Building College-University Partnerships for Nanotechnology Workforce Development

The Use of Probes, Beams, and Waves for Characterization at the Nano-Scale

Lecture 2 Outline

The tools for characterizing materials and structures at the nano-scale

Probes

Photon beams

Electron beams

Ion beams

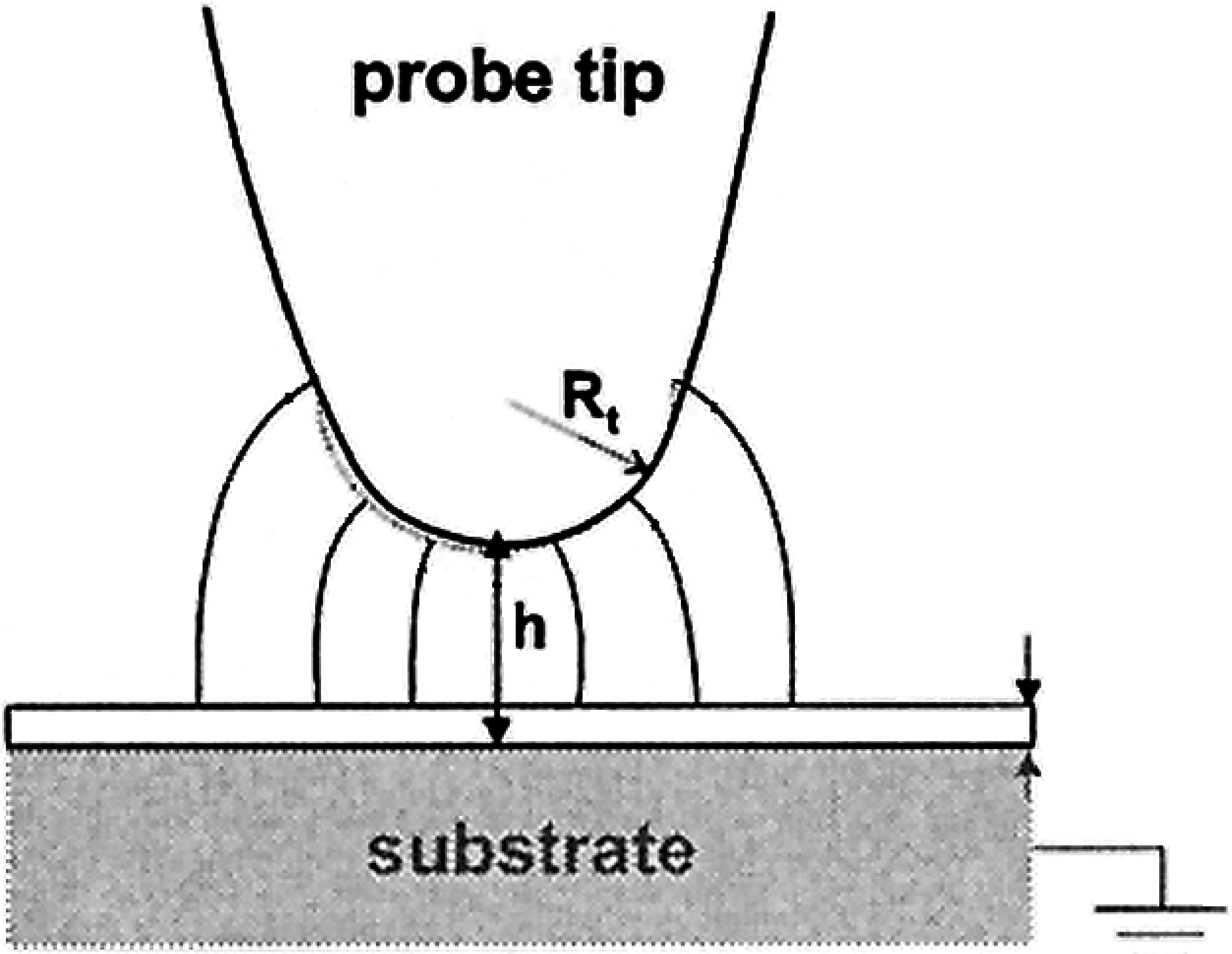
Acoustic waves

We saw last lecture that some techniques were termed microscopies and some were termed spectroscopies. What is the difference?

Microscopies produce images---they are for "seeing"

Spectroscopies measure energy or wavelength differences to deduce information---they are for uses such as chemical detection.
(Today the terms Spectroscopy and Spectrometry are generally used interchangeably)

Probe Tools



Some Probe Tools

Probe Techniques	Physics used to sense surface	Comments
Contact Profilometer(1)	Van der Waals forces Interatomic forces Electrostatic forces	Gives trace of surface profile
atomic force microscope (AFM)(2) (Contact AFM, Non-contact AFM, Dynamic Contact AFM ,Tapping AFM)	Van der Waals forces Interatomic forces Electrostatic forces	Operated in several modes
electrostatic force microscopy(3)	Electrostatic forces	Measures electrostatic force from surface charges
magnetic force microscopy(4)	Magnetic force	Magnetized tip scans sample and detects magnetic structure
piezoresponse force microscopy(5)	Electrostatic forces	Alternating current bias applied between tip and ferroelectric (piezoelectric} to excite deformation
scanning capacitance microscopy(6)	Electrostatic forces	Lateral variations of capacitance of a sample generate a capacitance image
Kelvin probe force microscopy(7)	Electrostatic Forces	Measures contact potential (workfunction) tip/surface difference under T.E.
chemical force microscopy(8)	Van der Waals forces Interatomic forces	Measures chemical bonding leading to friction and adhesion forces

Some Probe Tools (continued)

Probe Techniques	Physics used to sense surface	Comments
scanning electrochemical microscopy[9]	Oxidation/reduction currents	Uses oxidation/reduction reactions at solid-state material, electrocatalyst material, enzyme and other biophysical surfaces
scanning spreading resistance microscopy[10]	Current flow	Uses current to measure resistance and thereby resistivity and doping
scanning tunneling microscopy[11]	QM tunneling current flow	Uses QM current to image surface. Surface must be a conductor
spin polarized scanning tunneling[12]	QM tunneling current flow of specific spin orientations.	Uses tunneling with a magnetized tip. Electrons in sample with spins matching the tip's magnetization have better chance of tunneling. The tip/surface essentially acts as a spin valve. Magnetic imaging down to the atomic scale possible. Topological and magnetic information can be simultaneously obtained.

Adapted from http://en.wikipedia.org/wiki/Scanning_probe_microscopy

Some Probe Tools (continued)

Probe Techniques	Physics used to sense surface	Comments
photon scanning tunneling microscopy[13]	Near-field optical wave and photon tunneling	Near-field is created at a surface and photons tunnel from the surface to the probe. The received photons go to a detector that produces an output signal proportional to the number of photons received by the probe.
scanning thermal microscopy[14]	Flow of heat	Uses heat flows from the tip to sample to create a temperature and/or thermal conductivity map of the sample
photothermal microspectroscopy[15]	IR waves	IR spectroscopy with the nano-scale spatial resolution
near-field scanning optical microscopy (NSOM)[16]	Wave behavior of light	Uses near-field wave optical response
Fourier transform infrared nanospectroscopy)[17]	Molecular vibrations	Uses standard infrared databases of molecular vibrations for chemical identification
Adapted from http://en.wikipedia.org/wiki/Scanning_probe_microscopy		

References

(1) http://mmrc.caltech.edu/DektakXT/Manuals/DektakXT%20specifications.pdf

(2) Binnig, G.; C. F. Quate; Ch. Gerber (1986-03-03). "Atomic Force Microscope". *Physical Review Letters* **56** (9): 930–933.

(3) Weaver, J. M. R.; David W. Abraham (1991). "High resolution atomic force microscopy potentiometry". *Journal of Vacuum Science and Technology B* **9** (3): 1559–1561.

(4) Hartmann, U. (1988). "Magnetic force microscopy: Some remarks from the micromagnetic point of view". *Journal of Applied Physics* **64** (3): 1561–1564.

(5) Roelofs, A.; U. Bottger, R. Waser, F. Schlaphof, S. Trogisch, L. M. Eng (2000). "Differentiating 180 and 90 switching of ferroelectric domains with three-dimensional piezoresponse force microscopy". *Applied Physics Letters* **77** (21): 3444–3446.

(6) Matey, J. R.; J. Blanc (1985). "Scanning capacitance microscopy". *Journal of Applied Physics* **57** (5): 1437–1444.

(7) Nonnenmacher, M.; M. P. O'Boyle; H. K. Wickramasinghe (1991). "Kelvin probe force microscopy". *Applied Physics Letters* **58** (25): 2921–2923.

(8) *Noy, A; Dmitri V. Vezenov, and Charles M. Lieber (1997),* “Chemical Force Microscopy”, *Annual. Rev. Mater. Sci. 1997. 27:381–421*

(9) Kiani A, M. Alpuche-Aviles, P. Eggers, M. Jones, J. Gooding, M. Paddon-Row, A.Bard (2008) ,“Scanning electrochemical microscopy. 59. Effect of defects and structure on electron transfer through self-assembled monolayers”, Langmuir, Mar 18, 2008;24(6):2841-9.

(10) De Wolf, P.; J. Snauwaert, T. Clarysse, W. Vandervorst, L. Hellemans (1995). "Characterization of a point-contact on silicon using force microscopy-supported resistance measurements". *Applied Physics Letters* **66** (12): 1530–1532.

(11) Binnig, G.; H. Rohrer, Ch. Gerber, E. Weibel (1982). "Tunneling through a controllable vacuum gap". *Applied Physics Letters* **40** (2): 178–180.

(12) Wiesendanger, R.; M. Bode (2001-07-25). “Nano- and atomic-scale magnetism studied by spin-polarized scanning tunneling microscopy and spectroscopy”. *Solid State Communications* **119** (4-5): 341–355.

References (continued)

(13) Goudonnet, Jean-Pierre; L. Laurent; F. de Fornel; G. Chabrier; R. Warmack;T. T. Ferrell; “Photon scanning tunneling microscopy”, Proceedings of the SPIE, Volume 1400, p. 116-123 (1991).

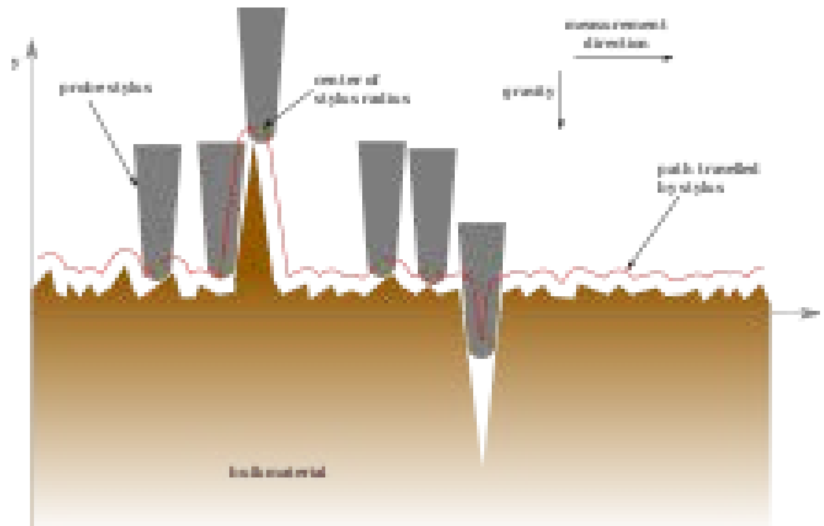
(14) Xu, J. B.; K. Lauger, K. Dransfeld, I. H. Wilson (1994). "Thermal sensors for investigation of heat transfer in scanning probe microscopy". *Review of Scientific Instruments* **65** (7): 2262–2266.

(15) http://en.wikipedia.org/wiki/Photothermal_microspectroscopy

(16) Reddick, R. C.; R. J. Warmack; T. L. Ferrell (1989-01-01). “New form of scanning optical microscopy”. *Physical Review B* **39** (1): 767.

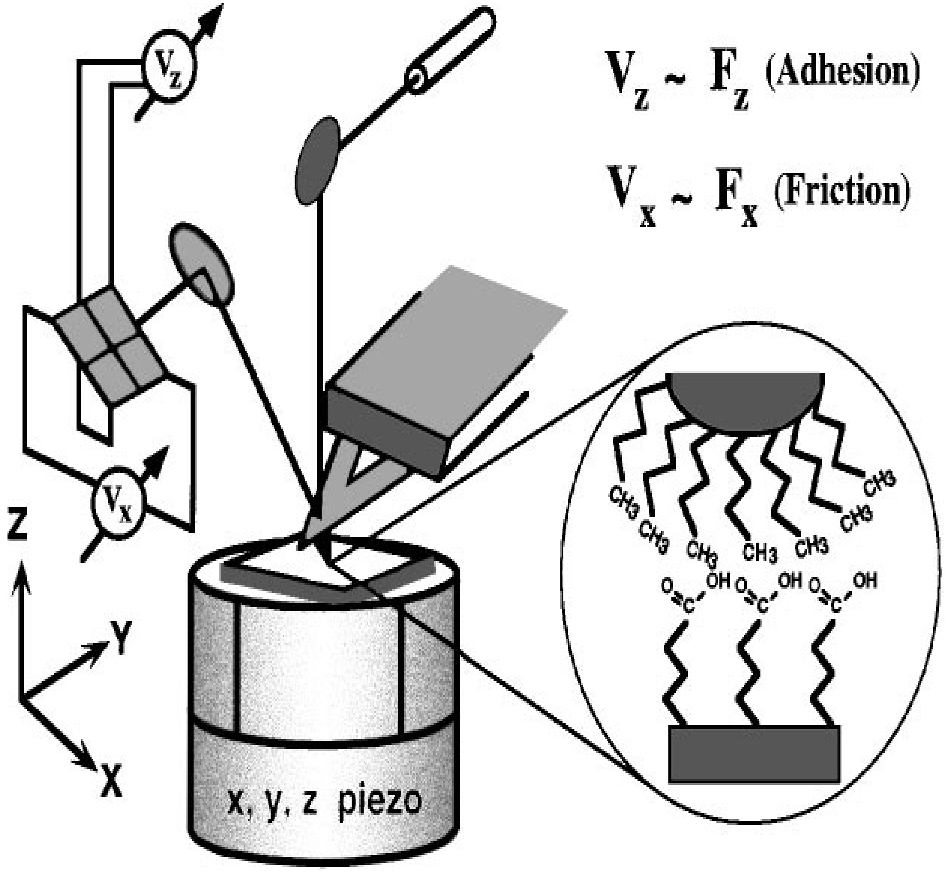
(17) Huth,F; Alexander Govyadinov; Sergiu Amarie; Wiwat Nuansing; Fritz Keilmann; and Rainer Hillenbrand; “Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution”, Nano Lett. 2012, 12, 3973−3978

Contact Profilometer



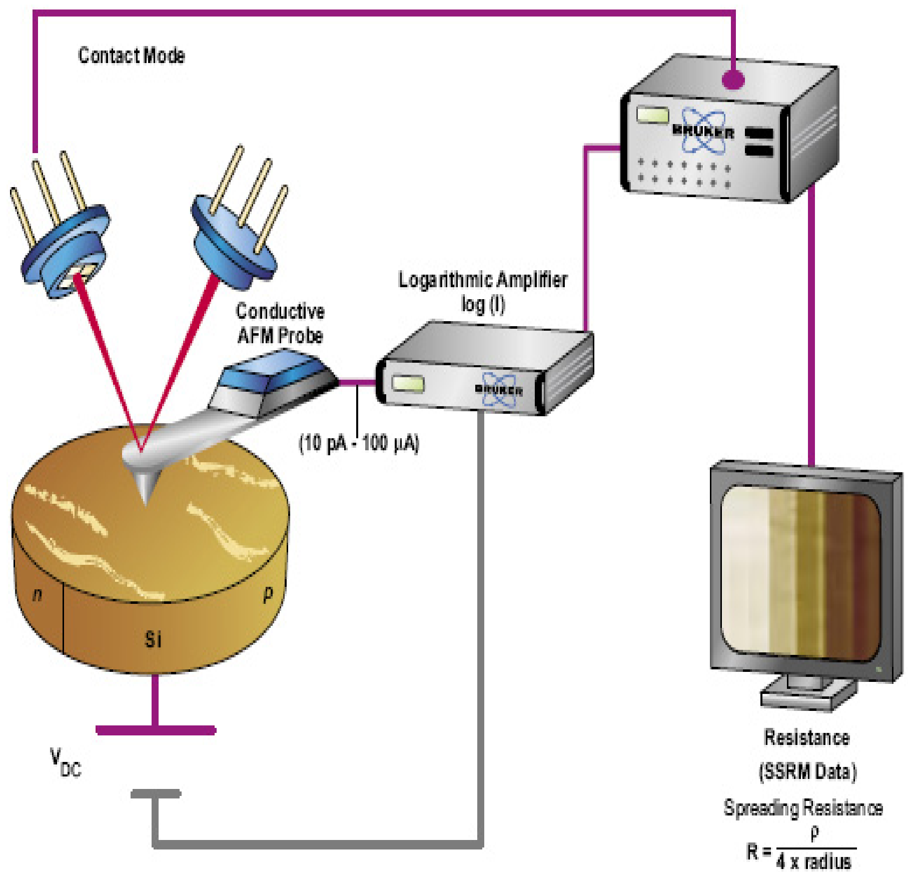
http://upload.wikimedia.org/wikipedia/commons/thumb/3/39/Mechanical_filtering_of_surface_finish_trace.svg/220px-Mechanical_filtering_of_surface_finish_trace.svg.png

Chemical Force Microscopy



Schematic drawing of the CFM setup. The sample rests on a piezoelectric x, y, z translator. A laser beam is reflected from the backside of the tip onto a photodiode to measure two types of tip-surface interactions. When the sample approaches, touches, and is withdrawn from the tip, the tip will move up and down in response to surface normal forces Fz, resulting in the vertical deflection signal Vz. The cantilever will also twist in response to friction forces Fx, yielding the lateral deflection signal Vx.The inset illustrates the chemically specific interactions between a Au-coated, CH3-terminated tip contacting a COOH-terminated region of a sample.(From ***Noy, A. et al.,Annu. Rev. Mater. Sci. 1997. 27:381–421))***

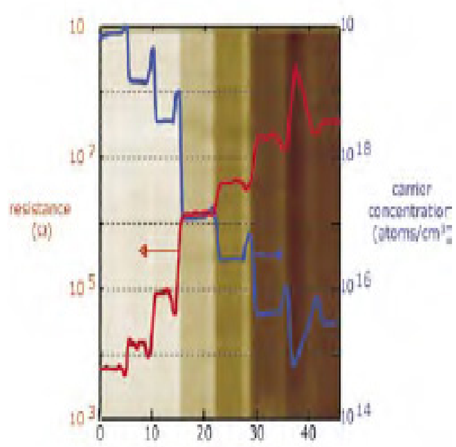
Scanning Spreading Resistance Microscopy



http://blog.brukerafmprobes.com/guide-to-spm-and-afm-modes/scanning-spreading-resistance-microscopy-ssrm/

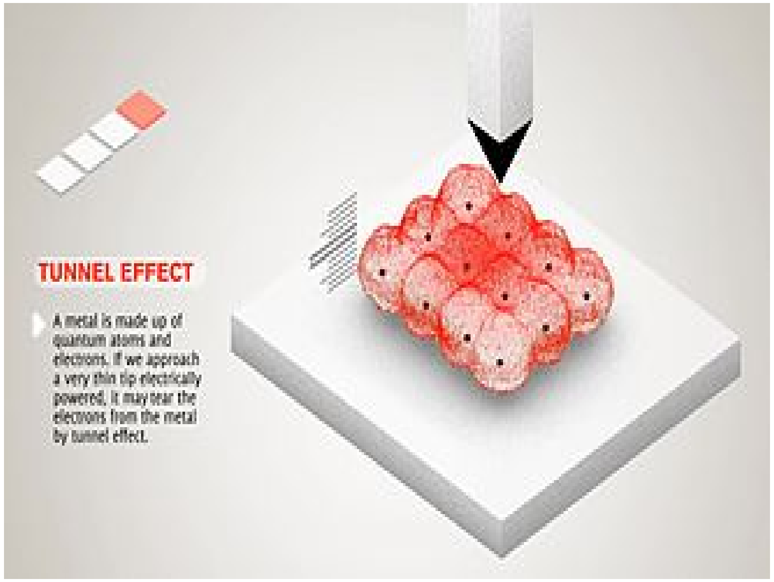
Scanning Spreading Resistance Microscopy
(continued)

Transistor cross section.



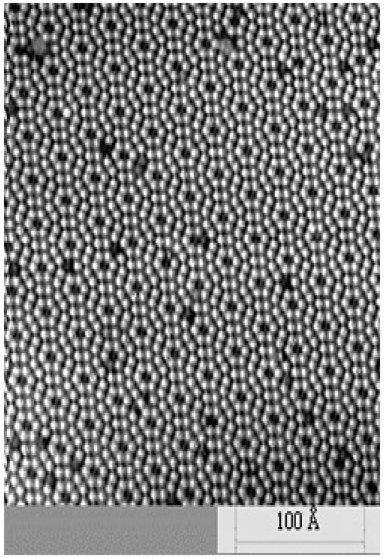
http://blog.brukerafmprobes.com/guide-to-spm-and-afm-modes/scanning-spreading-resistance-microscopy-ssrm/

Scanning Tunneling Microscopy



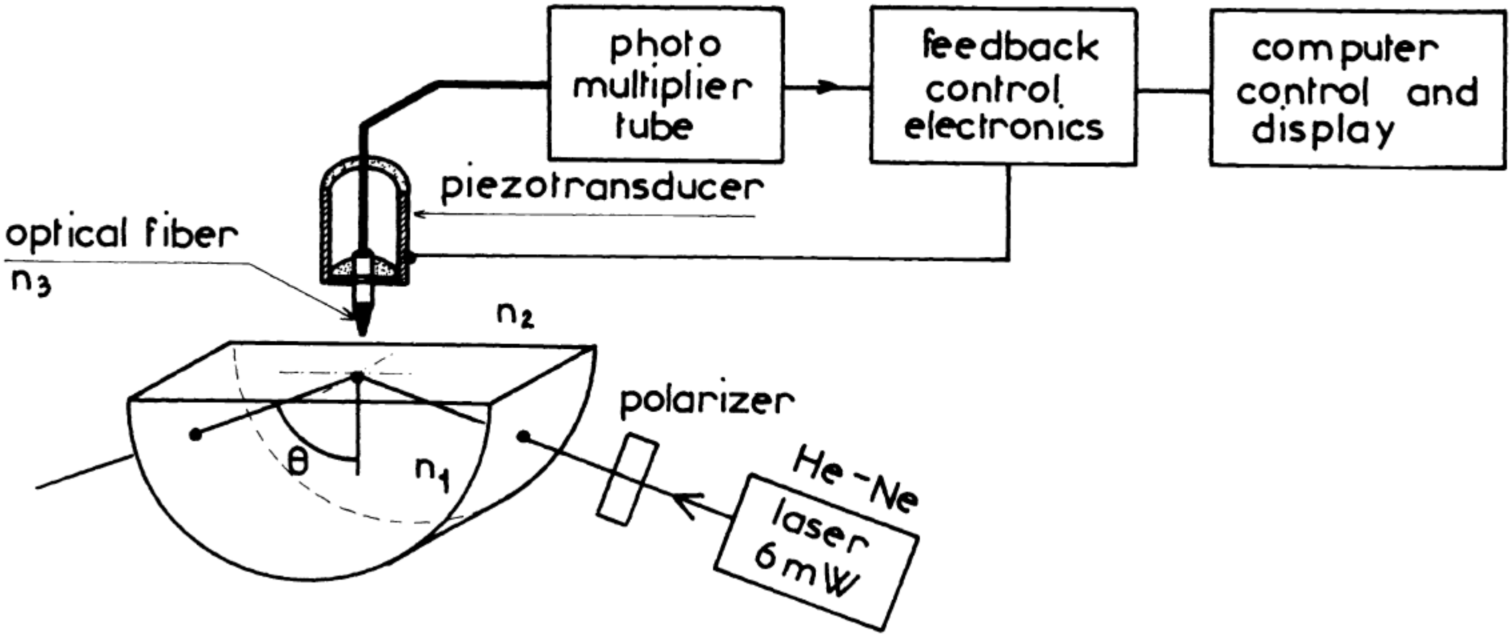
http://en.wikipedia.org/wiki/Scanning_tunneling_microscope

Scanning Tunneling Microscopy



http://www.nrel.gov/pv/measurements/images/photo_si_111_2d.jpg

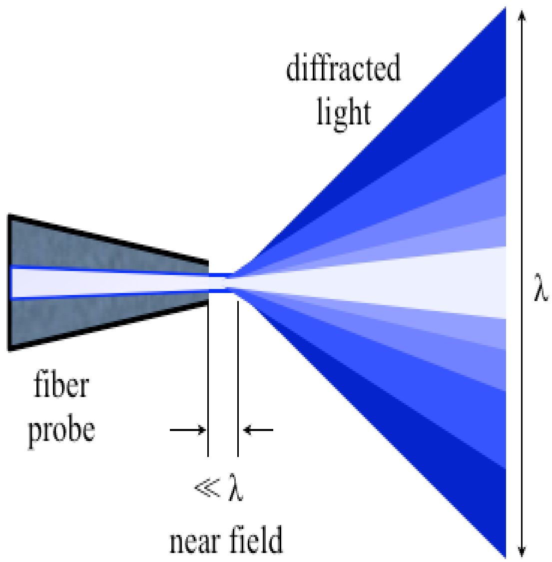
Photon Scanning Tunneling Microscopy



Schematic of experimental set up.

Goudonnet, Jean-Pierre; L. Salomon; F. de Fornel; G. Chabrier.; R. Warmack.; T. Ferrell; "Photon scanning tunneling microscopy", Proceedings of the SPIE, Volume 1400, p. 116-123 (1991).

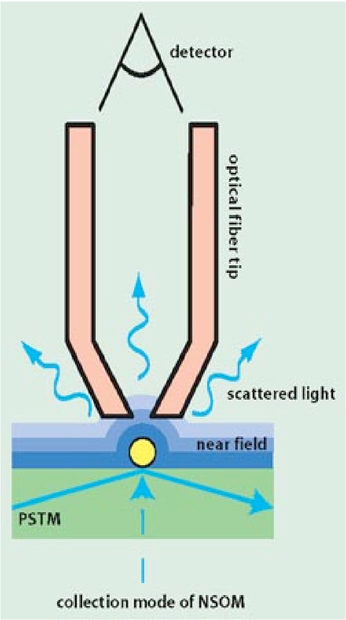
Near-field Scanning Optical Microscopy



"Nearfield optics" by Zogdog602 - Own work. Licensed under CC BY 3.0 via Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Nearfield_optics.png#/media/File:Nearfield_optics.png

Side-stepping the diffraction limit

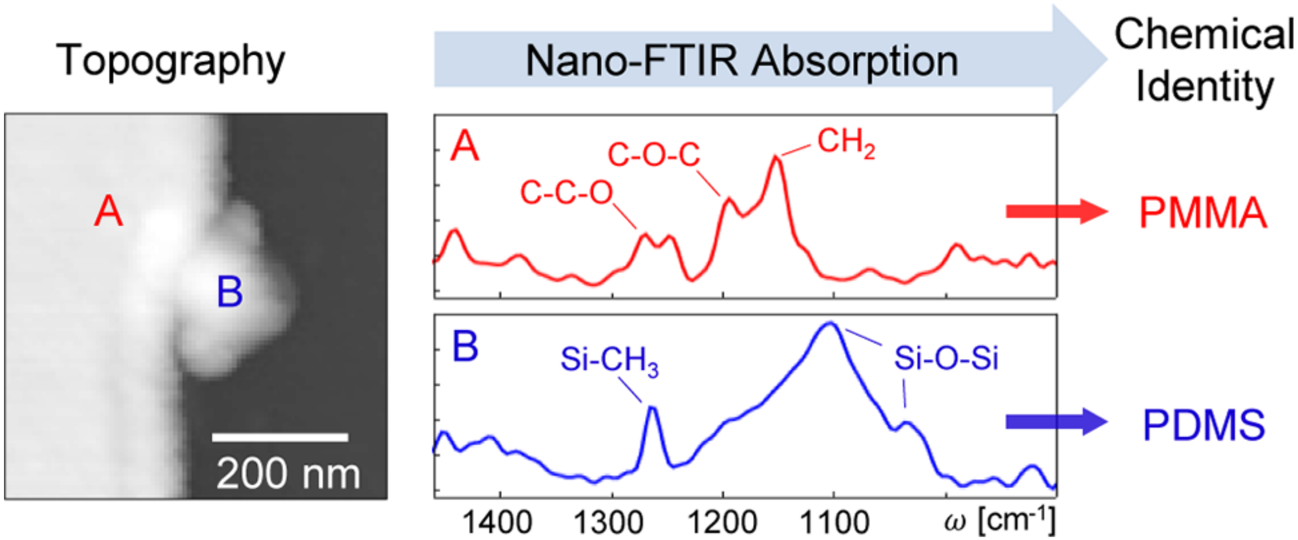
Near-field Scanning Optical Microscopy



Side-stepping the diffraction limit

http://www.bing.com/images/search?q=NSOM&FORM=HDRSC2#view=detail&id=E4BA304E0490CEADBC07BF2101A35EB6D735DA6D&selectedIndex=6

Fourier Transform Infrared Nanospectroscopy



Can match to standard infrared databases of molecular vibrations

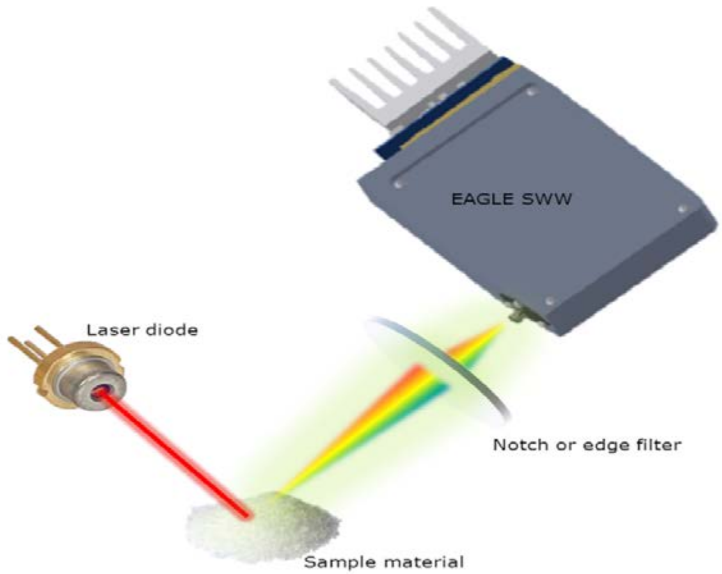
Huth,F; Alexander Govyadinov; Sergiu Amarie; Wiwat Nuansing; Fritz Keilmann; and Rainer Hillenbrand; "Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution", Nano Lett. 2012, 12, 3973−3978

Some Photon Beam Tools

Some Photon Beam Tools

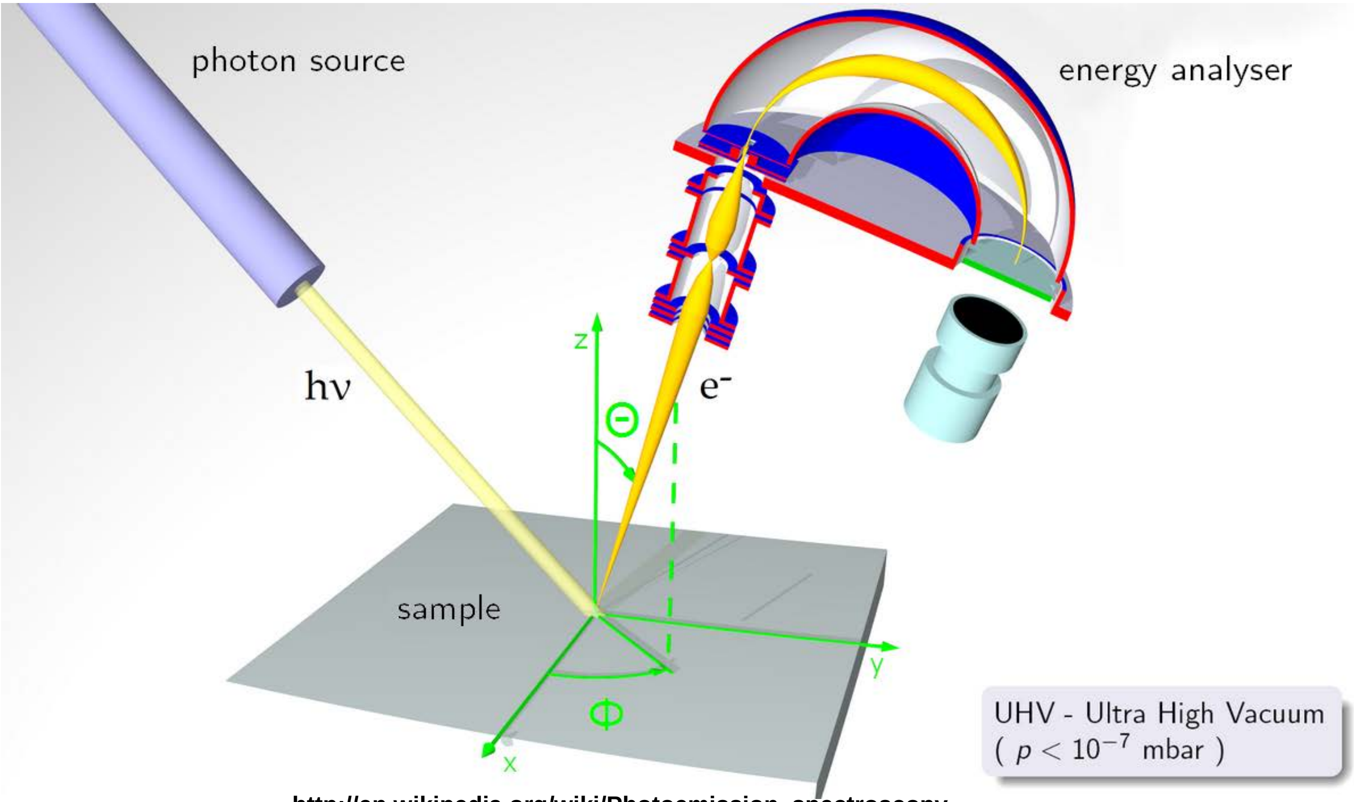
Photon Beam Techniques	Physics used to sense surface	Comments
Raman spectroscopy	Wave and particle nature of electromagnetic phenomenon Particle nature of vibrational phenomenon	Good for determining bonding structure; i.e., crystalline, amorphous
Photoelectron spectroscopy (Photoemission spectroscopy)	Particle nature of electromagnetic phenomenon Quantization of electron energy levels in solids	Chemical analysis uses
X-ray fluorescence (XRF) spectroscopy	Particle nature of electromagnetic phenomenon Quantization of electron energy levels in solids Fluorescence	Uses high-energy X-rays or gamma rays Used for chemical analysis uses

Raman Spectroscopy



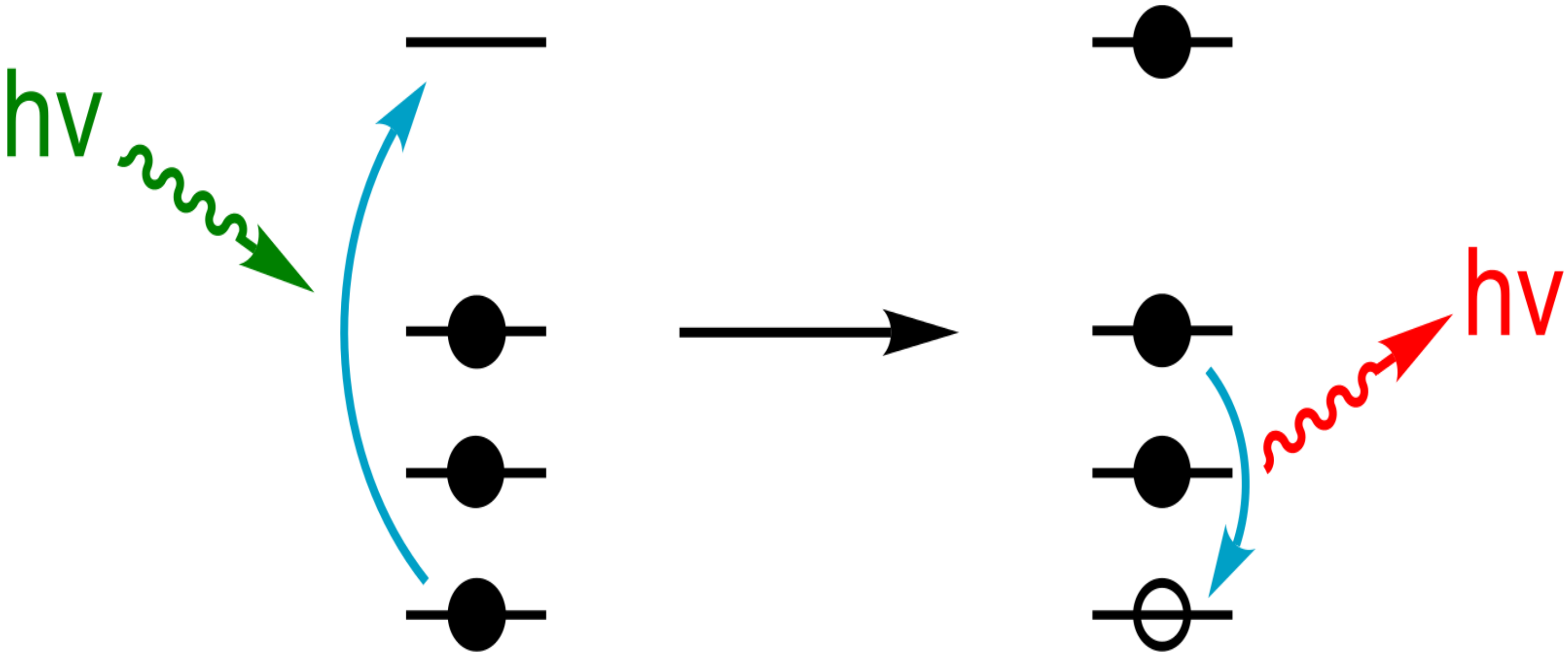
http://www.ibsenphotonics.com/wp-content/uploads/Raman-system.png

Photoelectron Spectroscopy



http://en.wikipedia.org/wiki/Photoemission_spectroscopy

X-ray Fluorescence Spectroscopy



http://en.wikipedia.org/wiki/X-ray_fluorescence#/media/File:X-ray_fluorescence_simple_figure.svg

Some Light Wave Tools

Some Light Wave Tools

Light Wave Techniques	Physics used to sense surface	Comments
Fluorescence Microscopy	Wave and particle nature of electromagnetic phenomenon Quantization of electron energy levels in solids Fluorescence	Can give an image locating individual molecules Side-steps the diffraction limit
Fourier Transform IR Spectroscopy	Wave and particle nature of electromagnetic phenomenon Vibrational levels in solids	Gives an infrared spectrum of absorption, emission Bonding energies Structure Chemical analysis

Some Light Wave Tools

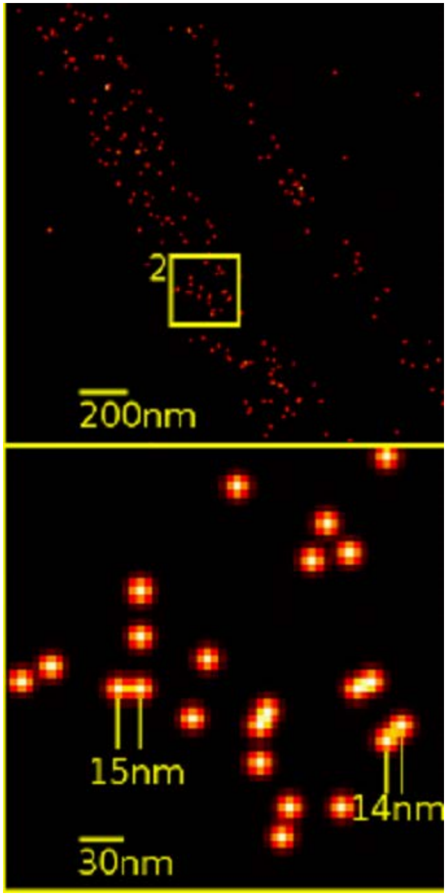
Fluorescence Microscopy

http://en.wikipedia.org/wiki/Optical_microscope

Uses fluorescence produced by incoming light to generate an image

Some Light Wave Tools

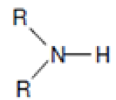
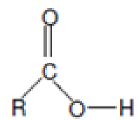
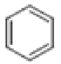
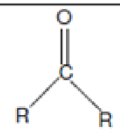
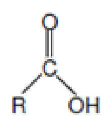
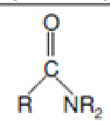
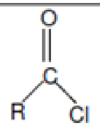
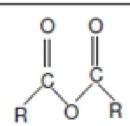
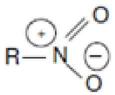
Fluorescence Microscopy



Single YFP molecule detection in a human cancer cell. Typical distance measurements in the 15 nm range

http://en.wikipedia.org/wiki/Fluorescence_microscope#/media/File:Single_YFP_molecule_superresolution_microscopy.png

Some Infrared Spectroscopy Data

Functional group	Structure (IR absorbing bond in bold)	IR frequency range (cm^{-1})	Functional group	Structure (IR absorbing bond in bold)	IR frequency range (cm^{-1})
Alkane (C-H)	R_3C-H (R= H or C)	3000-2800	Alkyne (C≡C)	RC≡CR (R=H or C)	2260-2100
Alcohol (O-H)	RO-H	3600-3200 (broad band)	Nitrile (C≡N)	RC≡N (R=C)	2260-2200
Amines, Amide (N-H)	 ------	3500-3300 (One band) 3500-3300 (two bands), 1650-1560 (bending)	Alkene (C=C)	R_2C=CR_2 (R=H or C)	1600-1680
Carboxylic acid (O-H)		3200-2500 (broad band)	Benzene ring (C=C)	 (C=C ring "breathing")	1450-1600 2 to 3 bands
Aldehydes or Ketones (C=O)		1750-1705	Alcohol or Ether (C-O)	--- (R=H or C)	1300-1000
Carboxylic acid (C=O)	 (R=H or C)	1790-1680	Alkyne (C-H)	RC≡C—H (R=C)	3300
Amide (C=O)	 (R-H or C)	1850-1800 and 1790-1730	Acid chloride (C=O)	 (R=H or C)	1815-1790
Acid anhydride (C=O)	 (R=H or C)	1850-1800 and 1790-1740 (two bands)	Nitro Compound (NO_2)	 (R = C)	1660-1500 (asymmetric stretch) 1390-1260 (symmetric stretch)

http://www.bing.com/images/search?q=IR+Spectra+Functional+Groups&Form=IQFRDR#view=detail&id=623B1375E5673B0F675A0A6DB45328906F1BF895&selectedIndex=0

Some Phonon Tools

Some Phonon Tools

Phonon Technique	Physics used to sense surface	Comments
Raman spectroscopy	Wave and particle nature of electromagnetic phenomenon Particle nature of vibrational phenomenon	Good for determining bonding structure; i.e., crystalline, amorphous

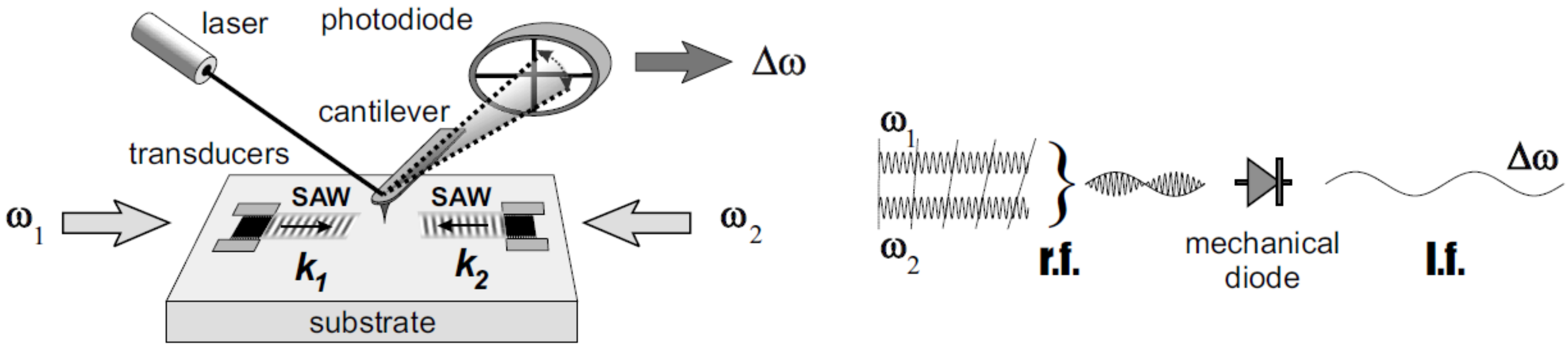
Some Acoustic Wave Tools

Some Acoustic Wave Tools

Photon Beam Techniques	Physics used to sense surface	Comments
Acoustic Wave Microscope	Use near-field to overcome diffraction	Used to study elastic properties of materials

Some Acoustic Wave Tools
Scanning Acoustic Wave Microscope

Acoustic methods are very useful tools for the investigation of elastic properties of crystalline and isotropic solids. In order to overcome the diffraction limit of quantitative acoustic methods, like scanning acoustic microscopy (SAM),[1] near-field setups either for the acoustic wave and/or for the probing wave have to be employed.



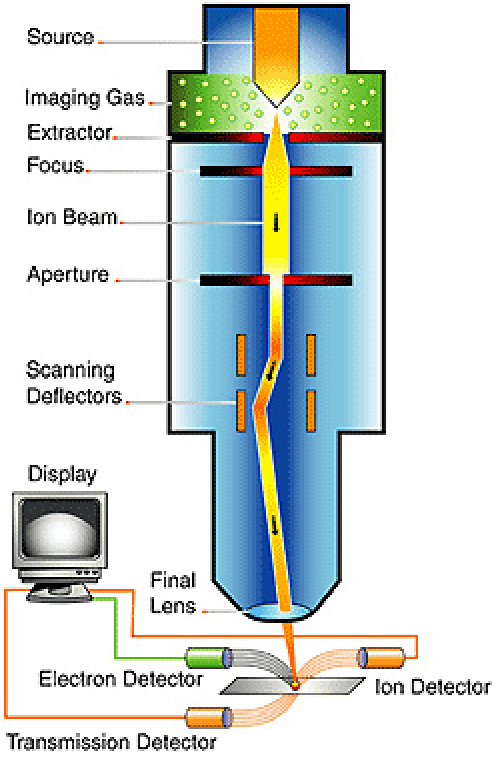
SAFM setup: SAW's are launched from transducers at slightly different frequencies towards the tip. The cantilever is unable to respond to the r.f. oscillations directly. At the nonlinearity of the tip-sample interaction, the waves are down-converted and a signal at the difference frequency is extracted, resembling the behavior of a mechanical diode.

Some Ion Beam Tools

Some Ion Beam Tools

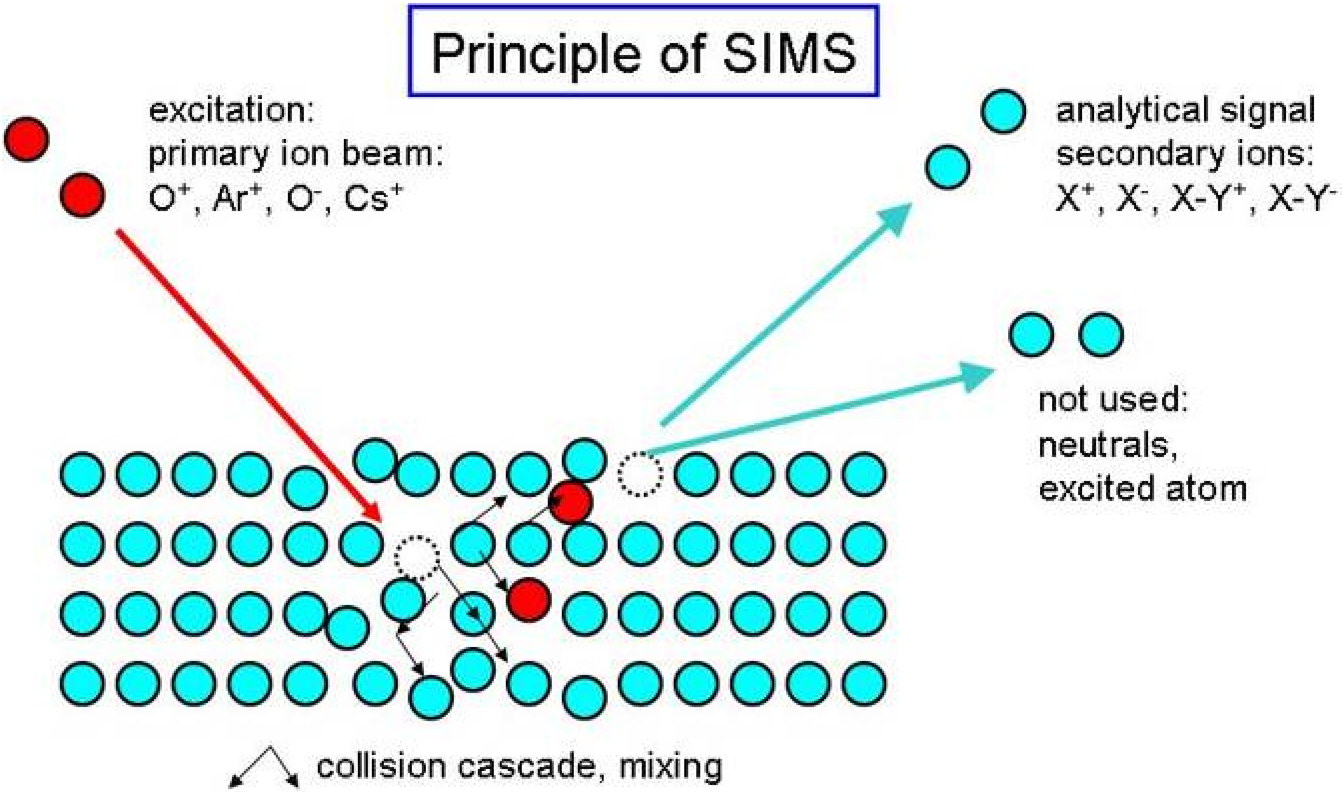
Photon Beam Techniques	Physics used to sense surface	Comments
Ion Microscope	Wave property of particles used to overcome diffraction de Broglie wavelength	Much smaller wavelength so much more relaxed diffraction issues.
Secondary ion mass spectroscopy	Particle bombardment	Uses ions to sputter the surface of a specimen with a focused primary ion beam while collecting and analyzing ejected secondary ions.

Ion Microscope



http://cdn.medgadget.com/img/542orr2.jpg

Secondary Ion Mass Spectroscopy



http://www.bing.com/images/search?q=Secondary+ion+mass+spectroscopy&FORM=HDRSC2#view=detail&id=80021274F5B229A8CE11544645BD7BBF56744F3B&selectedIndex=3

LECTURE SUMMARY

- Characterizing materials and structures at the nano-scale
- Probes
- Photon beams
- Electron beams
- Ion beams
- Acoustic waves