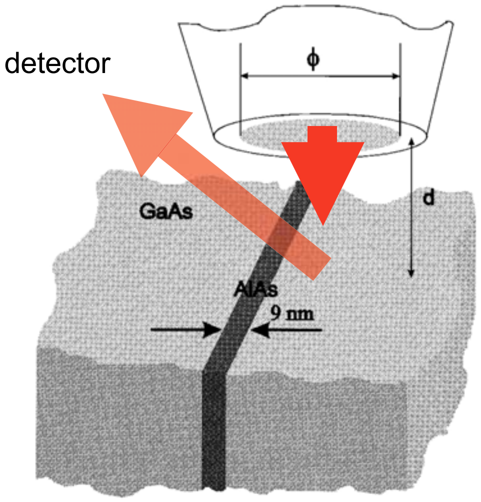
classical
far-field law
$1/d^2$

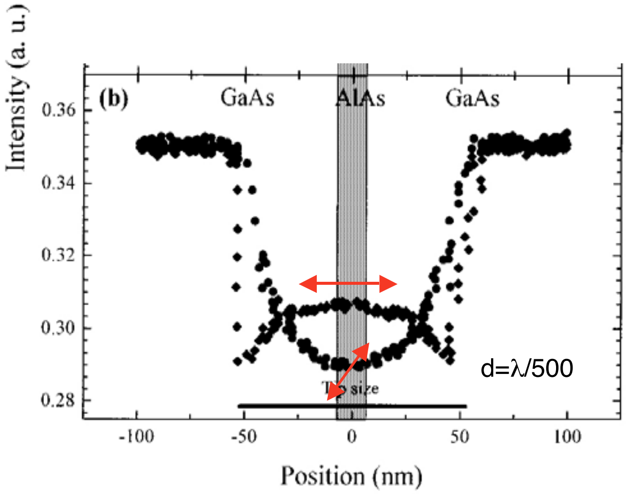
Scanning tip microscope principle



force (AFM)
shear-force
tunnel current (STM)
optically

Aperture SNOM performance

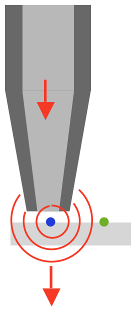




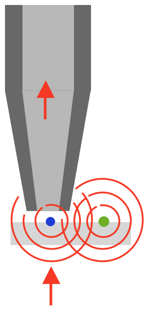
Appl. Phys. Lett. **70**, 1932, (1997)
R.S. Decca, H.D. Drew, and K.L. Empson

Aperture SNOM operation modes

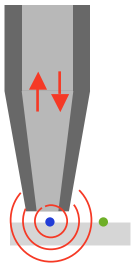
Illumination
in transmission



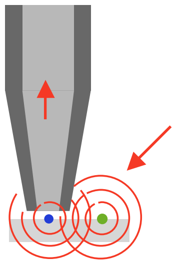
Collection
in transmission



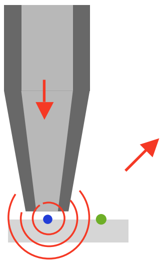
Illumination and collection
in reflection



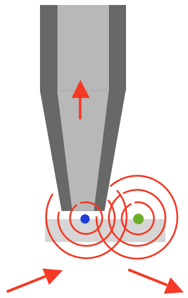
Collection in
oblique reflection



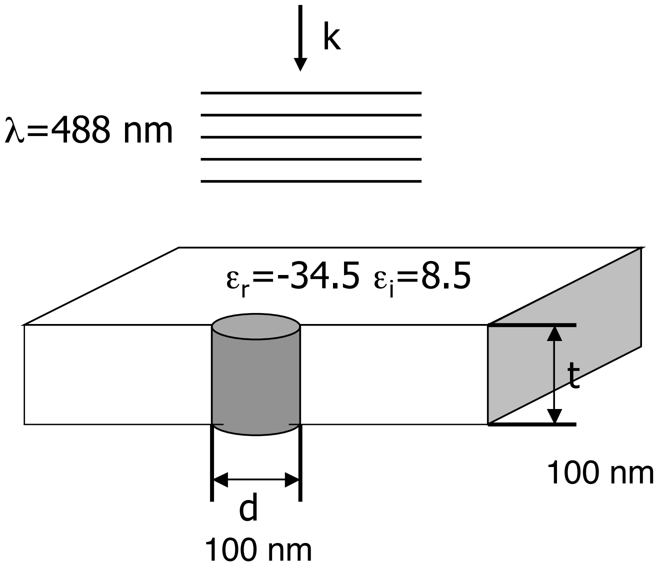
Illumination in
oblique reflection

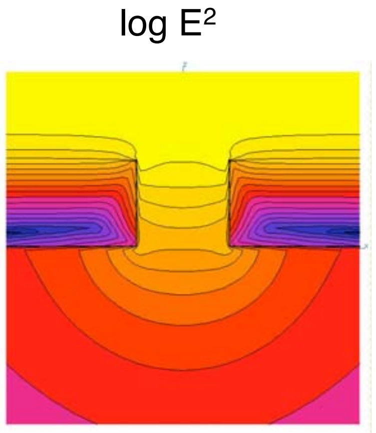


Collection in
TIR illumination



Thick metal screen - multiple multipole calculation



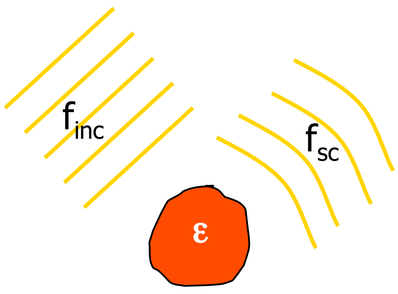


J. Renger (Dresden)

MMP concept

numerical methods in electrodynamics, e.g.

- domain methods: Finite-Difference Time-Domain (FDTD)
- boundary methods: Multiple Multipole Method[1] (MMP)



$$f(\mathbf{r}) = f_{inc} + f_{sc}$$

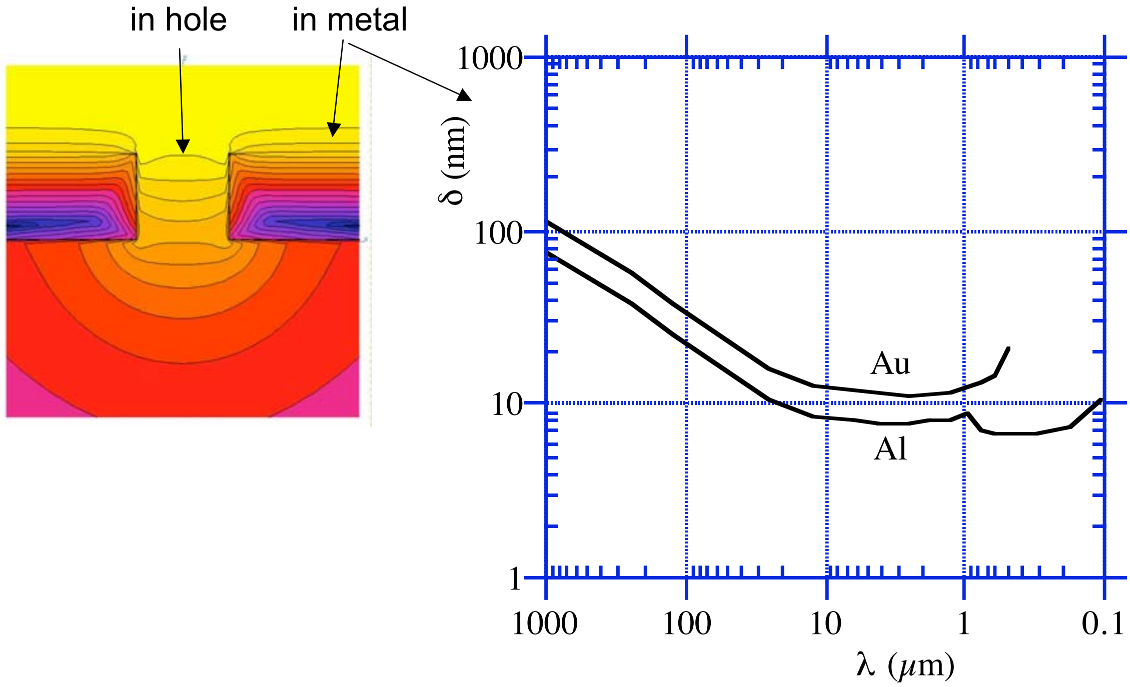
basis functions satisfy Maxwell's equations exactly (e.g. multipoles)

$$f = f_0 + \sum_k c_k f_k$$

MMP computes c_k by minimizing the error at the boundary

[1] C. Hafner, *The Generalized Multiple Multipole Technique for Computational Electromagnetics* (Artech, Boston, 1990).

Finite penetration depth

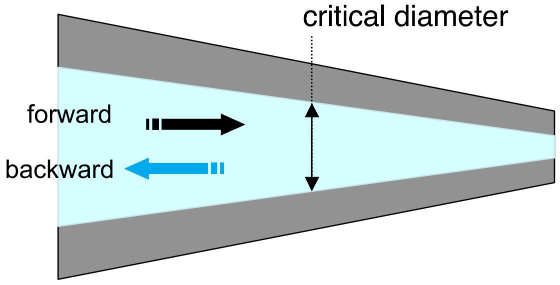


Evanescent transmission by mode ansatz

B. Knoll and F.Keilmann, Opt. Commun. **162**, 177 (1999)

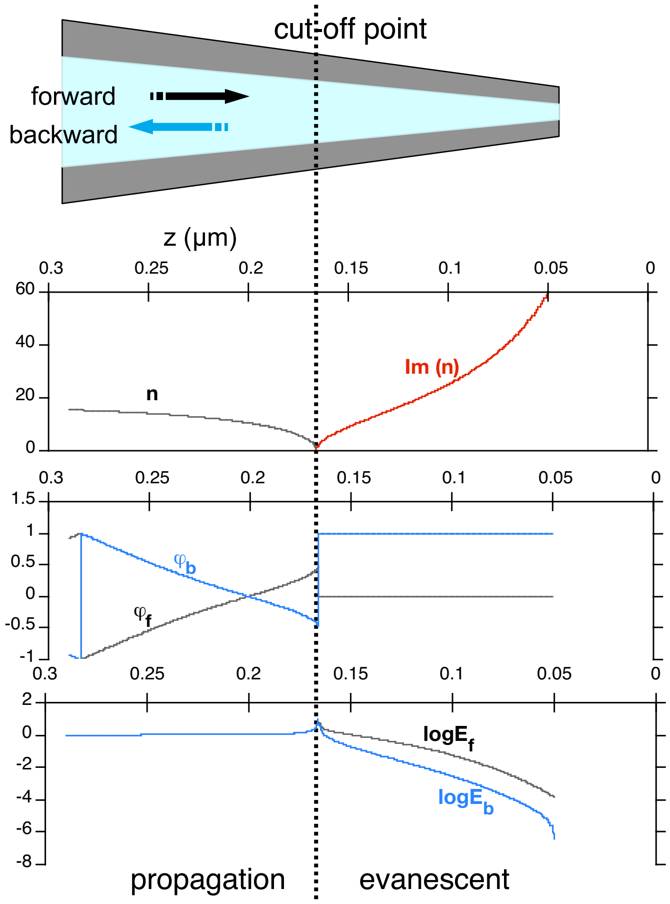
$$\omega > \sqrt{n^2+m^2}\,\frac{\pi c}{a\sqrt{\varepsilon}} = \omega_c(n,m)$$

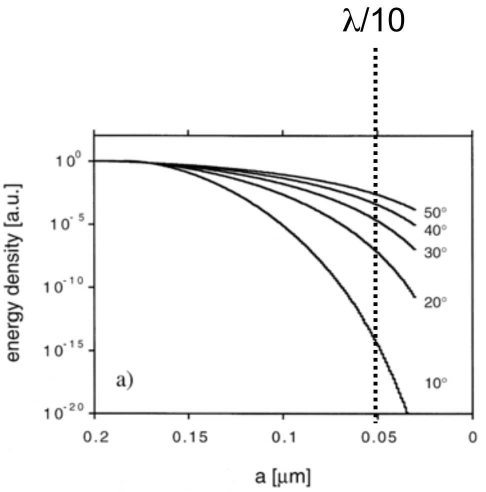
no propagation if a < λ/2



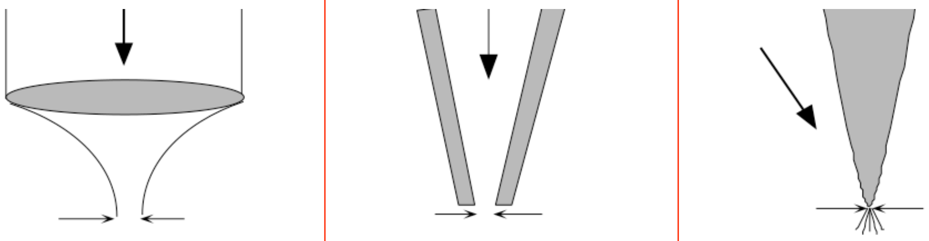
$$\frac{dE_f}{dz} = ik(z)E_f - \frac{1}{a}\frac{da}{dz}E_f - \frac{1}{2k(z)}\frac{dk(z)}{dz}\left(E_f - E_b\right)$$

$$\frac{dE_b}{dz} = -ik(z)E_b - \frac{1}{a}\frac{da}{dz}E_b - \frac{1}{2k(z)}\frac{dk(z)}{dz}\left(E_b - E_f\right)$$





Aperture SNOM limit: λ/10



λ/2

classical

diffraction-limited

λ/10

aperture SNOM

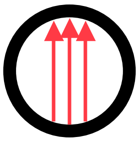
aperture-limited

< 30 nm

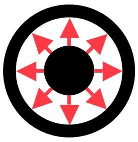
scattering SNOM

tip-limited

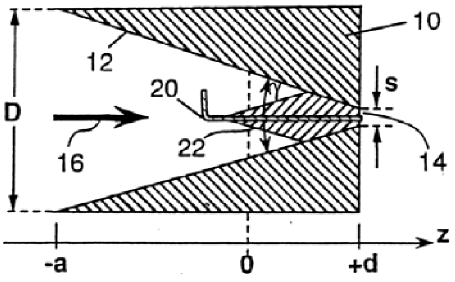
Coaxial taper for aperture SNOM ?

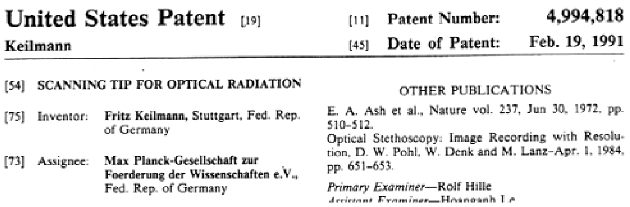


hollow guide has cutoff



coaxial guide has no cutoff





United States Patent [19]
Keilmann

[11] **Patent Number:** **4,994,818**
[45] **Date of Patent:** **Feb. 19, 1991**

[54] SCANNING TIP FOR OPTICAL RADIATION

[75] Inventor: **Fritz Keilmann,** Stuttgart, Fed. Rep. of Germany

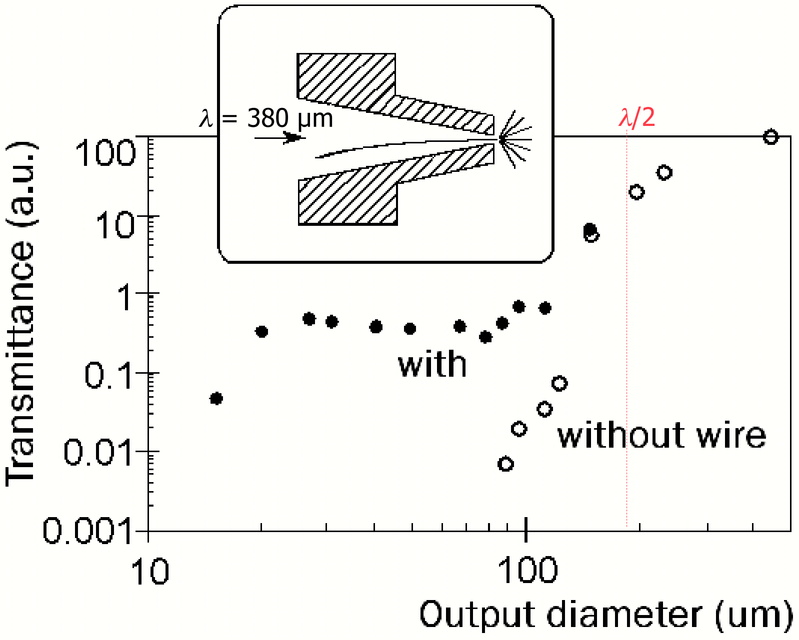
[73] Assignee: **Max Planck-Gesellschaft zur Foerderung der Wissenschaften e.V.,** Fed. Rep. of Germany

OTHER PUBLICATIONS

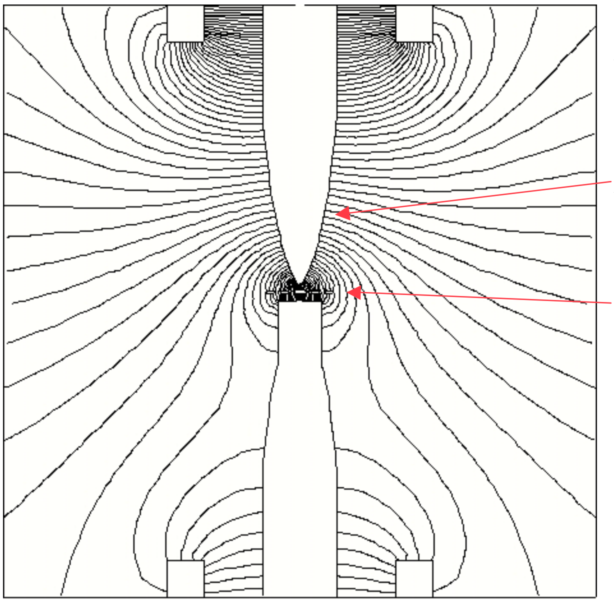
E. A. Ash et al., Nature vol. 237, Jun 30, 1972, pp. 510–512.
Optical Stethoscopy: Image Recording with Resolution, D. W. Pohl, W. Denk and M. Lanz–Apr. 1, 1984, pp. 651–653.

Primary Examiner—Rolf Hille
Assistant Examiner—Hoanganh Le

Coaxial taper in the far infrared



Radiowave microscope



coaxial cable from source

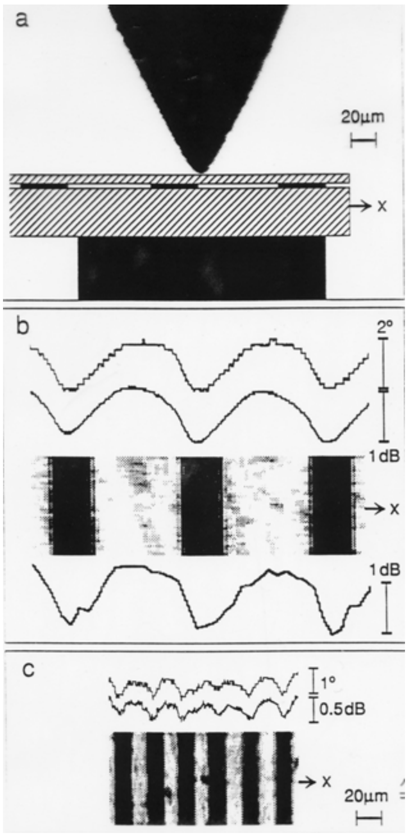
inner conductor sharpened to concentrate field lines

microstructured sample in "tip focus"

coaxial cable to receiver

F. Keilmann, D.v.d. Weide, J. Eickelkamp, R. Merz, and U. Stöckle, Opt. Comm. **129**, 15 (1996)

Radioimaging

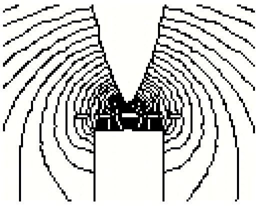


700 MHz

$\lambda = 40$ cm

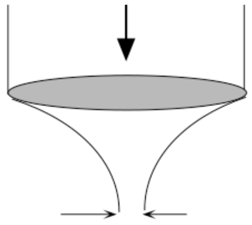
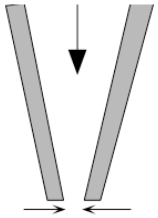
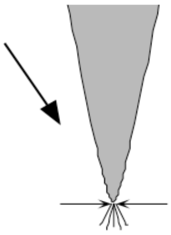
7 MHz

$\lambda = 40$ m



resolution $\lambda/2000000$!!

Microscope principles use different interaction concepts

λ/2 | λ/10 | < 30 nm

classical
diffraction-limited

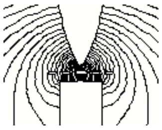
free-space

aperture SNOM
aperture-limited

guided

scattering SNOM
tip-limited

confined



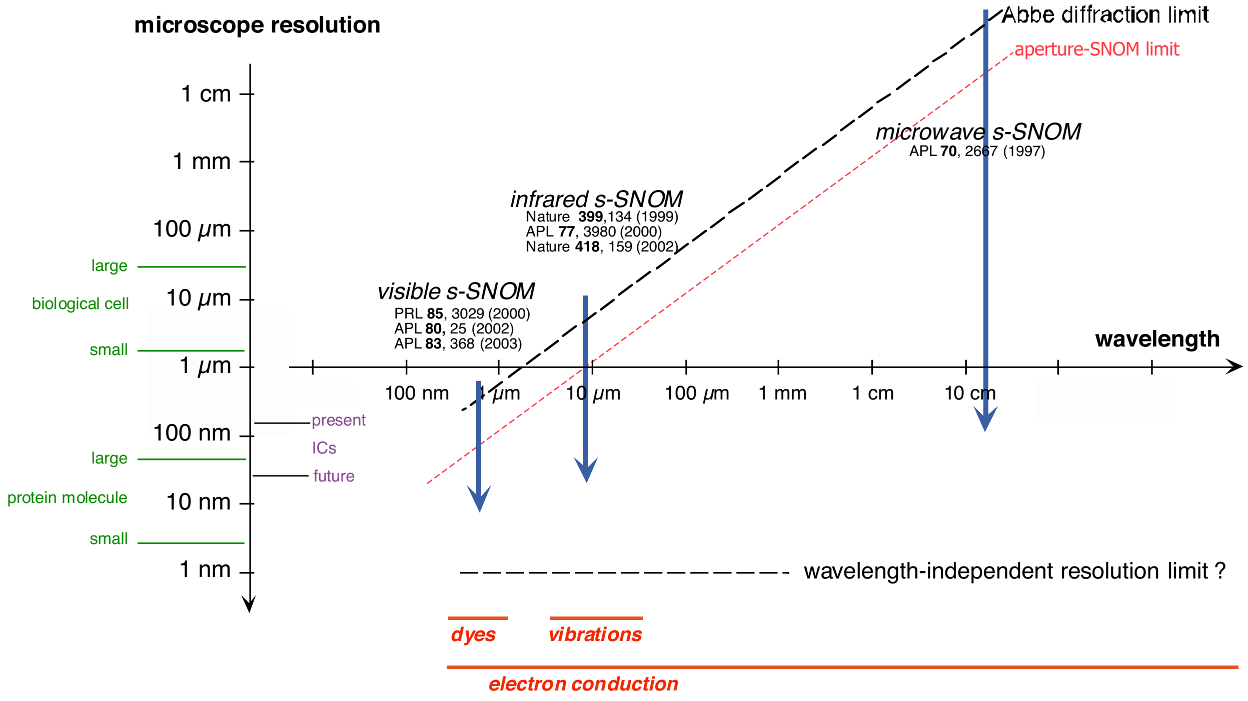
transverse polarisation

travelling wave

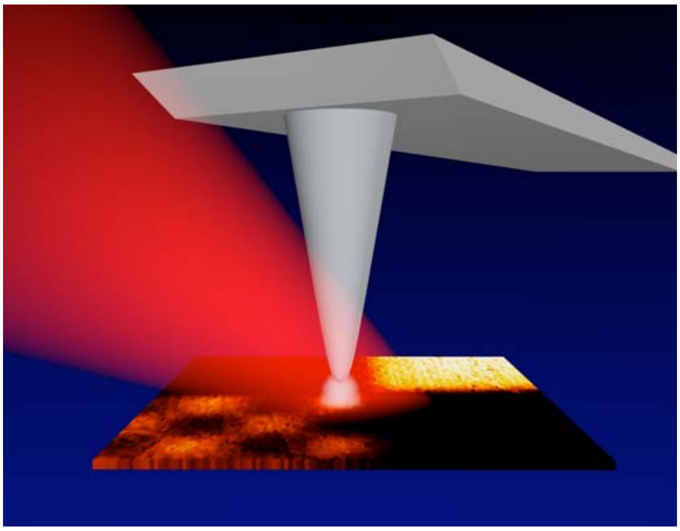
longitudinal polarisation

electrostatic field

Apertureless near-field microscopy chances

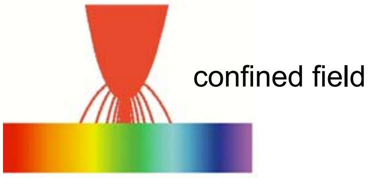


„Apertureless“ or s-SNOM

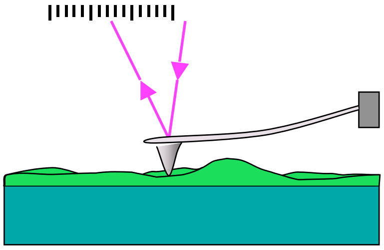


a cantilevered
metal tip
serves as antenna

near field with
≈ 20 nm spot size
probes surface

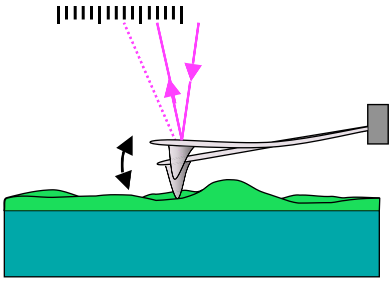


Cantilever height measured by laser reflection



feedback to keep cantilever
bending constant

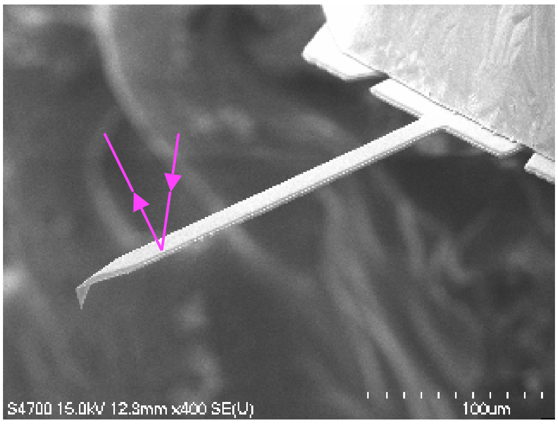
yields AFM topography

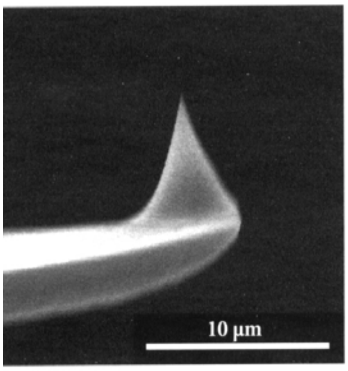


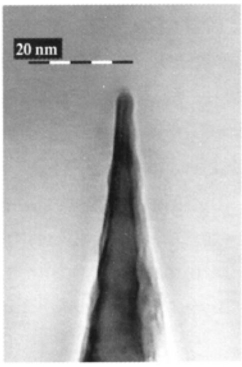
tapping oscillation

allows fast tip-sample
distance modulation

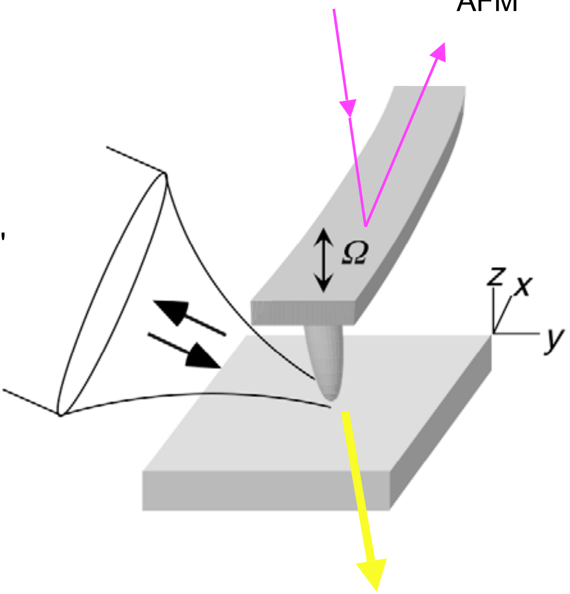
Commercial Si cantilever tips





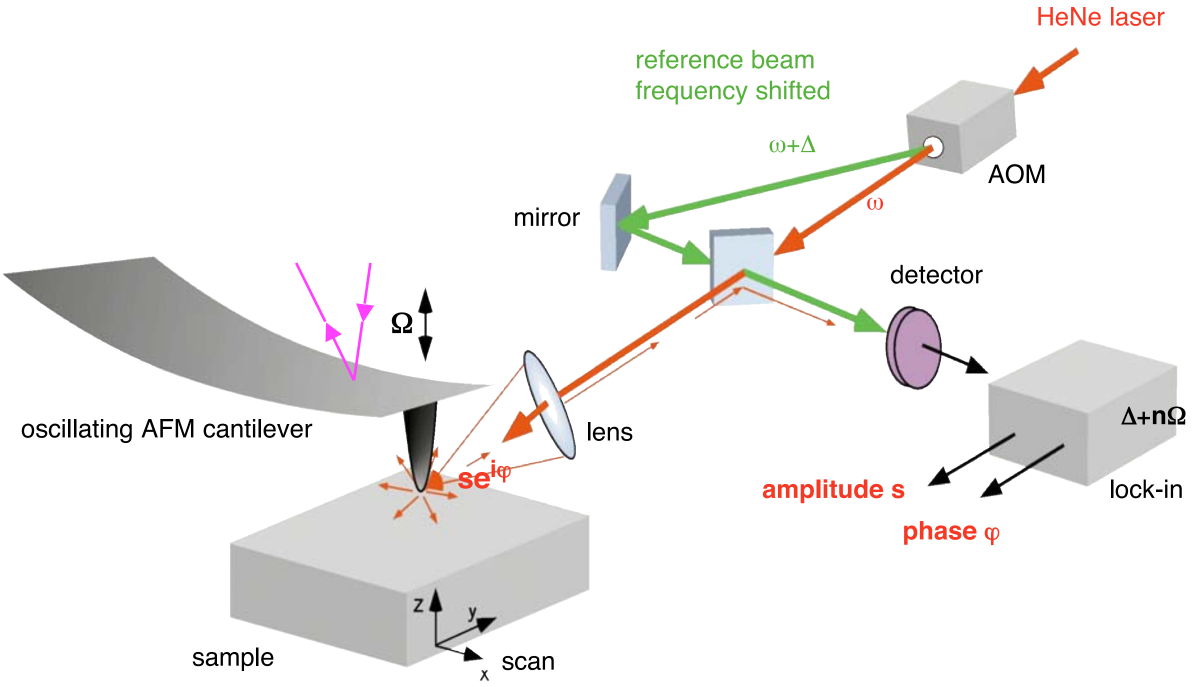


Backscattering geometry



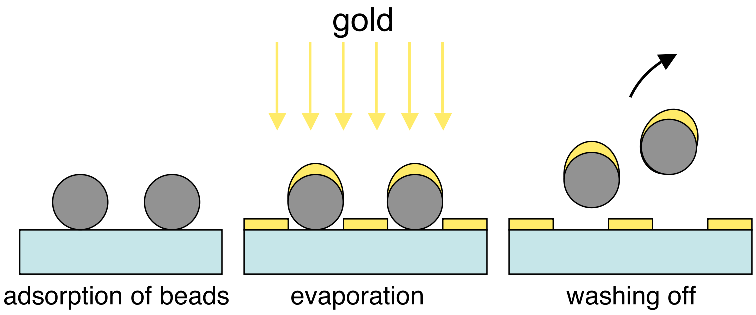
the "tapping" tip-sample distance
modulation Ω
modulates the optical near-field interaction

s-SNOM with heterodyne detection of backscattering

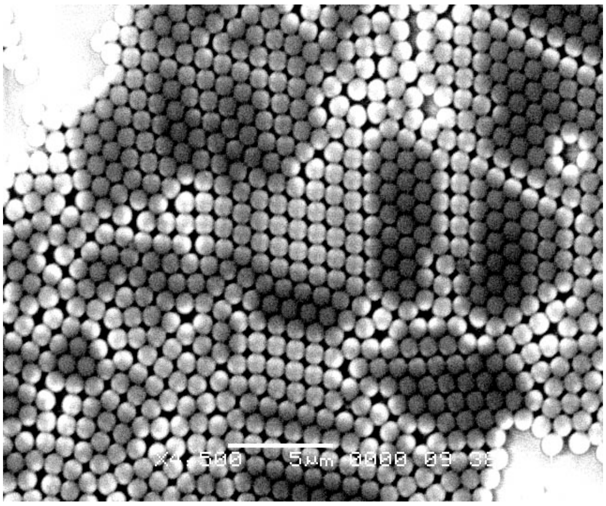


R. Hillenbrand, F. Keilmann, Phys. Rev. Lett. **80**, 3029 (2000)

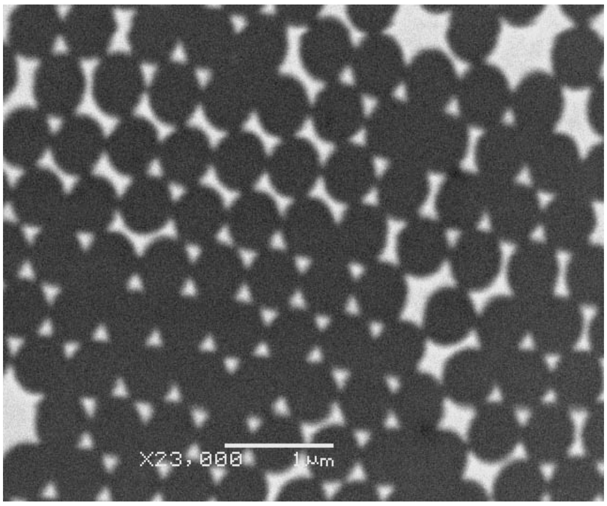
Test sample by colloidal lithography



Test sample Au on Si

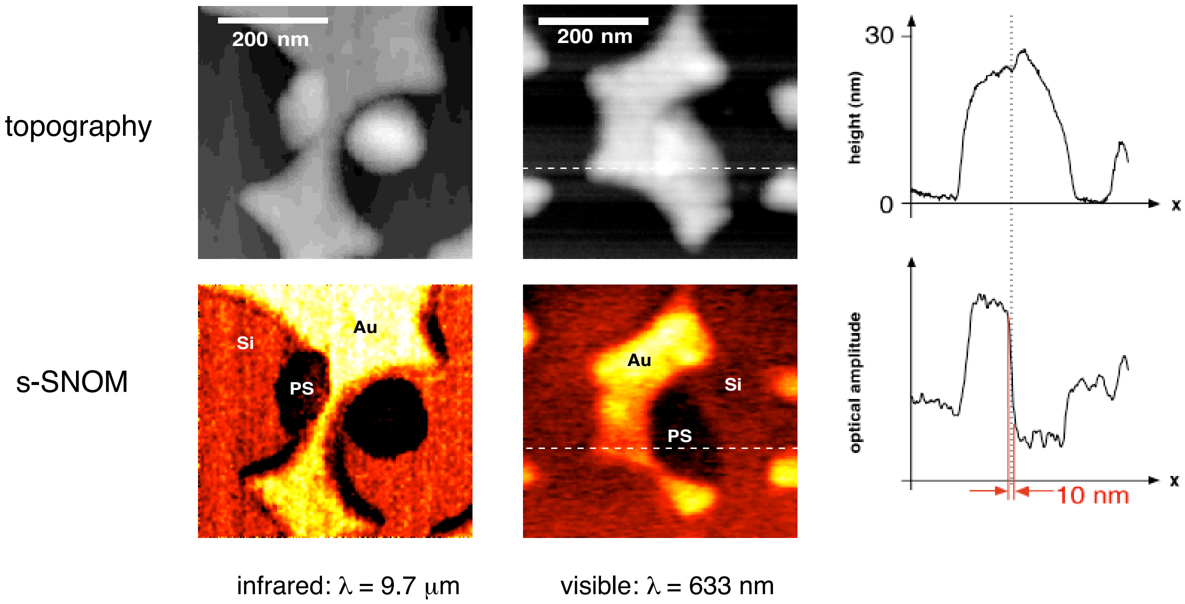


SEM image of self-assembled
monolayer of polystyrene (PS) beads

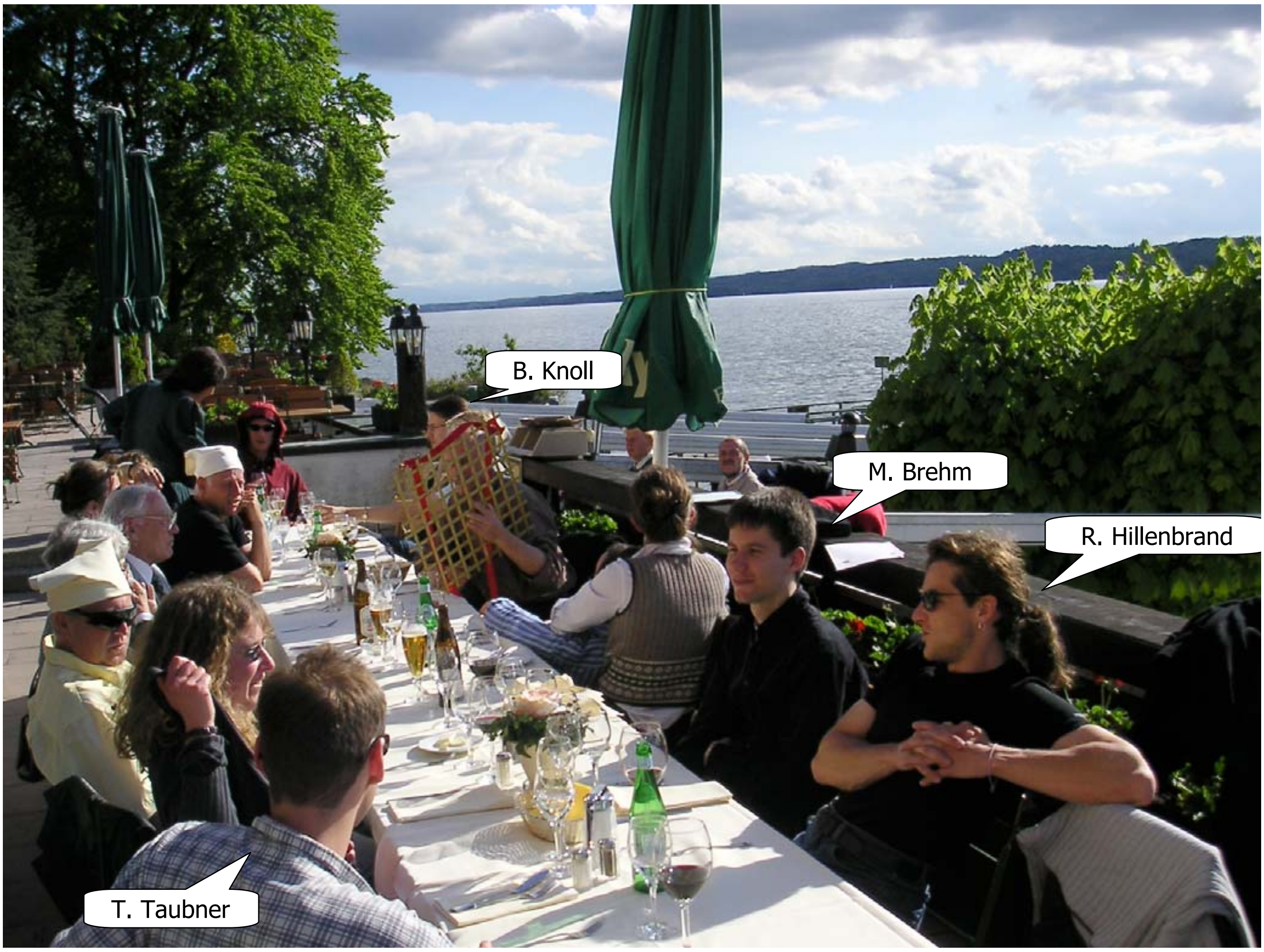


SEM image after Au evaporation
and dissolving the beads

Material-dependent, λ-independent near-field contrast



T. Taubner, R. Hillenbrand, F. Keilmann, J. Microscopy **210**, 311 (2003)

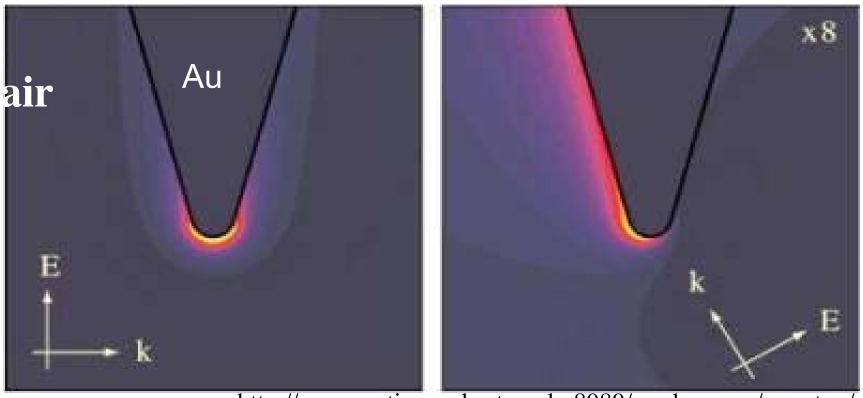


s-SNOM issues and challenges

- Resolution was ultimate goal -> advantage over aperture-SNOM
- to explain the contrast, physical theory
- But: Artefacts by topography (tip-sample distance changes) and background scattered light (lots of „doubtful“ images!)
- Modulation techniques are necessary
- Field enhancement is there, but how big is it really?
- **tip-enhanced** microscopies evolve, such as probing Raman-scattered light, Rayleigh-scattered light (VIS, IR and THz, microwave), fluorescence, second-harmonic-generation, writing with tip-enhanced fields

Tip focusing

incident light becomes enhanced, on a highly confined spot



http://www.optics.rochester.edu:8080/workgroups/novotny/

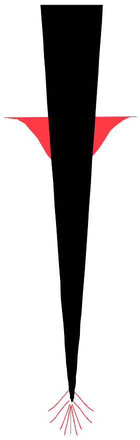
such narrow confinement prequisite for s-SNOM
physical concepts: antenna, surface waves

how does this spot interact with the sample
analytic theory

Surface waves

Maxwell equations allow solutions of bound waves on "conductive" surfaces (i.e. negative ε)

metal	surface plasmon polariton
dielectric	surface phonon polariton
	surface exciton polariton



a Sommerfeld wave = a wire plasmon
travels along a metal wire;
can it "focus" at the tip?

any connections?

an electrostatic field is intensified at a metal tip
(lightning rod effect)

Surface plasmon polaritons

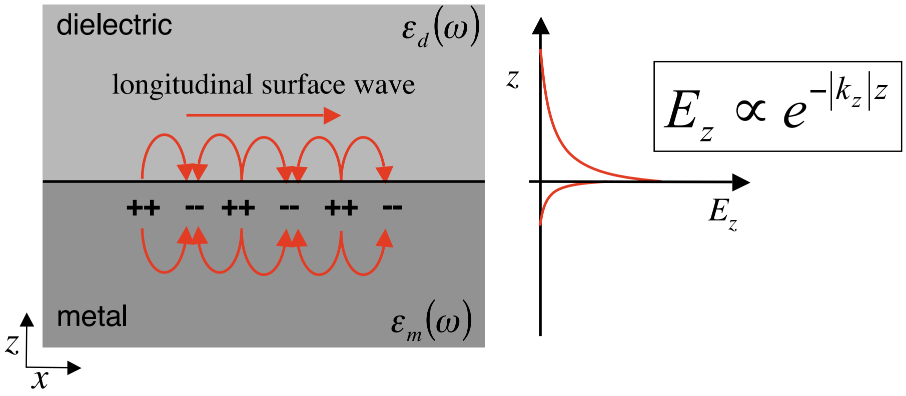
Radiative surface plasmons are coupled with propagating EM waves

Nonradiative surface plasmons do not couple with propagating EM waves

On perfectly flat surfaces SPPs are always nonradiative!

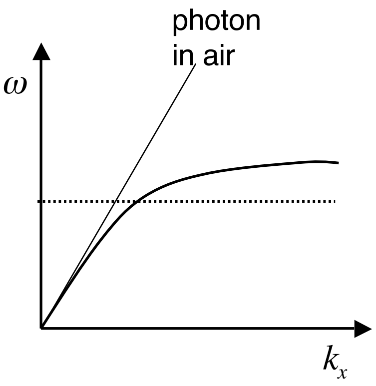
Mixed transversal and longitudinal EM field

In contrast to TIR the plasmon field on both sides of the interface are evanecent



$$E_z \propto e^{-|k_z| z}$$

Surface plasmon polariton dispersion

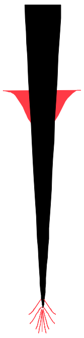


for a given ω: k of photon in air < k of SPP

↓

no excitation of SPP is possible

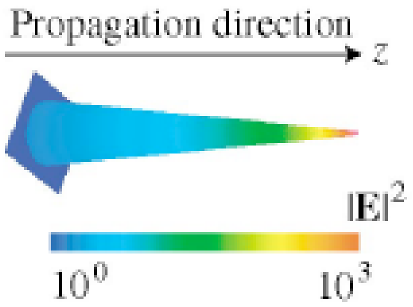
(on flat surface;
remedy: grating or prism coupling)



a Sommerfeld wave = a wire plasmon
travels along a metal wire;
can it "focus" at the tip?

Stockman theory: yes!

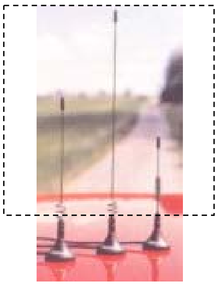
PRL 93, 137404 (2004)



how to launch the surface wave?

Antenna

a device to catch the wind



a device to catch radio

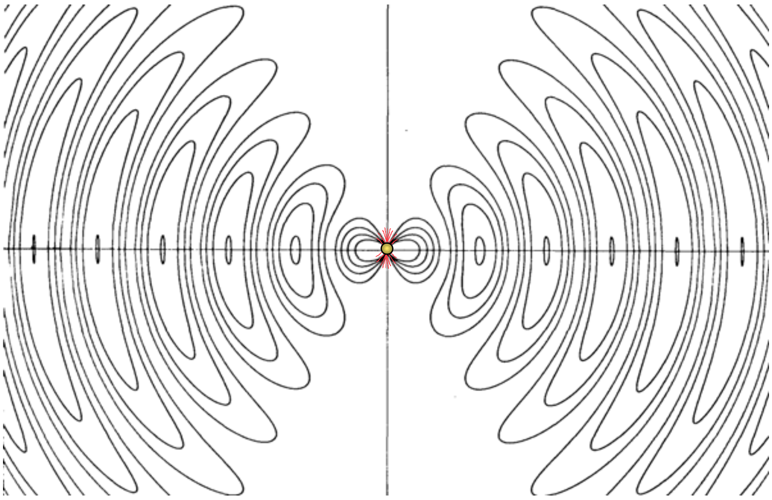
optimal length:
L=λ/4

absorption
cross section:
L^2

generally, a device to **couple** electromagnetic energy from one mode into an other:

Gaussian beam
fiber guide
hollow metal guide
coaxial guide
surface wave
  2dim
  1dim
  0dim

Molecular/atomic dipole emitter/absorber

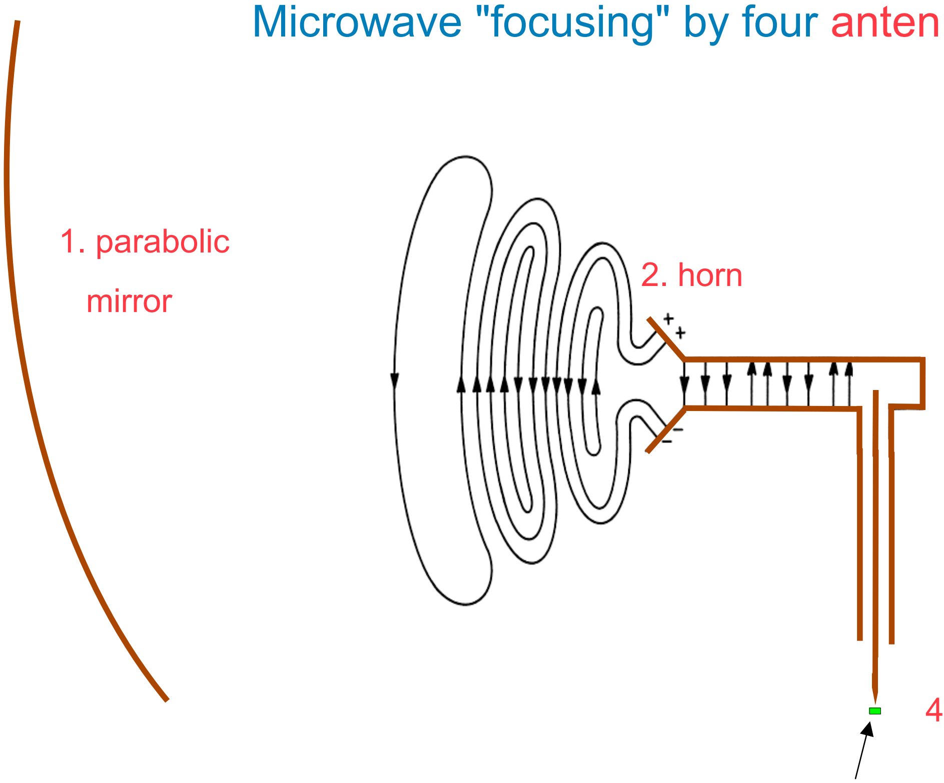


has very bad antenna efficiency:

even if the absorption cross section were unusually large e.g., 10^{-14} cm^2 = 1 nm^2

the antenna efficiency, at λ=400 nm, is still only $(1\text{nm} / 100\text{nm})^2 = 10^{-4}$

Microwave "focusing" by four antennae



1. parabolic mirror

2. horn

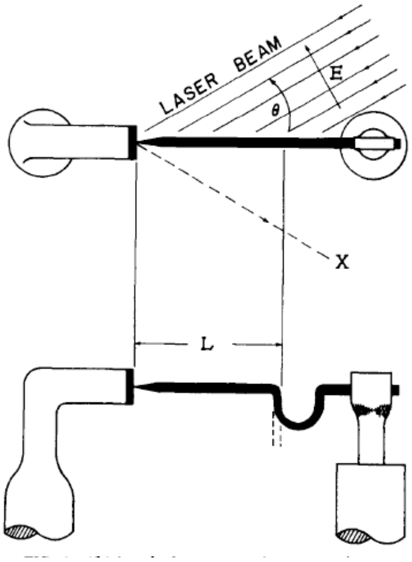
3. wire antenna

4. tip focus

at λ = 10 cm overall efficiency to reach 1 µm transistor/diode >50% !!!!

Antenna lobes in the infrared

Evenson APL **17**, 8 (1970)



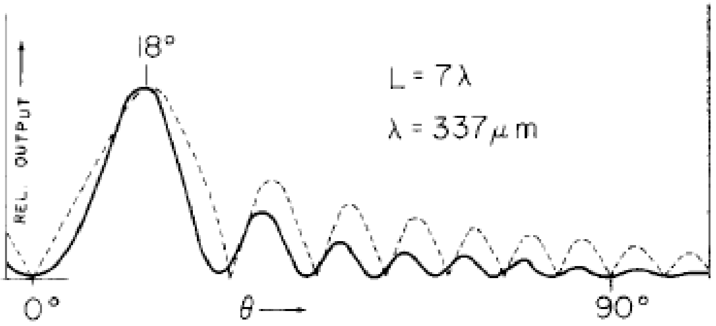
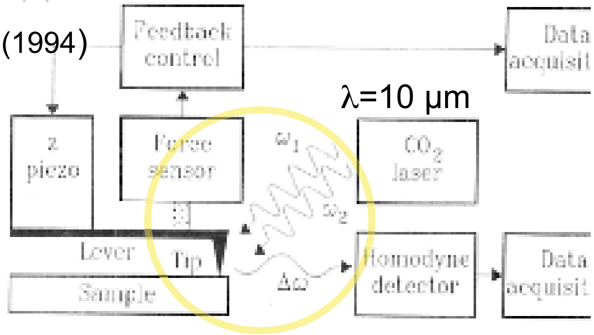


FIG. 2. Portion of the antenna pattern of a whisker seven wavelengths long. Solid curve, experimental; dashed curve, theoretical.

Efficiency obtained with infrared antenna

Völcker, Krieger, Walther, J.Vac.Sci.Tech.B **12** 2129 (1994)

(a)



λ=10 μm

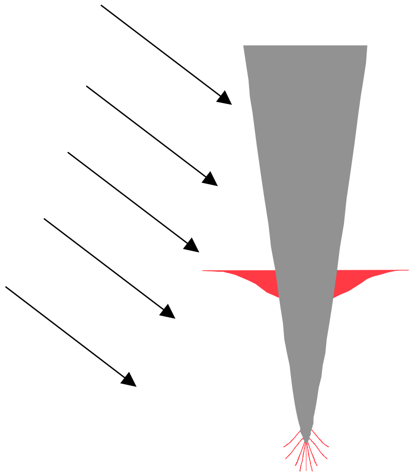
STM

TABLE I. Power conversion in the tip–sample junction.

Applied laser power	$P^l_{\omega_1} + P^l_{\omega_2}$	30	mW	0
Power received by the tip	$P^a_{\omega_1} + P^a_{\omega_2}$	730	μW	1.6
Power at ω in the gap	$P^g_{\omega_1} + P^g_{\omega_2}$	41	nW	5.8
Power at $\Delta\omega$ in the gap	$P^g_{\Delta\omega}$	130	pW	8.3
Total power emitted at $\Delta\omega$	$P^t_{\Delta\omega}$	640	aW	10.7
Detected power at $\Delta\omega$	$P^d_{\Delta\omega}$	200	aW	11.2

[a] Experimental value.

What we learn: two steps



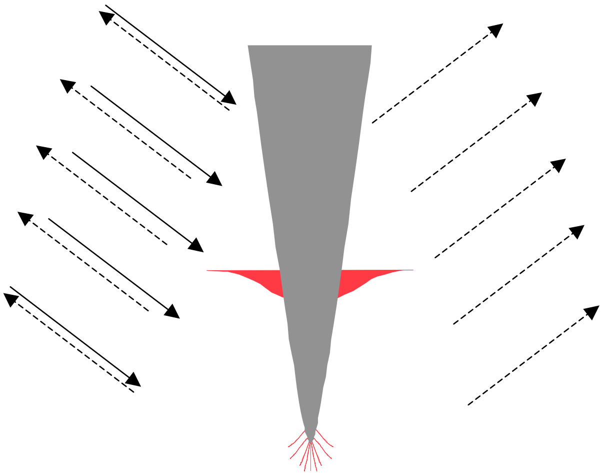
in order to create a strong near field at the solid tip

1. light from the free-space has to be intercepted by an antenna, i.e., by a structure longer than the imediate apex region

2. currents or surface waves distributed along the antenna should exite the apex region

---

Three more

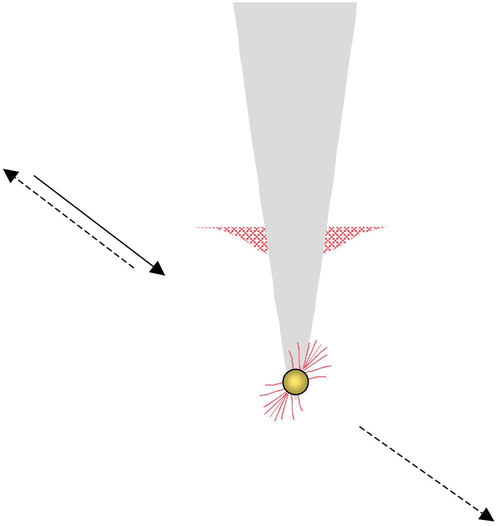


3. to interact with the sample

4. to excite currents or surface waves distributed along the antenna

5. to emit a free-space beam

Is antenna needed?



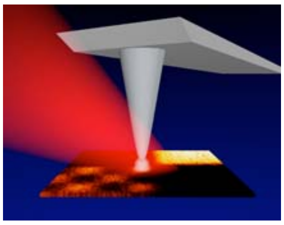
if the tip were replaced by a very small particle

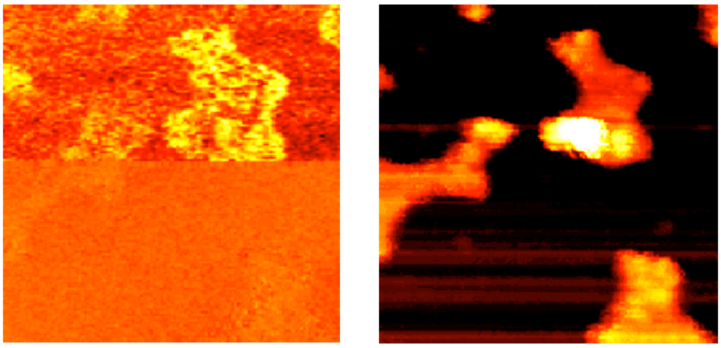
confined near fields also occur

but possibly much weaker

(exception: dielectric resonance e.g. from particle plasmon)

Polarization test at λ=10µm





p-polarization

s-polarization

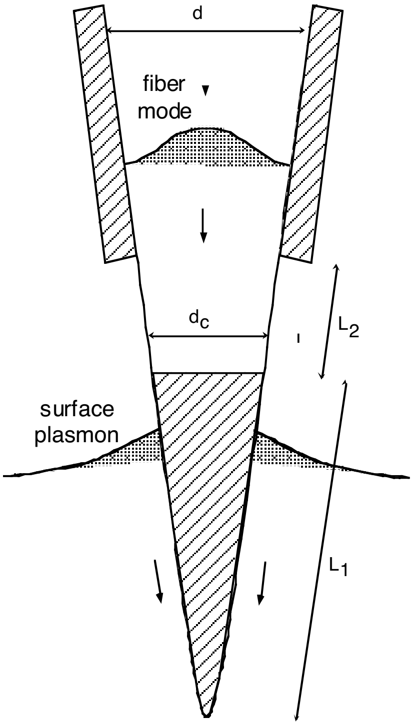
infrared

topography

Tip-on-aperture

aperture SNOM
is used...

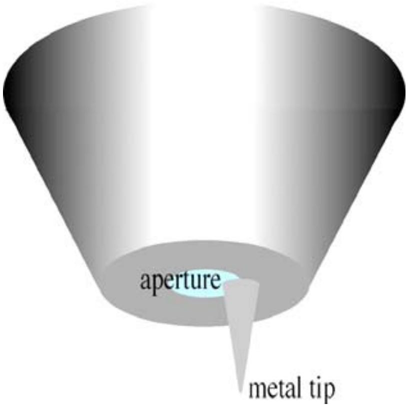
...to illuminate
solid tip

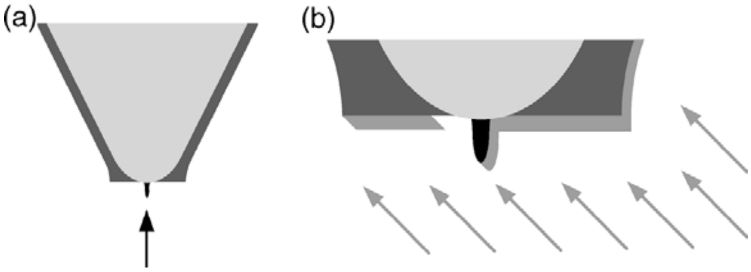


resonant
sections

F. Keilmann, R. Guckenberger
Patent DE 19522546 (1995)

Tip-on-aperture experimental



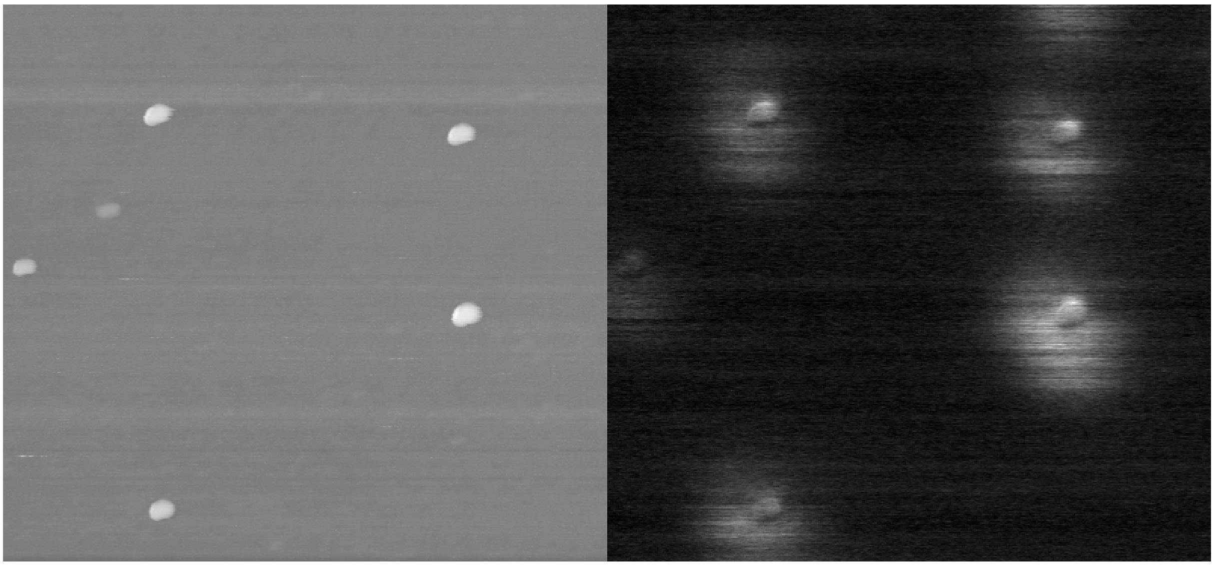


growth of C tip

metallization

H.G. Frey, A. Kriele, F. Keilmann, and R. Guckenberger, APL **81**, 5030 (2002)

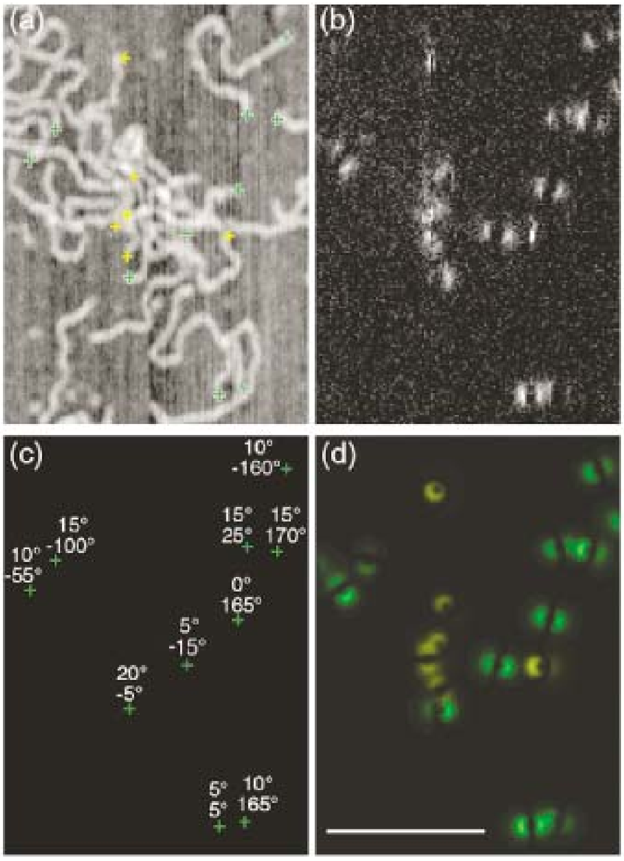
Fluorescent beads



topography

fluorescence

DNA with single dye molecules



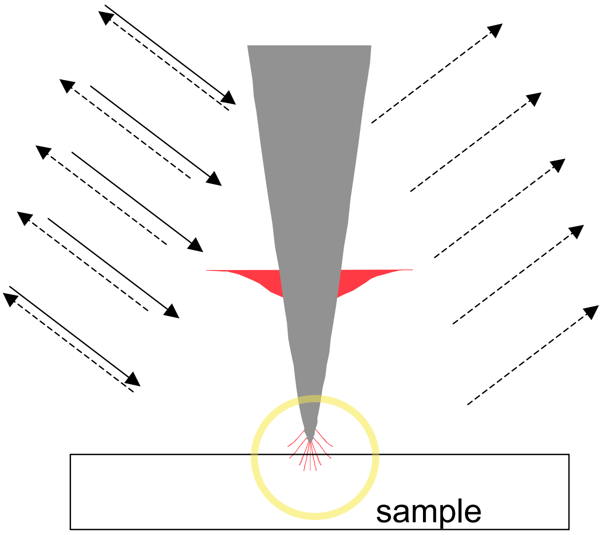
topography

fluorescence

modelling of fluorescence

Guckenberger et al.
PRL Nov. 2004

How can one understand step 3. near-field interaction ?

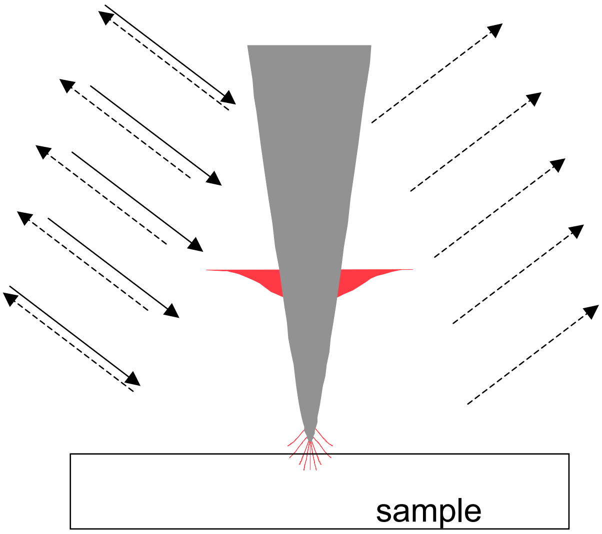


3. to interact with the sample

4. to excite currents or surface waves distributed along the antenna

5. to emit a free-space beam

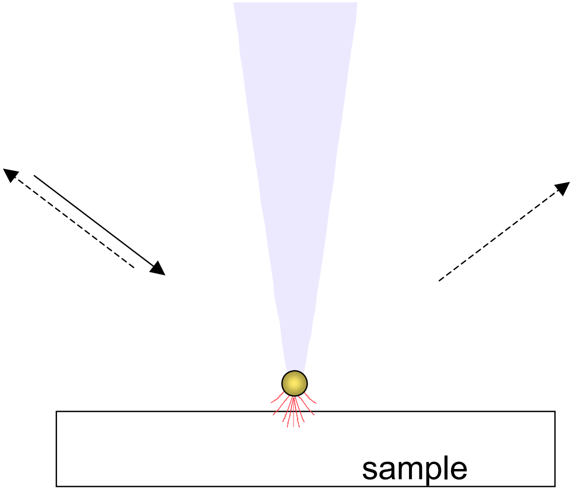
Only apex counts



idea:

near-field shape does not depend on long shaft

Point dipole theory



to model the near-field interaction

we approximate the tip by a small sphere

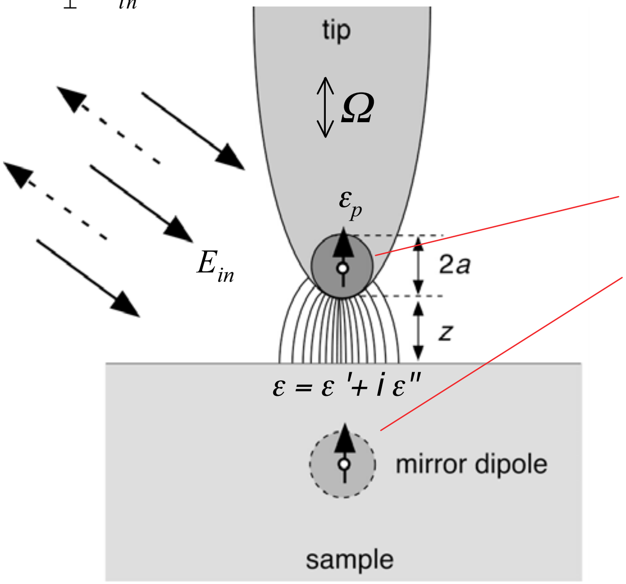
but retain z-orientation of near field due to tip shaft

calculate dipole moment of point dipole in sphere center

Near-field interaction between point dipole and sample

measured far-field:

$$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$$



treated by combining the scattering from two dipoles

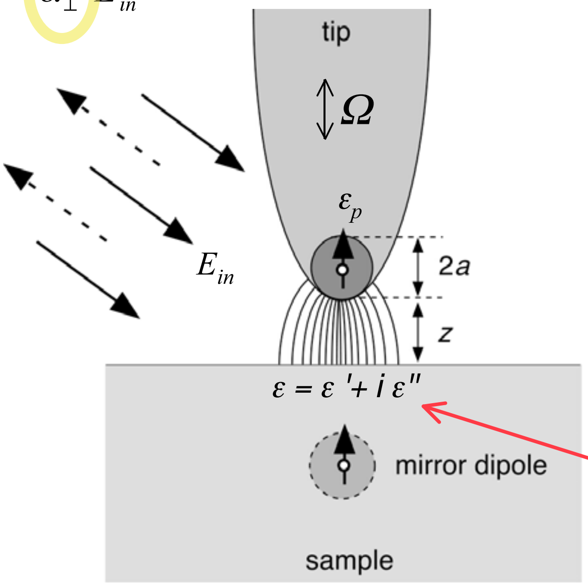
point dipole in tip apex interacting with mirror dipole in the sample

P. Aravind and H. Metiu, Surf. Sci. **124**, 506 (1983)

Near-field interaction measures ε=ε'+iε" of sample

measured far-field:

$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$



polarizability of tip dipole:

$$\alpha = 4\pi a^3 \frac{(\varepsilon_p - 1)}{(\varepsilon_p + 2)}$$

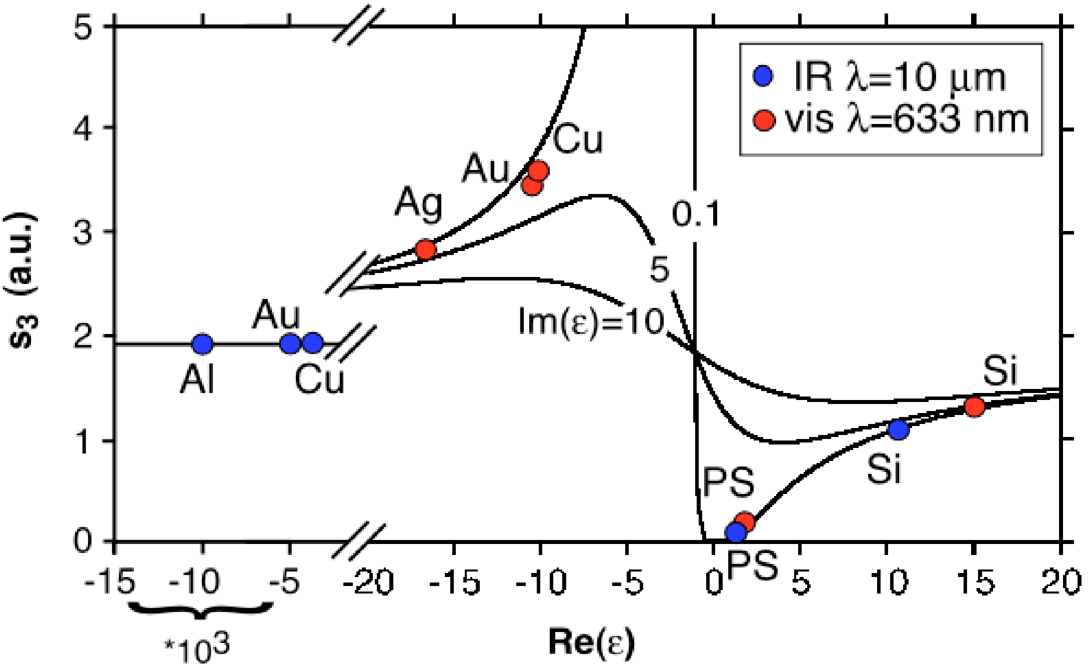
effective polarizability of tip and sample:

$$\alpha_{\perp}^{eff} = \frac{\alpha(1+\beta)}{1 - \frac{\alpha\beta}{16\pi(z+a)^3}}$$

with $$\beta = \frac{(\varepsilon - 1)}{(\varepsilon + 1)}$$

complex ε determines scattering amplitude and phase

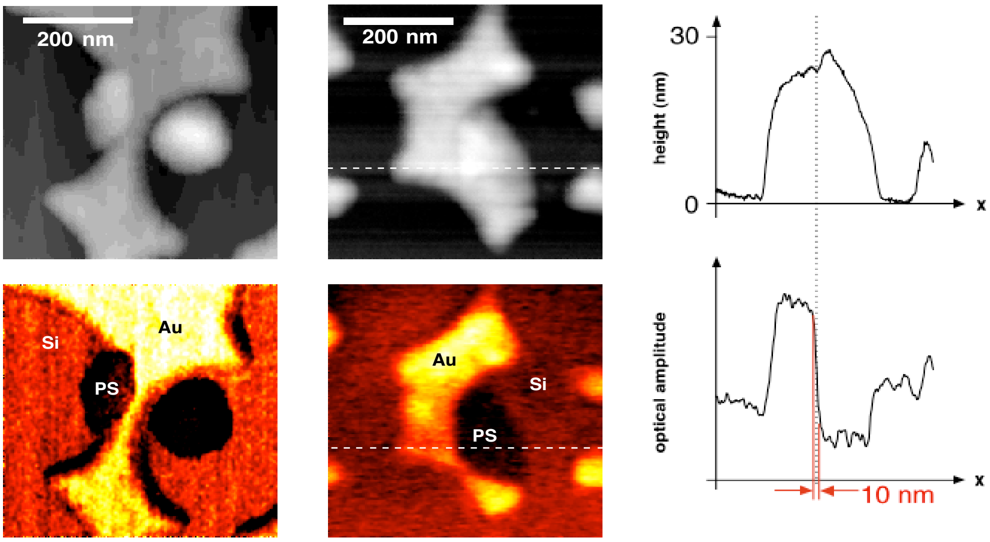
Predicted scattering amplitude from point d. model



Material-dependent, λ-independent near-field contrast

topography

s-SNOM



infrared: λ = 9.7 µm

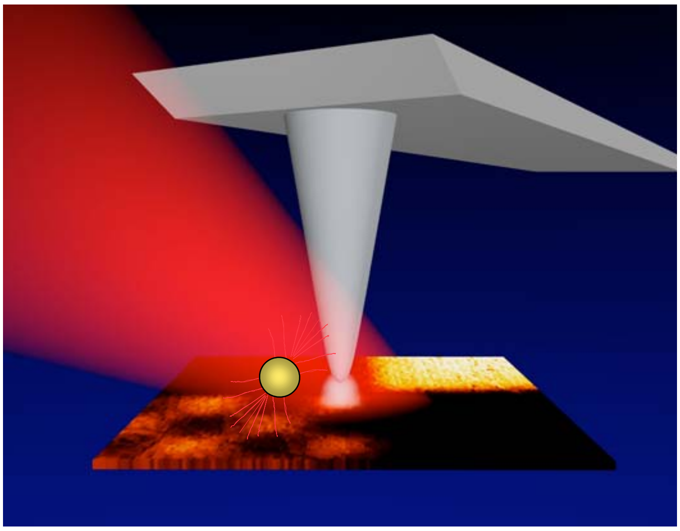
visible: λ = 633 nm

T. Taubner, R. Hillenbrand, F. Keilmann, J. Microscopy **210**, 311 (2003)

---

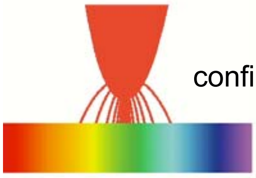
break

„Apertureless“ or s-SNOM

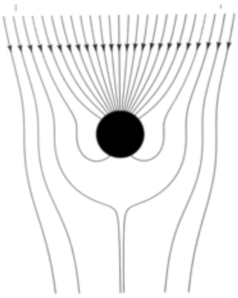


a cantilevered
metal tip
serves as antenna

near field with
≈ 20 nm spot size
probes surface



Dielectric resonance of a small particle



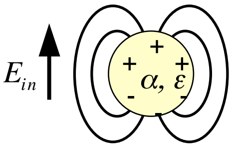
small particles can become optically resonant

condition $\varepsilon' = -2$, ε'' small

(dielectric antenna)

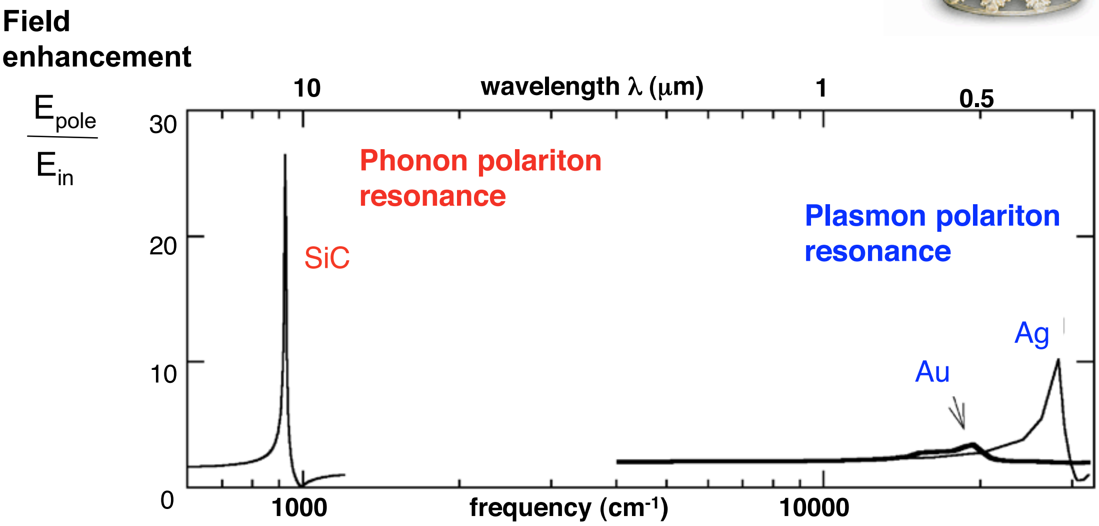
consequences
- enhanced near field
- enhanced Raman scattering
- enhanced nonlinear conversion

Examples



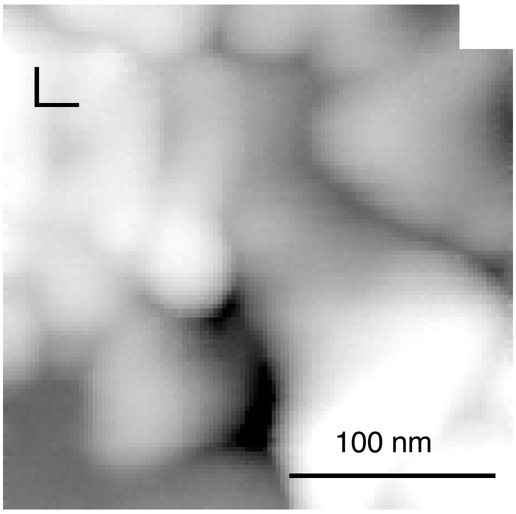
$$\alpha = 4\pi a^3 \frac{\varepsilon - 1}{\varepsilon + 2}$$

resonance at
$\varepsilon = -2$

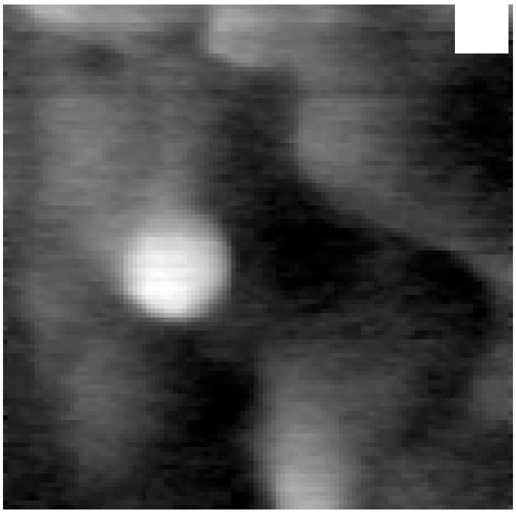


Example

λ = 633 nm



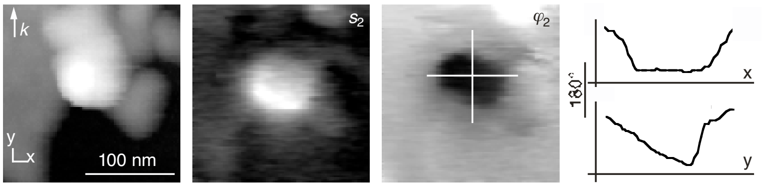
topography



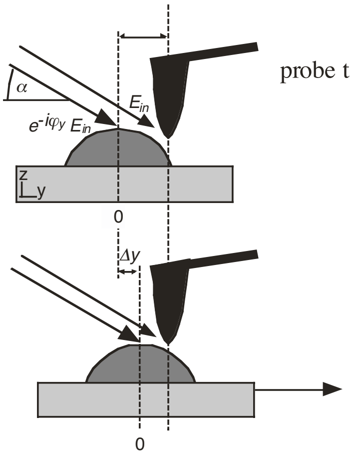
optical amplitude

Phase gradient in scan direction

λ = 633 nm



topography optical amplitude optical phase



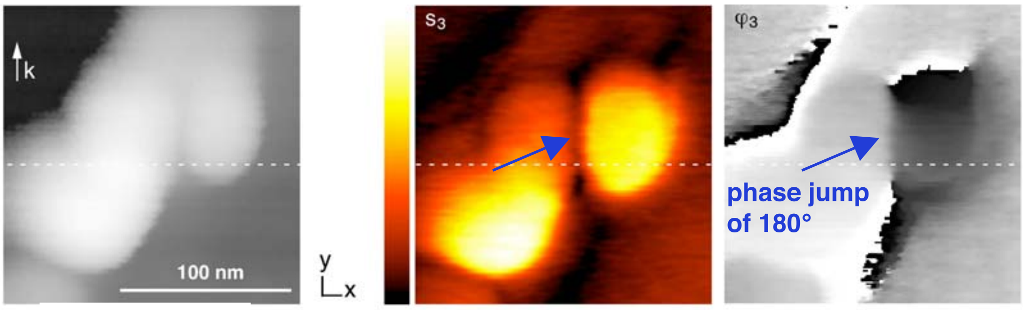
probe tip stays fixed in space

sample advances

→ the oscillation phase ϕ_p of the particle appears linearly retarded in y-direction (not in x-direction) by

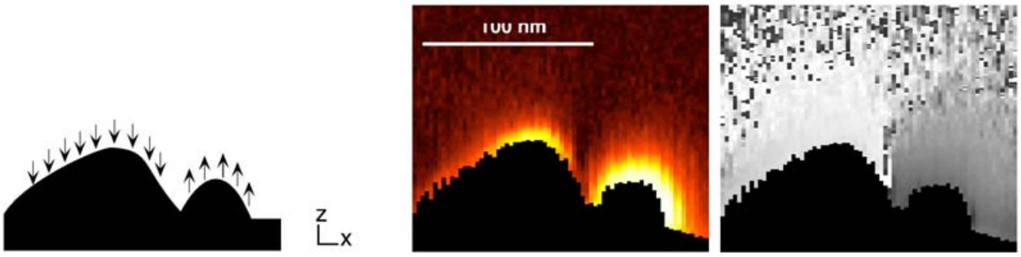
$$\varphi_p = \Delta y \frac{2\pi}{\lambda} \cos(\alpha)$$

Particle with quadrupolar mode



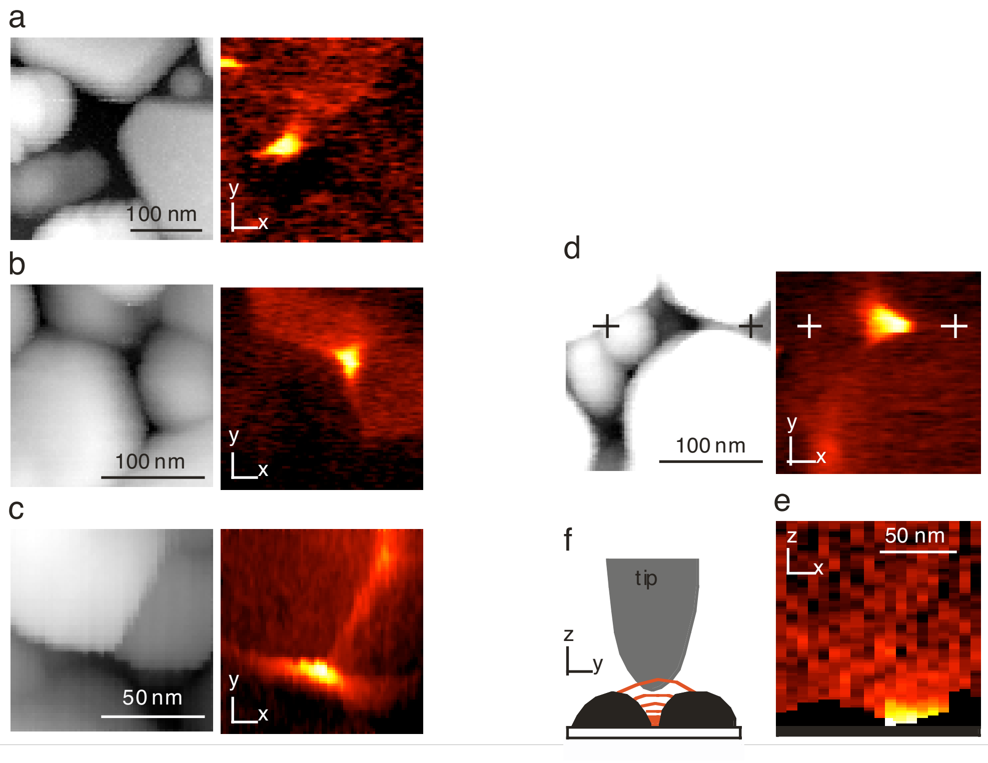
phase jump of 180°

topography **amplitude** **phase**



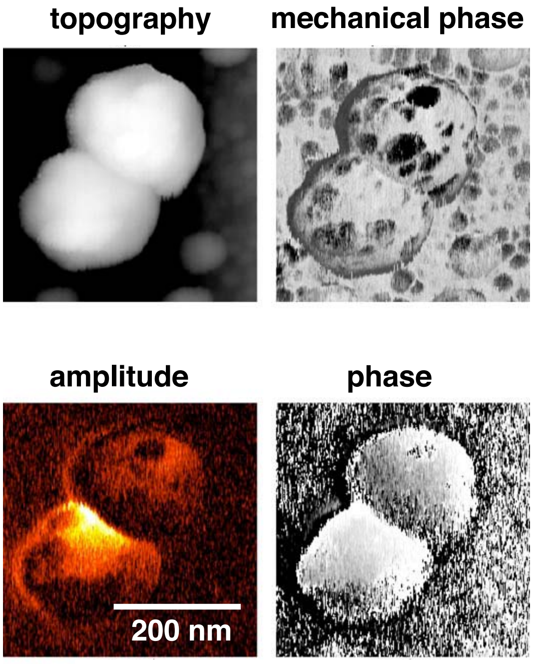
R. Hillenbrand, F. Keilmann, Appl. Phys. B **79** (2001)

Highly localized fields in gaps



Gap field in Ag dimer

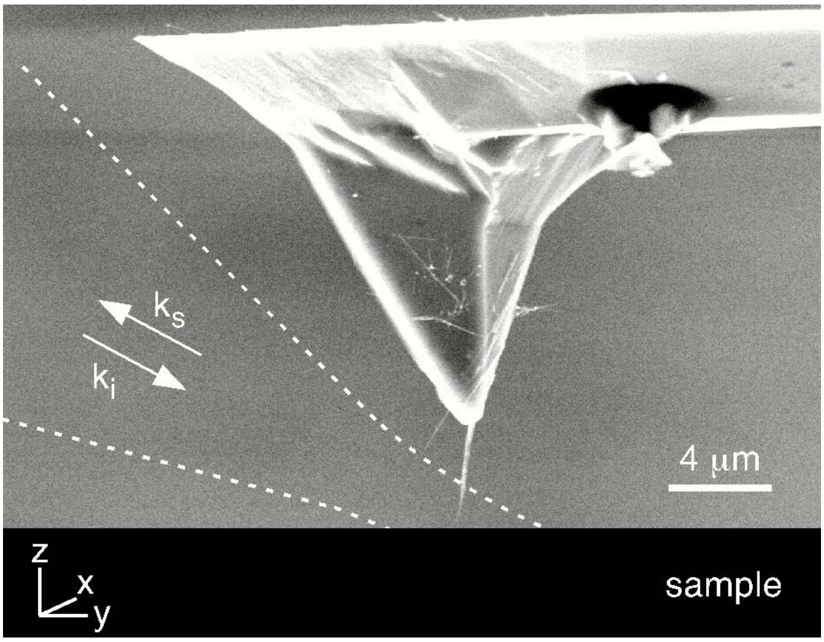
sample from H. Xu and M. Käll (Göteborg)



s-SNOM at λ=633nm

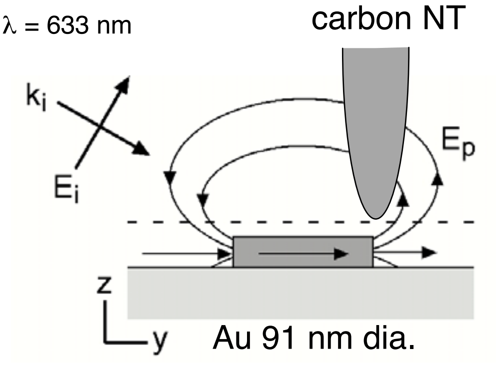
Quantitative study using carbon nanotube bundle as tip

supplied by npoint

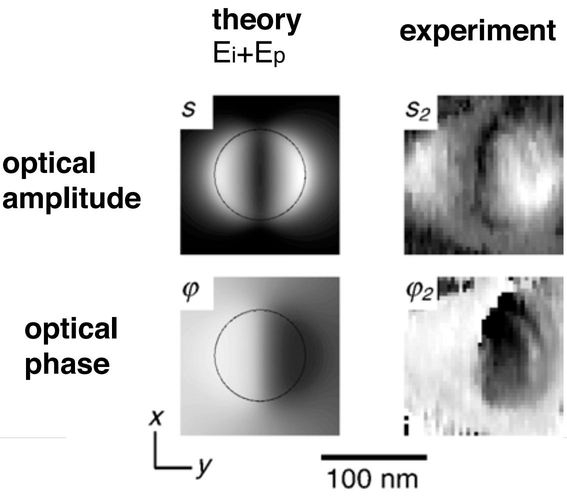


Imaging enhanced near field of tailor-made Au disk

λ = 633 nm

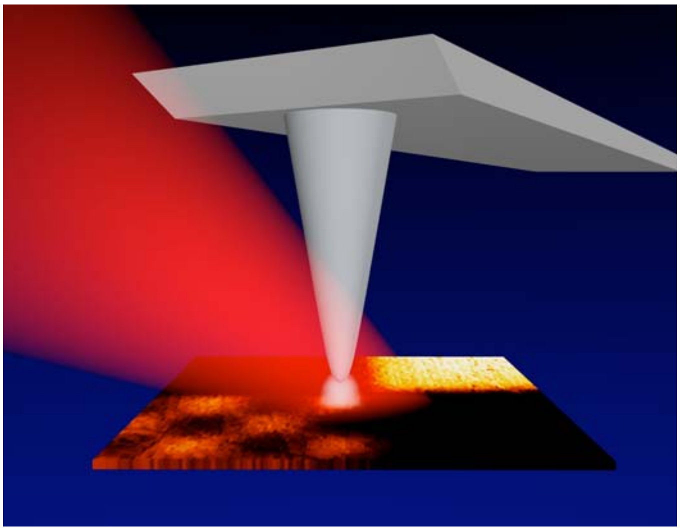


$$E_{sca} \propto \alpha_{eff}\left(E_i + E_p\right)$$



R. Hillenbrand, F. Keilmann, P. Hanarp,
S.D. Sutherland, and J. Aizpurua
APL **83**, 368 (2003)

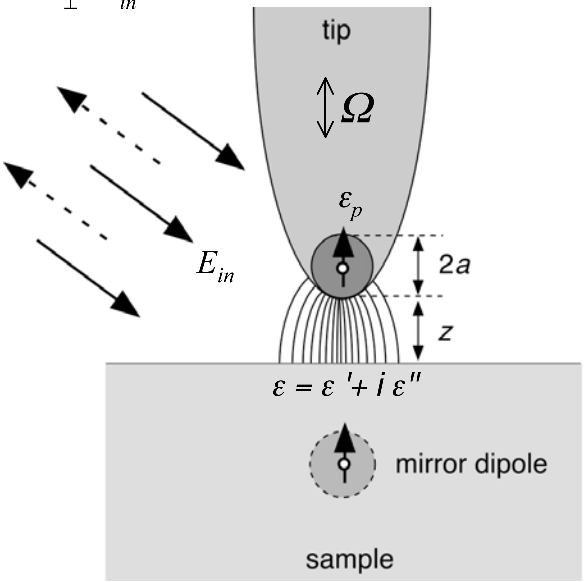
back to local spectroscopic probing



Near-field interaction is nonlinear in z

measured far-field:

$$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$$



polarizability of tip dipole:

$$\alpha = 4\pi a^3 \frac{(\varepsilon_p - 1)}{(\varepsilon_p + 2)}$$

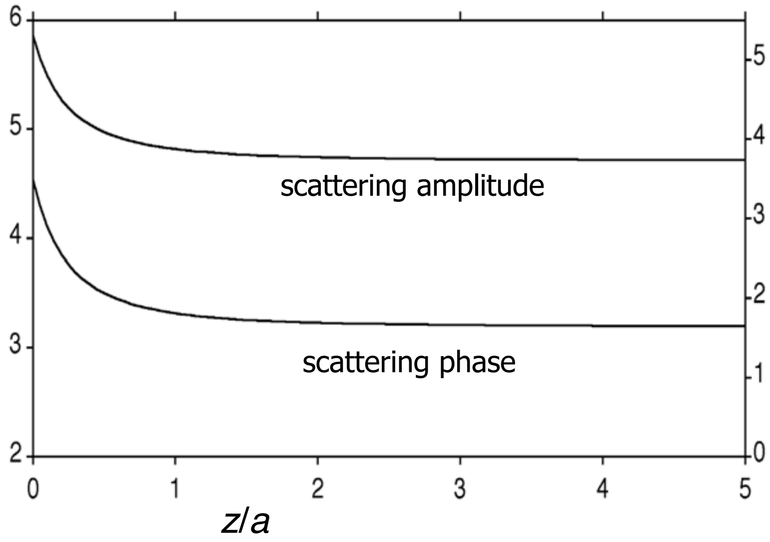
effective polarizability of tip and sample:

$$\alpha_{\perp}^{eff} = \frac{\alpha(1+\beta)}{1 - \dfrac{\alpha\beta}{16\pi(z+a)^3}}$$

with $\beta = \dfrac{(\varepsilon - 1)}{(\varepsilon + 1)}$

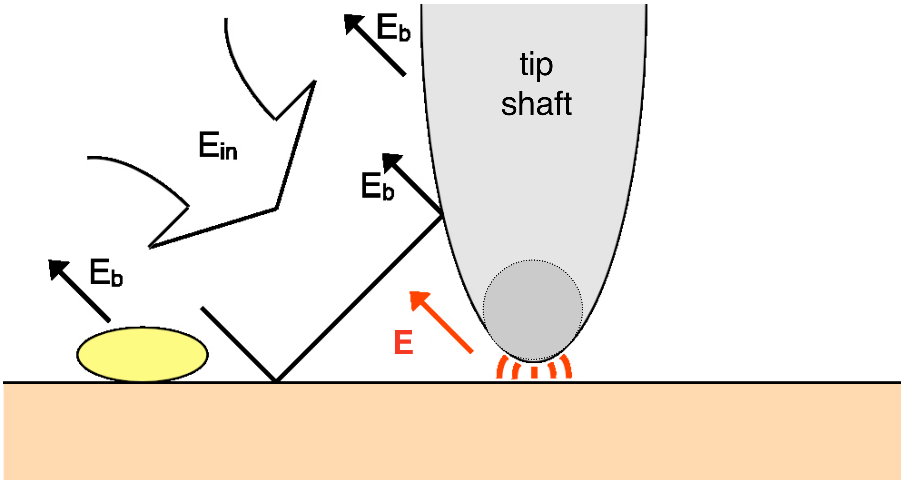
nonlinear characteristic

Approach from point dipole theory



...allows suppression
of background scattering:

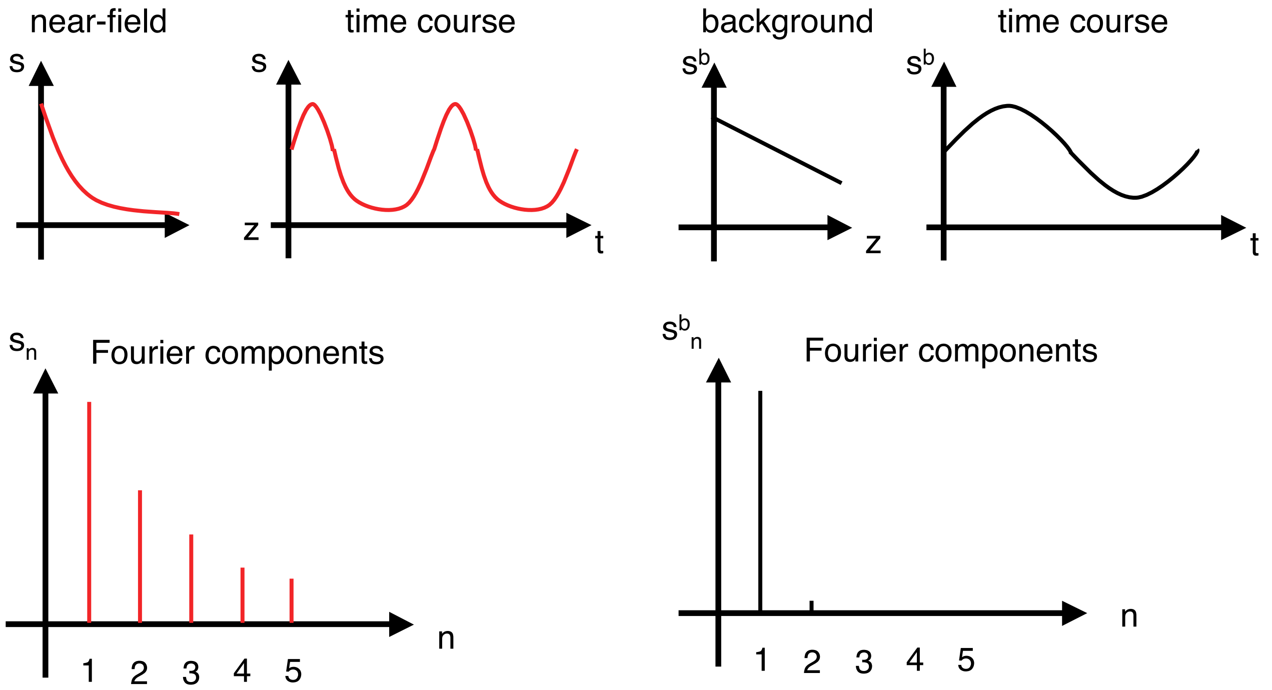
Disturbing scattering "background"



E_b : background scattered light

E: scattered light from near-field interaction

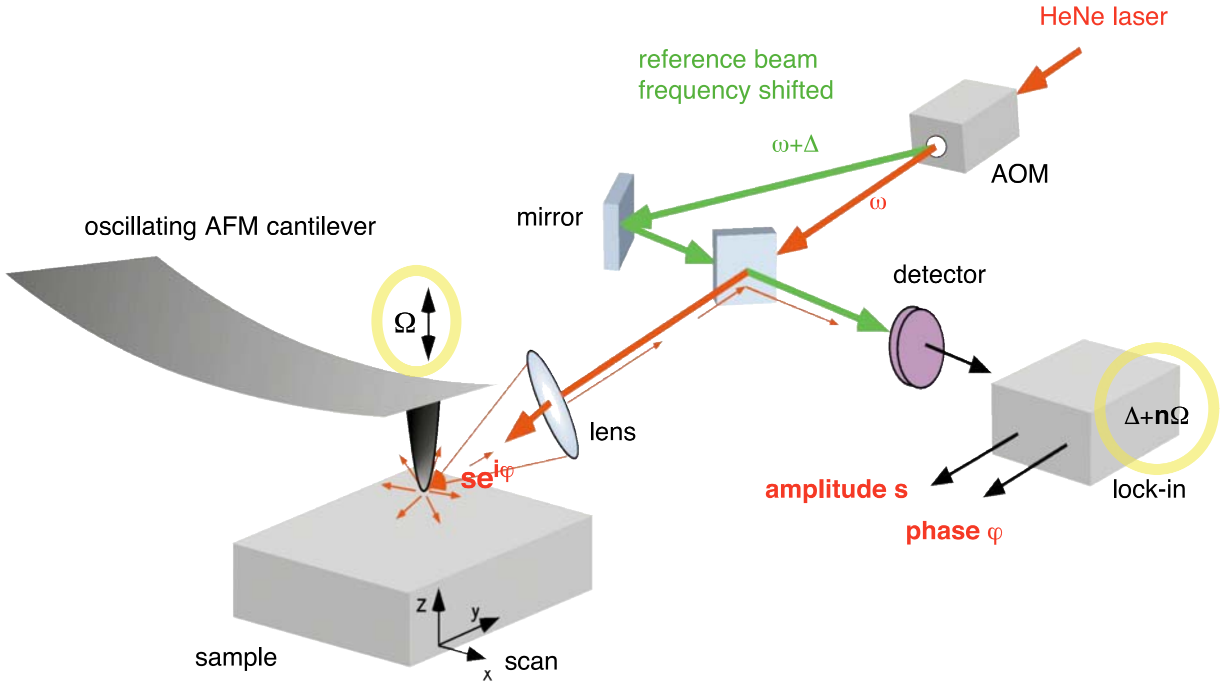
Fourier components in scattered intensity



➡ if *n* is chosen high enough then: $s_n > s_n^b$

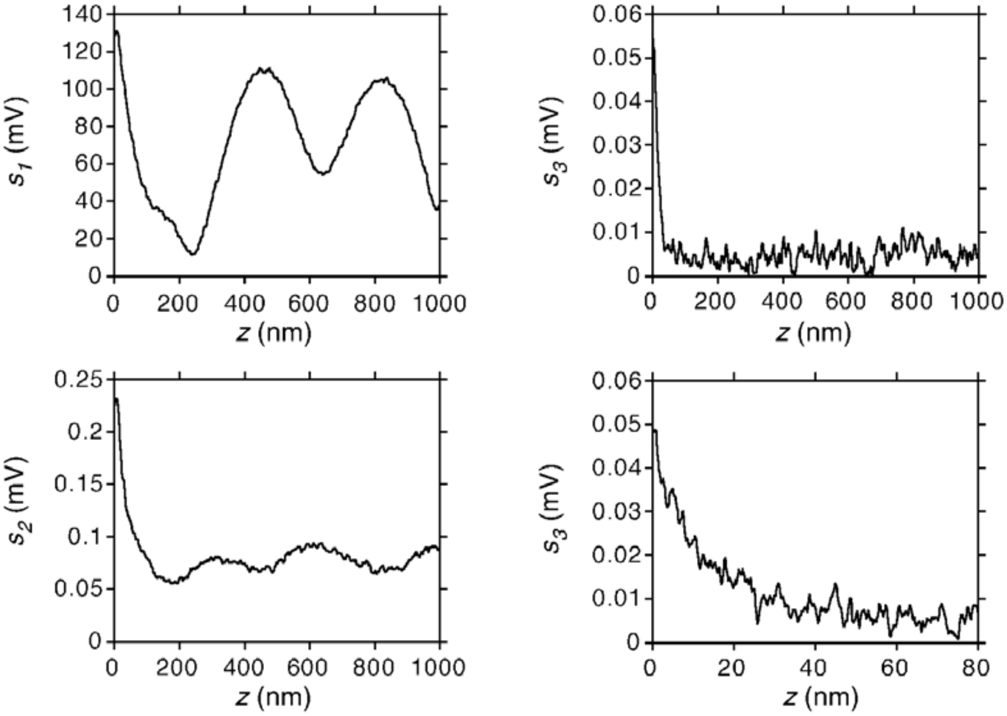
Near-field amplitude dominates over background amplitude

s-SNOM with heterodyne detection of backscattering



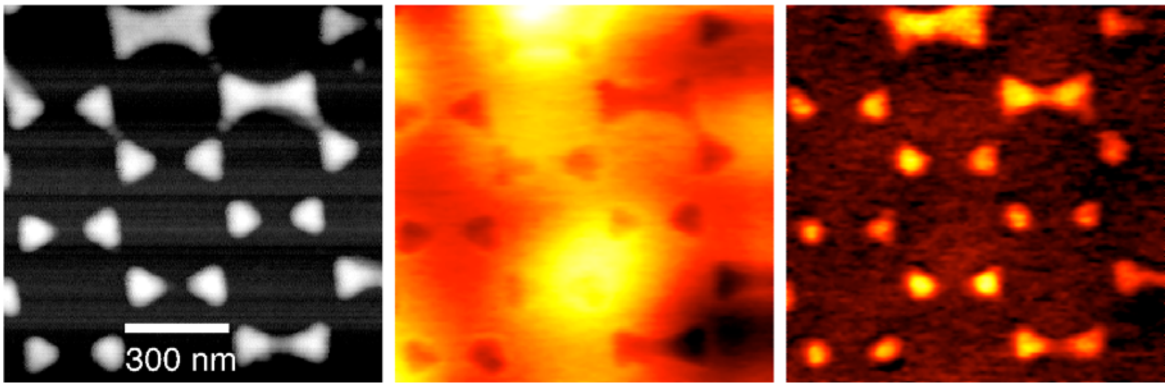
R. Hillenbrand, F. Keilmann, Phys. Rev. Lett. **80**, 3029 (2000)

Approach curves at nΩ demodulation



Example of background suppression

Au islands on Si



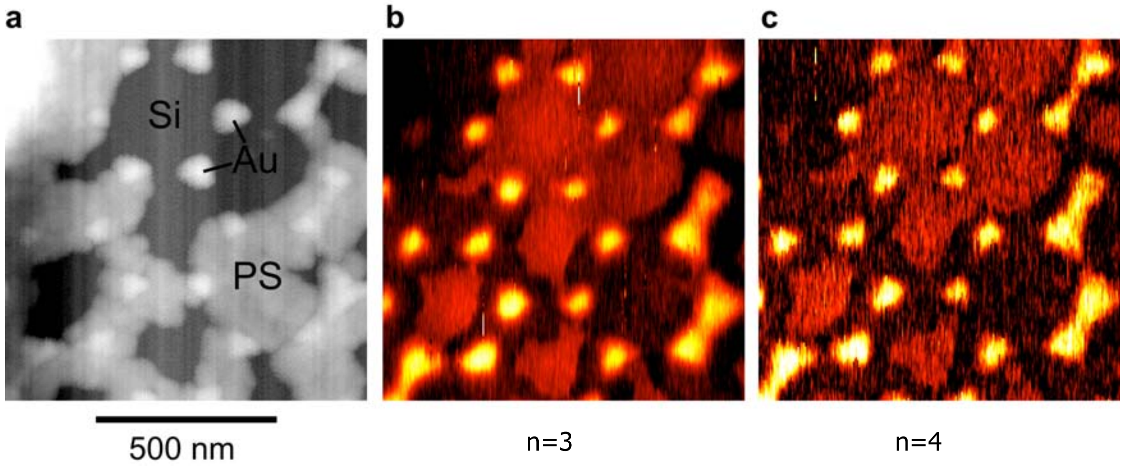
topography

s_1

s_3

Stable contrasts

Au islands on Si, partly covered with PS film



n=3

n=4

contrast not affected by choice of n

Broken tip

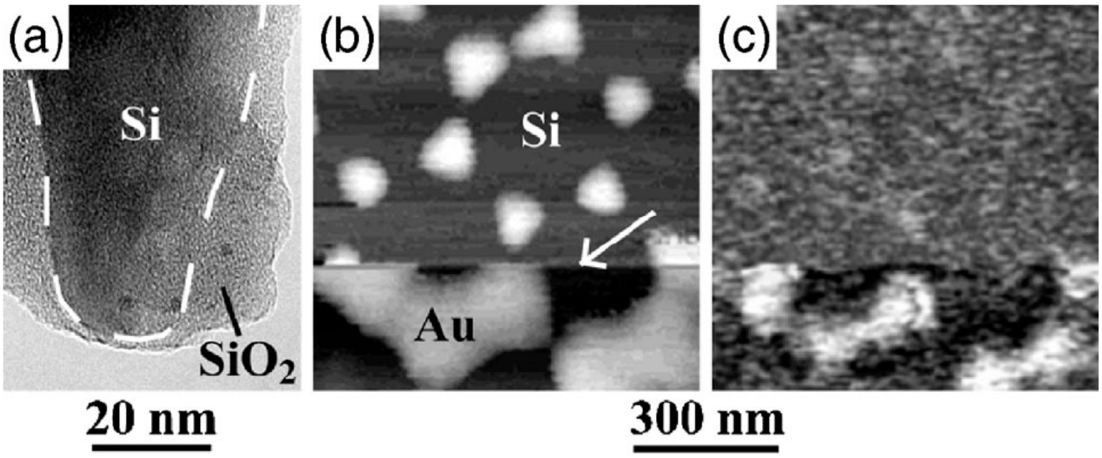


FIG. 4. *s*-SNOM with a crashed Si tip. (a) TEM image of a typical Si tip crashed during probing. (b) Topography and (c) simultaneously acquired near-field optical image taken at demodulation order $n=3$. The tip crash is marked by an arrow.

$\lambda = 633$ nm

D. Häfliger, J. Plitzko, R. Hillenbrand, Appl. Phys. Lett **85**, 4466 (2004)

Inhibiting oxide

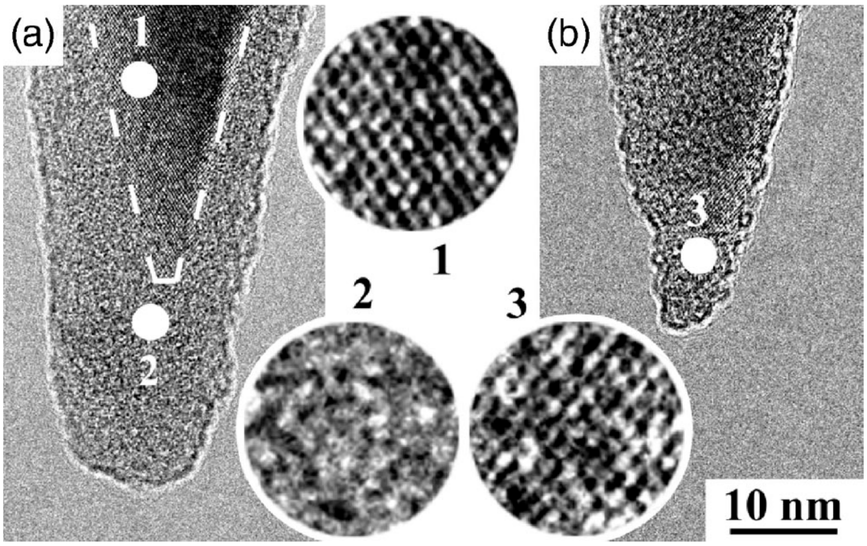


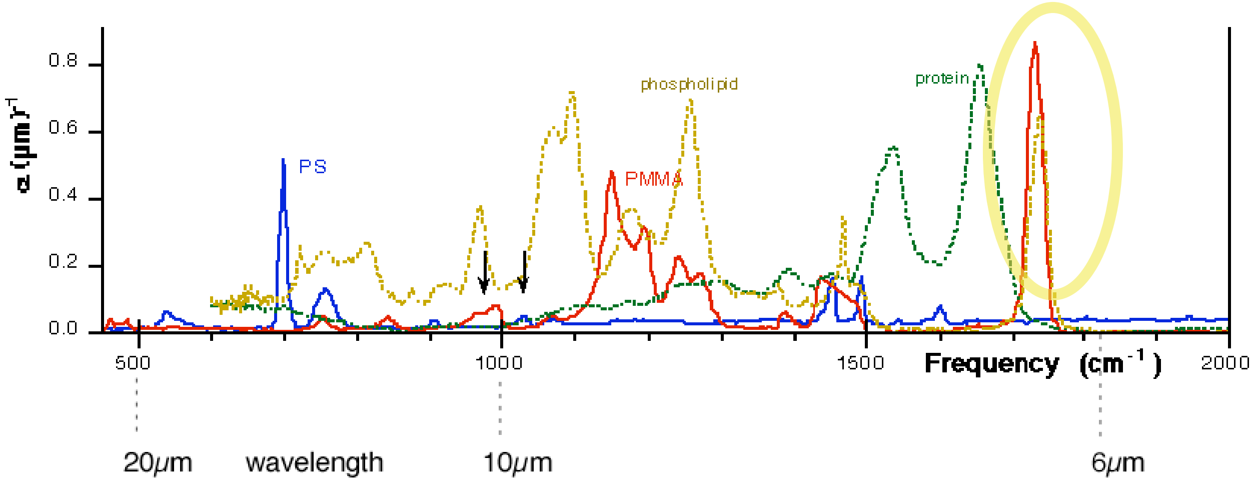
FIG. 3. TEM image of the tip apex of a typical (a) off-the-shelf Si probe and (b) Si probe etched in buffered HF. The insets 1–3 are scaled-up images of the probe's atomic structure in the white areas marked in (a) and (b).

Application in polymers

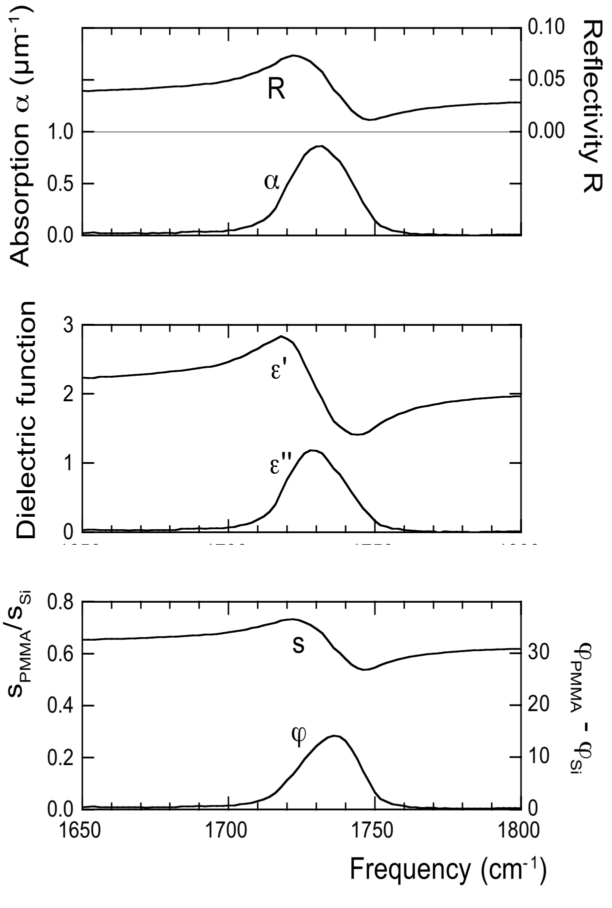
Typical Vibrational Absorption Spectra

measured ellipsometrically

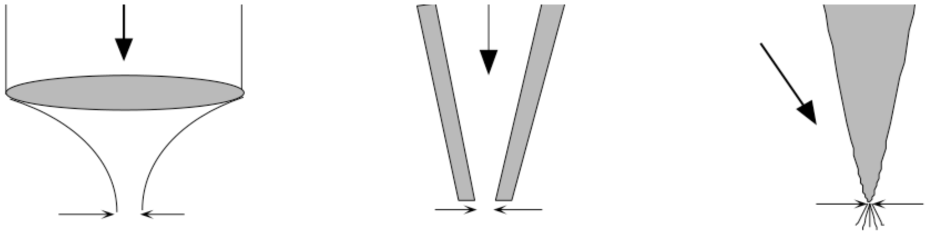
recalculated for α - absorption coefficient



Predicted near-field response of a molecular oscillator
(data of PMMA)



Microscope principles use different interaction concepts



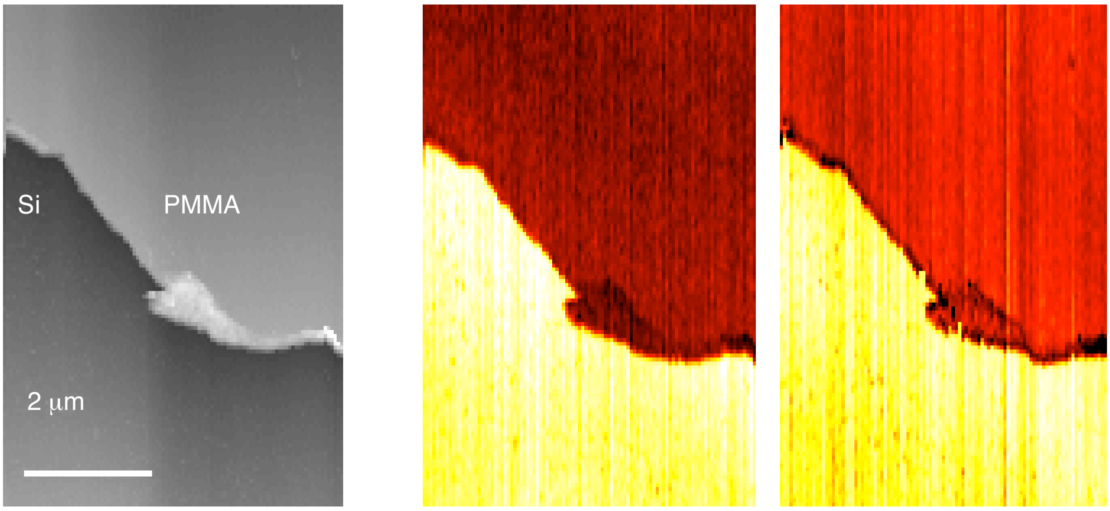
$\lambda/2$	$\lambda/10$	< 30 nm
classical	**aperture SNOM**	**scattering SNOM**
diffraction-limited	aperture-limited	tip-limited
free-space	guided	confined

transverse waves **longitudinal field**

Pairs of optics observables

	to determine n + ik unambiguously
α absorption coefficient	Transmission spectrometer
R reflectivity	Reflection spectrometer
R reflectivity φ phase of reflection	Interferometer
R_p / R_s reflectivity ratio $\varphi_p - \varphi_s$ reflection phase difference	Ellipsometer
s / s_{ref} scattering amplitude $\varphi - \varphi_{ref}$ scattering phase	scattering near-field microscope (s-SNOM)

s-SNOM of 50 nm PMMA on Si

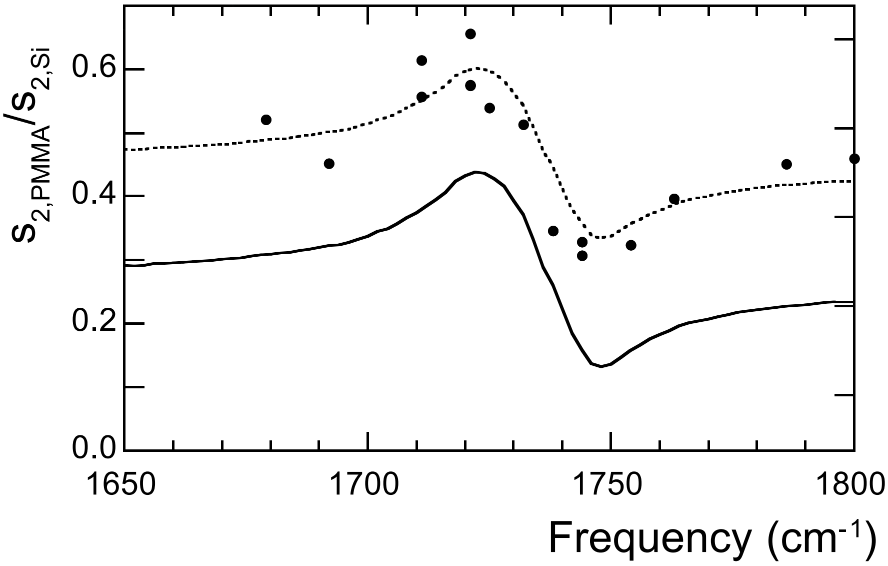


topography

infrared

5.7 5.8 μm

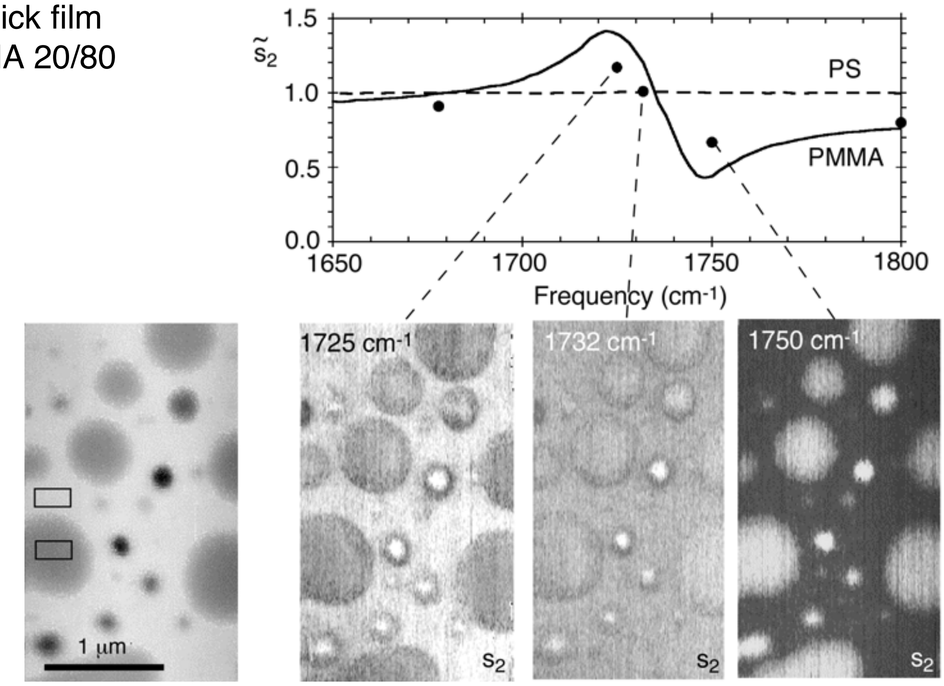
Resulting near-field spectrum



T. Taubner, R. Hillenbrand, and F. Keilmann, *Nanoscale polymer identification by spectral signature in scattering infrared near-field microscopy*, APL **85**, 5064 (2004)

Polymer blend

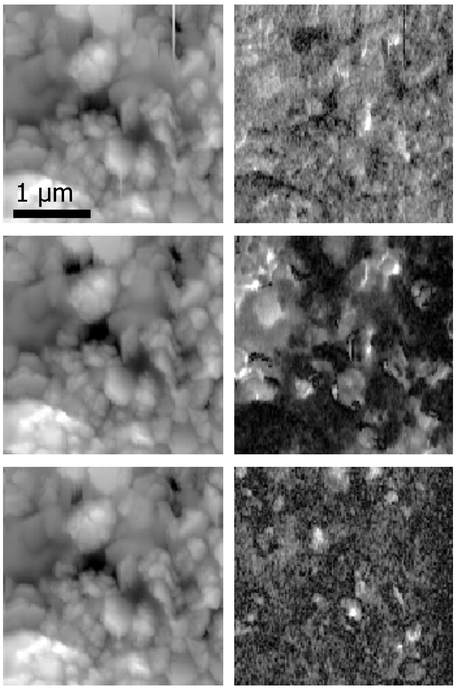
70 nm thick film
PS/PMMA 20/80



topography IR:1725 cm^{-1} 1732 cm^{-1} 1750 cm^{-1}

Infrared s-SNOM of industrial paper coating

topography infrared



λ = 9.2 µm

λ = 9.7 µm

λ = 10.6 µm

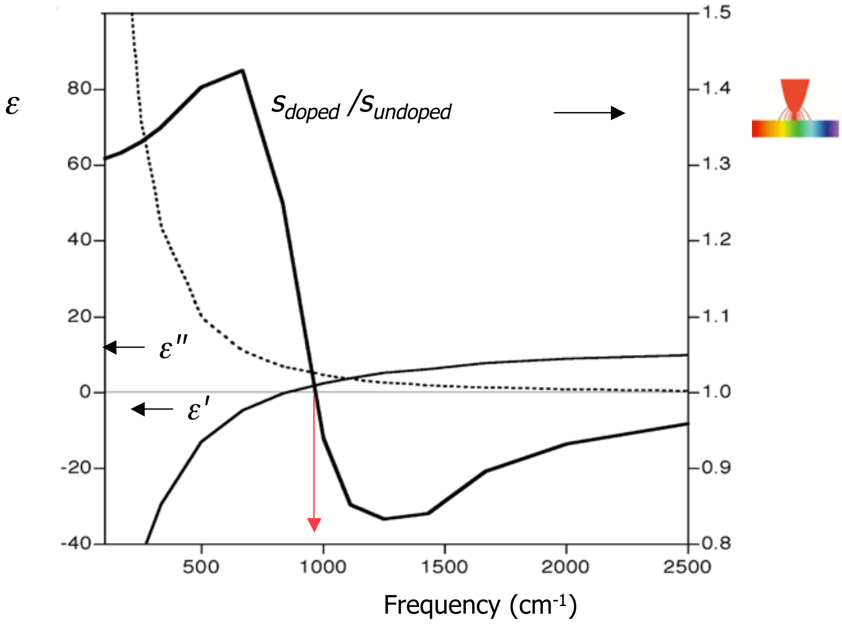
Application in nanoelectronics

Free carrier mapping in Si

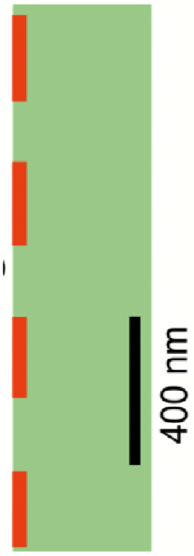
Drude model of free carrier response

$\varepsilon(\omega) = -\omega_p^2 / (\omega^2 + i\omega_t^{-1})$ where $\omega_p^2 = n_e e^2/\pi c^2 m^*$

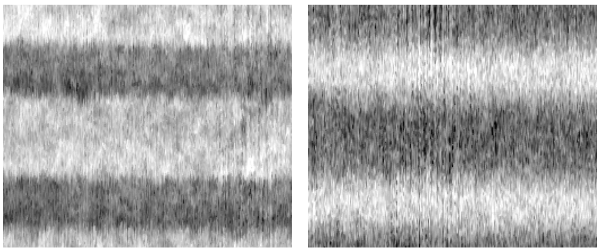
$n_e = 4\text{x}10\ \text{cm}^{-3}$



Imaging subsurface electrons



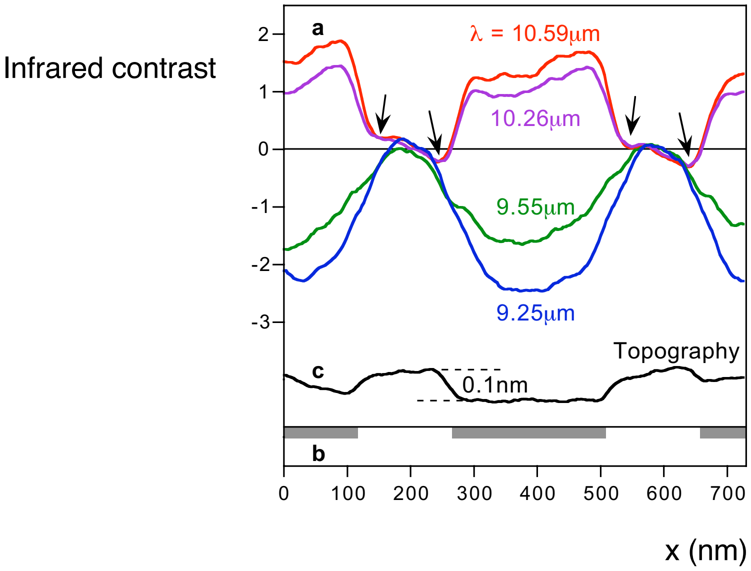
implanted stripes, 250 nm wide, 30 nm deep
n_e = 4x10 cm^{-3} (nom.)



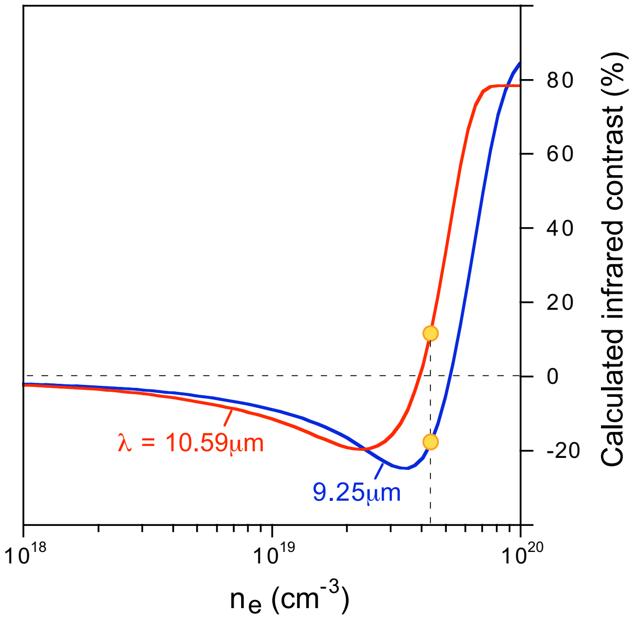
λ = 10.6 µm λ = 9.3 µm

B. Knoll and F. Keilmann, *Infrared conductivity mapping for nanoelectronics*, APL **77**, 3980 (2000)

Free carrier contrast of doped Si

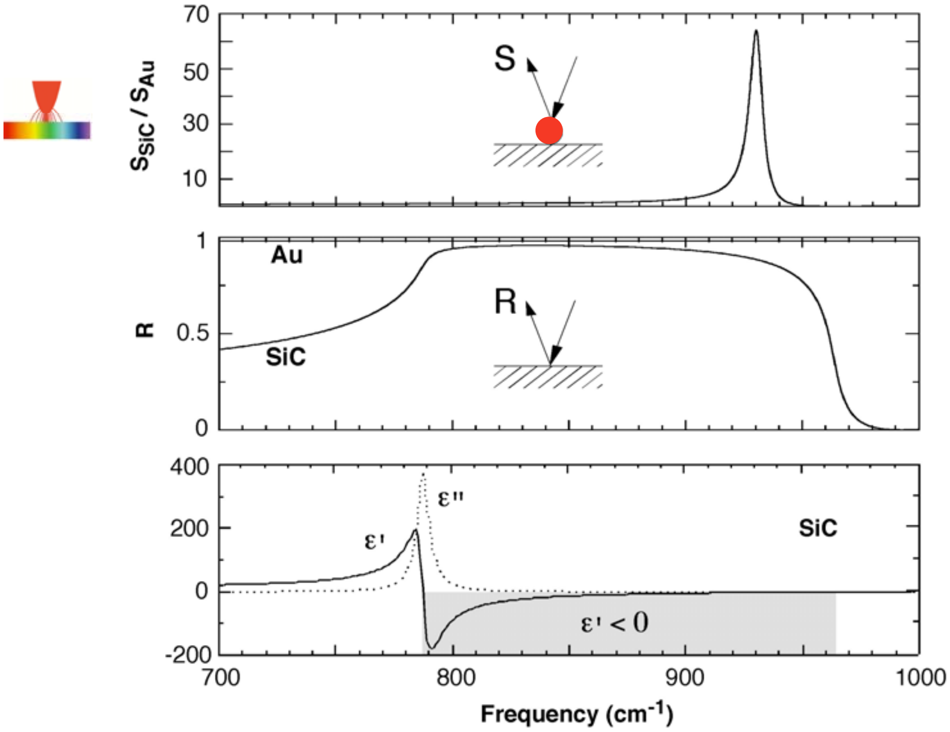


Determination of carrier density

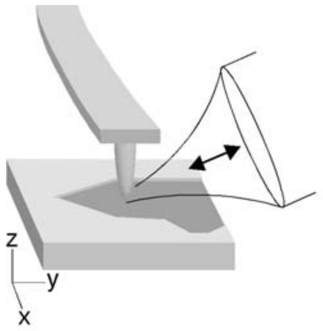


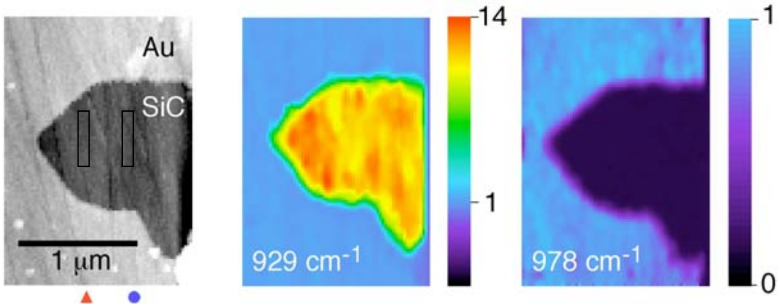
Application in crystal quality assessment

Predicted s-SNOM response of phonon oscillator



s-SNOM imaging of partly Au-covered SiC

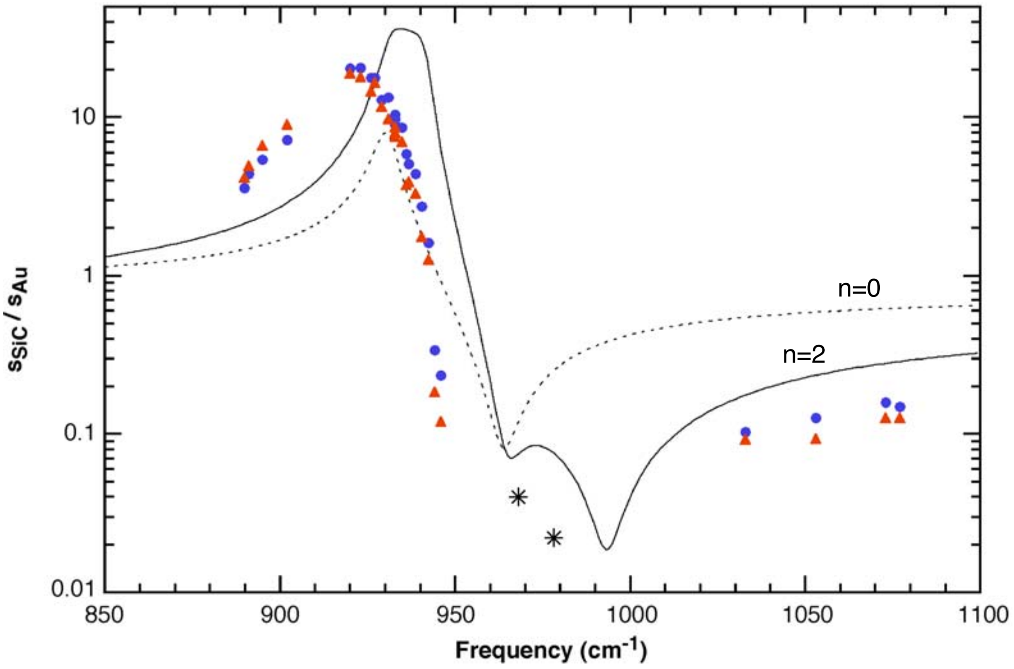




topography

infrared amplitude

Verification of phonon resonance

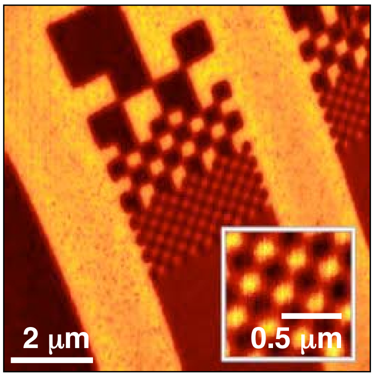


R. Hillenbrand, T. Taubner, F. Keilmann, Nature **418**, 159 (2002)

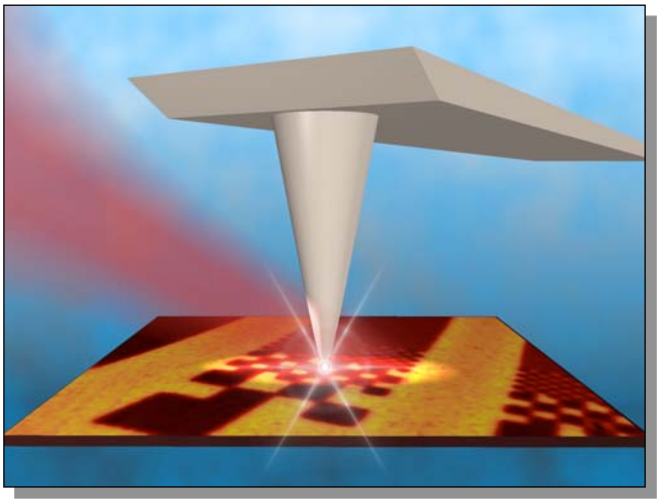
Nanoscale tailoring of surface phonon polaritons

by transforming crystalline to amorphous SiC by focused ion beam (FIB)

λ = 10.22 µm



infrared contrast



➡ **durable, longterm, high-density IR-ROM**

N. Ocelic, R. Hillenbrand, Nature Materials **3**, 606-609 (2004)

Summary

* nanoscopic field concentration at metal tip

brings spectroscopic power to the nanosciences

* Infrared s-SNOM chances

- * same <10 nm resolution as in visible
- * but better antenna efficiency
- * opportunities to highlight specific contrasts
  - rotational
  - vibrational
  - low-energy electronic
    - superconductivity
    - cyclotron resonance...