Basics Material Characterization Techniques

Structural (bulk and surface) Optical

Basic Electron Microscopy

Why electron microscopy

Primary reason: Spot size

$$\lambda = \frac{h}{p} = \frac{h}{mv} \sqrt{1 - \frac{v^2}{c^2}}$$

DeBroglie wavelength of a particle

 $\lambda_B = \frac{h}{n}$

If speeds are large or total acceleration voltage is close to rest mass of particle You should better use relativistic formulas for energy, momenta etc.

For an electron with KE = 1 eV and rest mass energy 0.511 MeV, the associated DeBroglie wavelength is 1.23 nm, about a thousand times smaller than a 1 eV photon.

Electron Microscopy

- Developed in the 1930s that use electron beams instead of light.
- because of the much lower wavelength of the electron beam than of light, resolution is far higher.

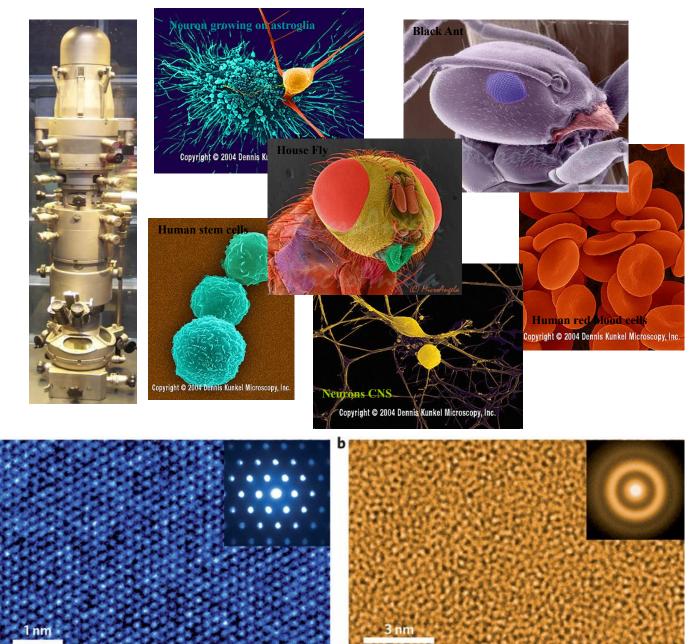
TYPES

- Transmission electron microscopy (TEM) is principally quite similar to the compound light microscope, by sending an electron beam through a very thin slice of the specimen. The resolution limit is less than 0.03 nanometer.
- Scanning electron microscopy (SEM) visualizes details on the surfaces of cells and particles and gives a very nice 3D view. The magnification is in the lower range than that of the transmission electron microscope.

Transmission Electron Microscopy (TEM)

- beam of <u>electrons</u> beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a <u>fluorescent</u> beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of <u>photographic film</u> beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of <u>photographic film</u> beam of electrons is transmitted through a specimen, then an image is formed, magnified and directed to appear either on a fluorescent screen or layer of photographic film or to be detected by a sensor (e.g. <u>charge-coupled device</u>, <u>CCD camera</u>.
- involves a high <u>voltage</u> involves a high voltage electron beam emitted by a <u>cathode</u> involves a high voltage electron beam emitted by a cathode, usually a tungsten filament and focused by electrostatic and <u>electromagnetic</u> lenses.
- electron beam that has been transmitted through a specimen that is in part transparent to electrons carries information about the inner structure of the specimen in the electron beam that reaches the imaging system of the microscope.

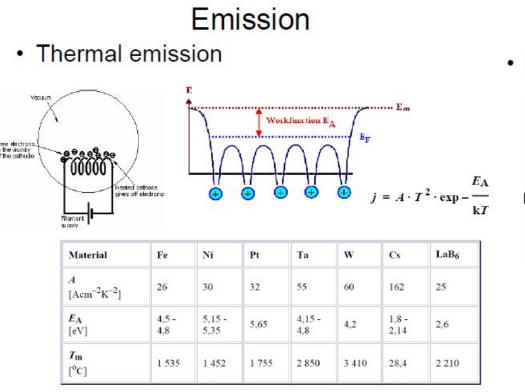
Transmission Electron Microscopy (TEM)



Scanning Electron Microscopy (SEM)

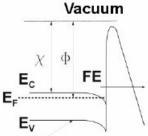
- type of <u>electron microscope</u> capable of producing high-resolution images of a sample surface.
- due to the manner in which the image is created, SEM images have a characteristic 3D appearance and are useful for judging the surface structure of the sample.
- Resolution
- depends on the size of the electron spot, which in turn depends on the magnetic electron-optical system which produces the scanning beam.
- is not high enough to image individual atoms, as is possible in the TEM ... so that, it is 1-20 nm

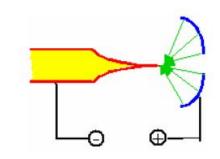
the electron gun



Emission

Field emission





Semiconductor

Field emission starts for E > 10^7 V/cm High current density: J(E) = A·E² ϕ exp (-B $\phi^{1.5}$ /E)

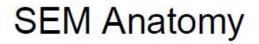
Strong nonlinear current-voltage characteristic Very short switching time (t <ns)

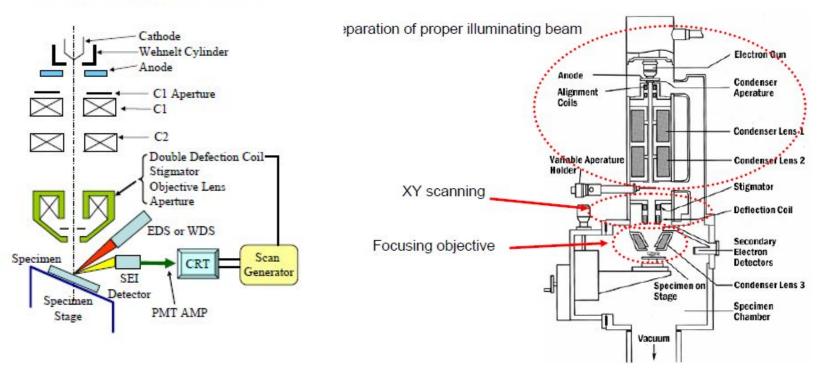
Small spot size due to field enhancement at the tip apex

Scanning Electron Microscope

- Sequential imaging similar to the optical scanning confocal microscope
- Can be used in reflection or transmission modes (STEM)

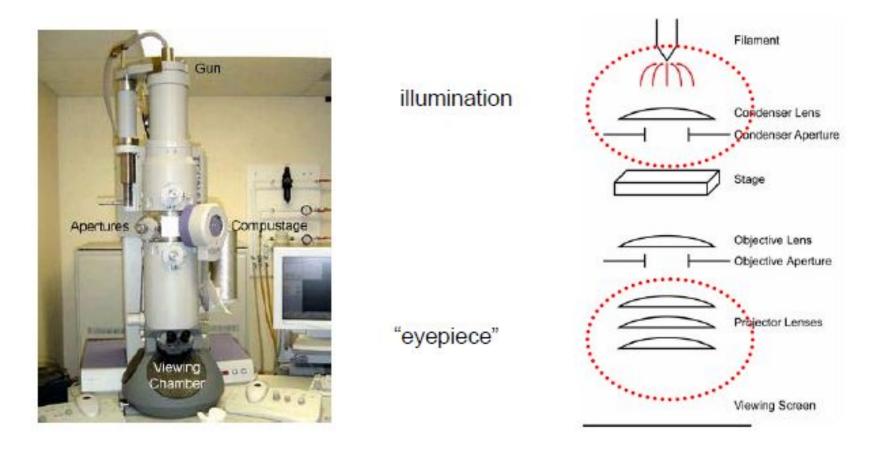
Lens System of SEM

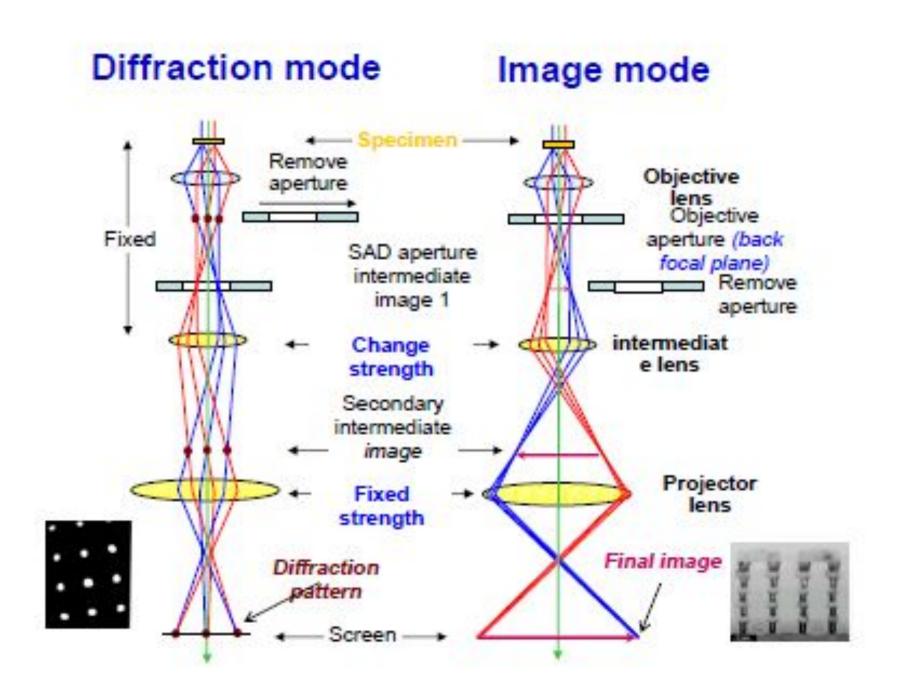




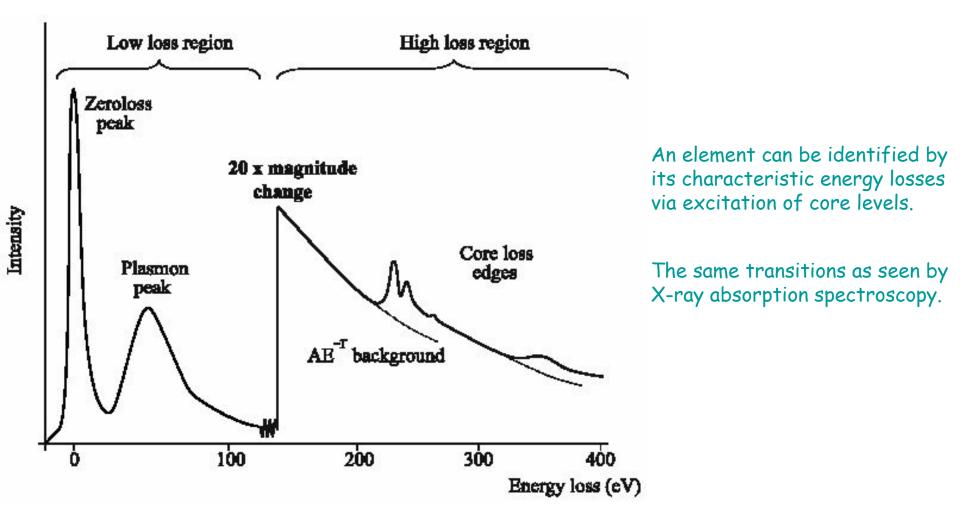
Transmission Electron Microscope

More analogous to an optical microscope

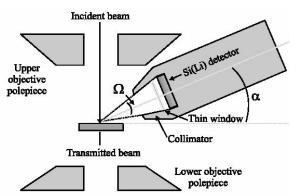




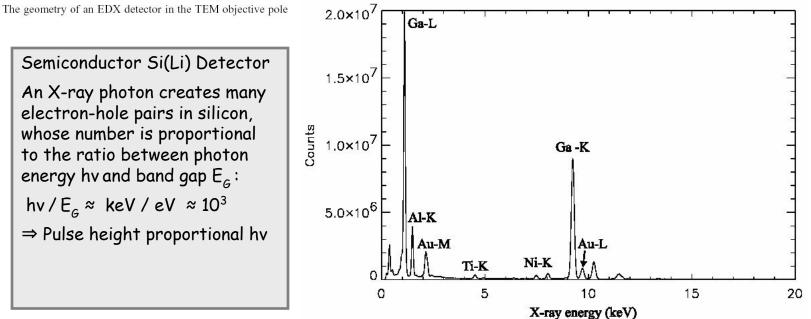
Identify Elements by EELS (Electron Energy Loss Spectroscopy)



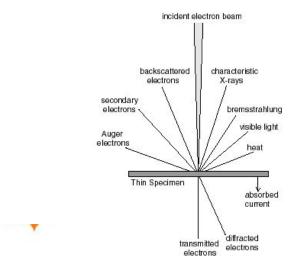
Identify Elements by EDX (Energy-Dispersive X-ray Analysis)



Identify an element by its core level fluorescence energy.



An example EDX spectrum, taken from an AlGaN based ohmic contact



Technique	Excitation Source/ Signal Detected	Elements Detected	Detection Limits	Depth Resolution	Lateral Resolution
Auger Electron Spectroscopy (AES)	Focused Electron Beam/ Auger Electrons	Li to U	0.5 at.%	0-100Å* *Auger electron escape depth	150Â
X-ray photoelectron Spectroscopy (XPS/ESCA)	Monochromatic X-rays/ Photoemitted electrons and Auger electrons	Li to U	0.5 at.%	0-100Å	26µm
Secondary Ion Mass Spectrometry (SIMS)	Primary lons (cs, o, ar)/ Secondary lons	H to U All elements and isotopes	To 1 pp b (at/cm³)	<100A	0.3µm
Static SIMS or Time-of-Flight SIMS (TOF- SIMS)	Primary lons (Ar, Ga, O)/ Secondary lons	H to U All elements and isotopes	To 1 pp m (at/cm³)	<50Å	<0.2µm

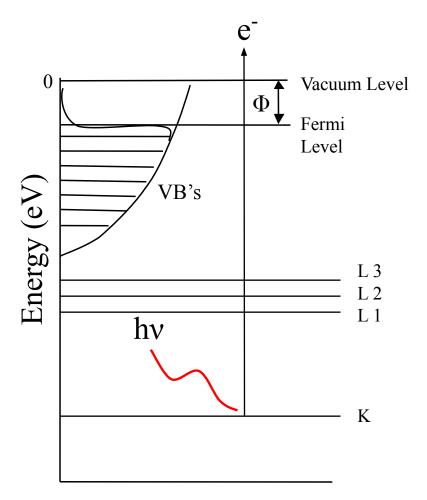
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XPS spectoscopy

• Photon removes a bound electron according to:

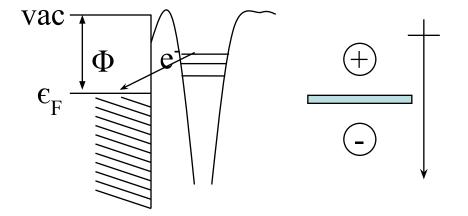
 $KE = hv - BE - \Phi$

- KE is the energy of the ejected electron
- BE is the energy of the core level
- Typical x-rays come from thermionic emission of Al, Mg, Cu, etc.



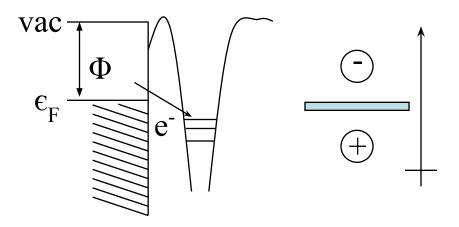
Work Function

Consequence of the photoelectric effect

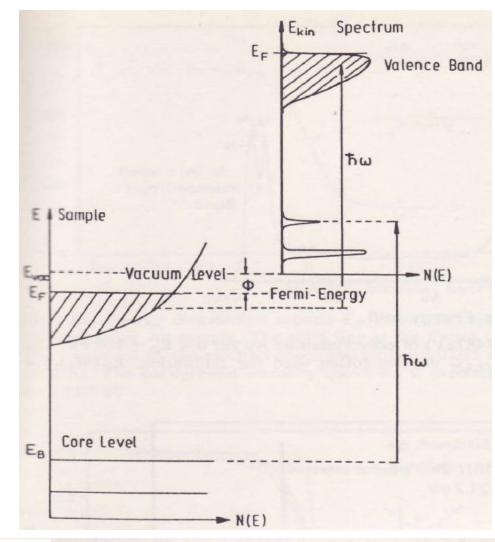


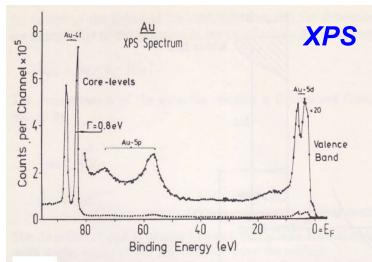
•
$$\boldsymbol{\Phi} = \boldsymbol{E}_{VAC} - \boldsymbol{\epsilon}_{F}$$

- Important indicator of physical and chemical changes
- Adsorbates can increase or decrease *Φ*

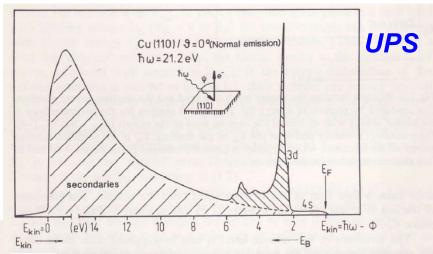


Photoemission spectroscopy





XPS spectrum ($\hbar\omega = 1487$ eV) of polycrystalline Au for $0 \le E_B \le 100$ eV. The 5d valence band and the $4f_{7/2,5/2}$ doublet (often used for calibration: $E_B(4f_{7/2}) = 84.0$ eV) are clearly seen



Relation between the energy levels in a solid and the electron energy distribution produced by photons of energy $\hbar\omega$. The natural abscissa for the photoelectrons is the kinetic energy with its zero at the vacuum level of the sample $(E_{kin} = \hbar\omega - |E_B| - \phi)$. Experimenters generally prefer to use E_B as the abscissa. E_B is the so-called binding energy of the electrons, which in solids is generally referred to the Fermi level and in free atoms or molecules to the vacuum level

UPS (He I, $\hbar\omega = 21.2 \text{eV}$) spectrum from a (110) face of Cu (normal emission, $\vartheta = 0$, ϑ being the polar angle with respect to the surface normal). The flat 4s band and the structured 3d band are seen. The cutoff marks the point where $E_{kin} = 0$ and via (1.2) the work function can then be derived

Electron Energy Loss Spectroscopy (EELS)

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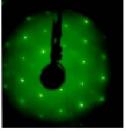
Low Energy Electron Diffraction (LEED)

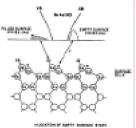
 $\lambda = h/p = h/(2mE)^{1/2}$

 $E = 20 \text{ eV} \rightarrow \lambda \approx 2.7 \text{Å};$ $200 \text{ eV} \rightarrow 0.87 \text{ Å}$

Small penetration depth (few tens of Å)

- surface analysis

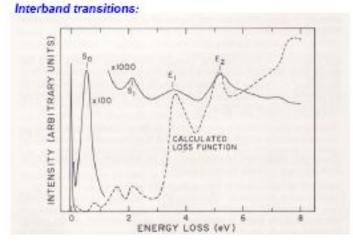


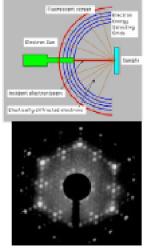


Because electrons are light, charge particles, they interact withthe electrons within the lattice and do not penetrate far.

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Electron Energy Loss Spectroscopy (EELS)





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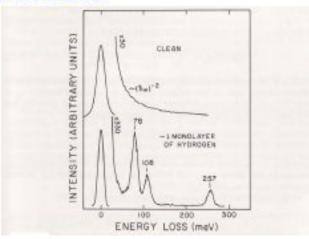
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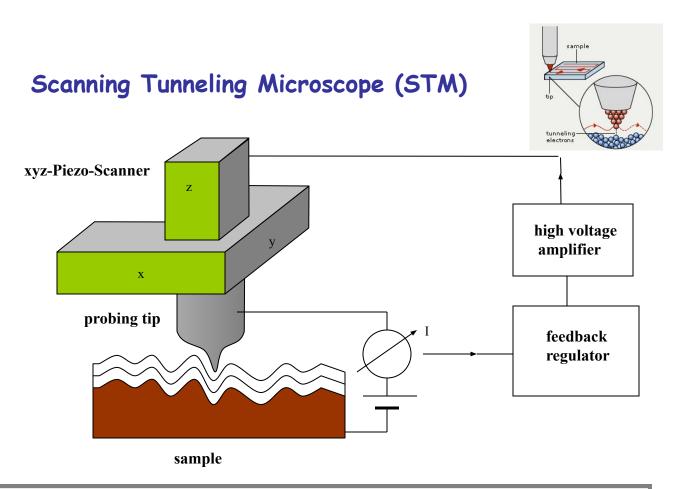
BLECTED

wisesone.

MINUNE







Negative feedback keeps the current constant (pA-nA) by moving the tip up and down. Contours of constant current are recorded which correspond to constant charge density.

Technology Required for a STM

- Sharp, clean tip (Etching, ion bombardment, field desorption by pulsing)
- Piezo-electric scanner (Tube scanner, xyz scanner)
- Coarse approach (Micrometer screws, stick-slip motors)
- Vibrational damping (Spring suspension with eddy current damping, viton stack)
- Feed-back electronics (Amplify the current difference, negative feedback to the z-piezo)

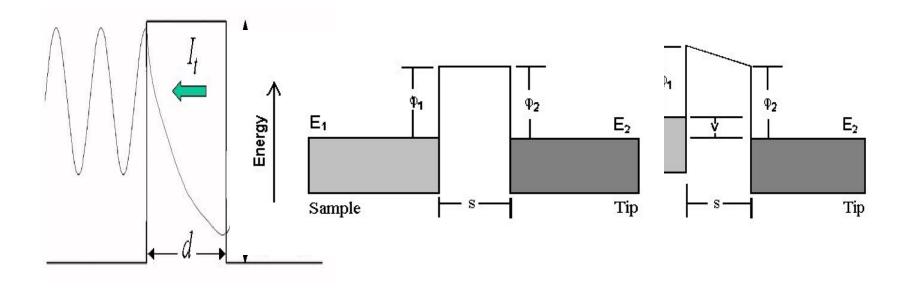
Atomic resolution, several orders of magnitude better than the best electron microscope

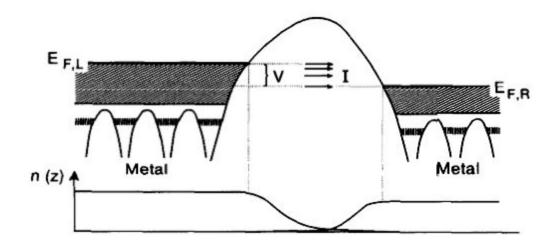
- Quantum mechanical tunnel-effect of electron
- In-situ: capable of localized, non-destructive measurements or modifications
- material science, physics, semiconductor science, metallurgy, electrochemistry, and molecular biology
- Scanning Probe Microscopes (SPM): designed based on the scanning technology of STM

Theory and Principle

Tunneling Current

- A sharp conductive tip is brought to within a few Angstroms of the surface of a conductor (sample).
- □ The surface is applied a bias voltage, Fermi levels shift
- □ The wave functions of the electrons in the tip overlap those of the sample surface
- Electrons tunnel from one surface to the other of lower potential.

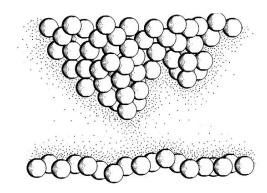




$$\Psi(d) = \Psi(0)e^{-\kappa d} \quad \text{where} \quad \kappa = \frac{\sqrt{2m(\Phi - E)}}{\hbar}$$
$$W(d) = |\Psi(d)|^2 = |\Psi(0)|^2 e^{-2\kappa d}$$
$$I = f(V) e^{-2Kd}$$

Theory and Principle

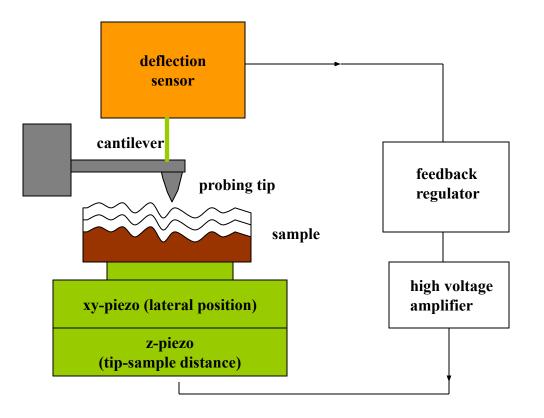
- In classical physics e flows are not possible without a direct connection by a wire between two surfaces
- On an atomic scale a quantum mechanical particle behaves in its wave function.
- □ There is a finite probability that an electron will "jump" from one surface to the other of lower potential.



$$I \propto e^{-2Kd}$$

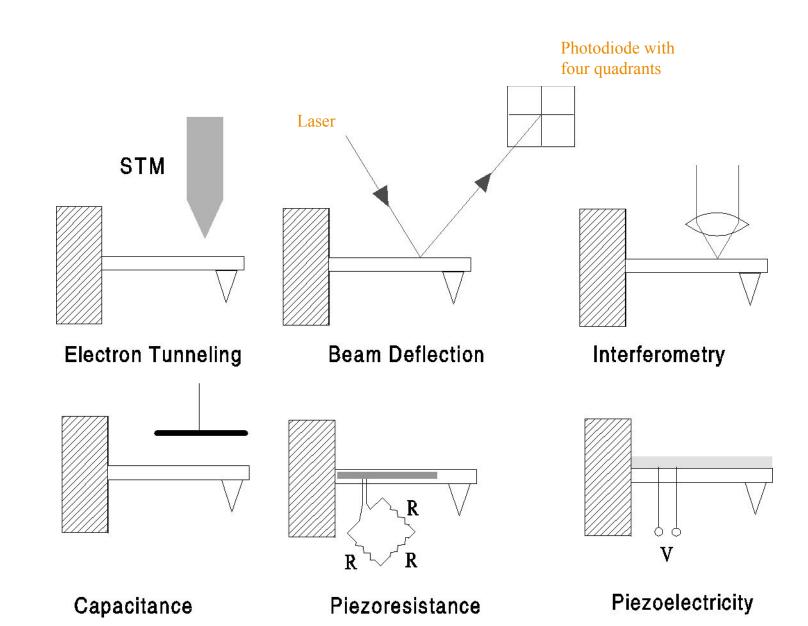
$$\kappa \approx \frac{\sqrt{2m\Phi}}{\hbar}$$

Atomic Force Microscope (AFM)

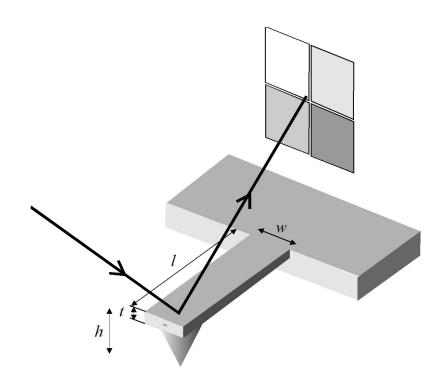


Negative feedback keeps the force constant by adjusting the z-piezo such that the up-down bending angle of the thin cantilever remains constant.

Deflection sensors



Beam-deflection method



A light beam is reflected from the cantilever onto a photodiode divided into 4 segments.

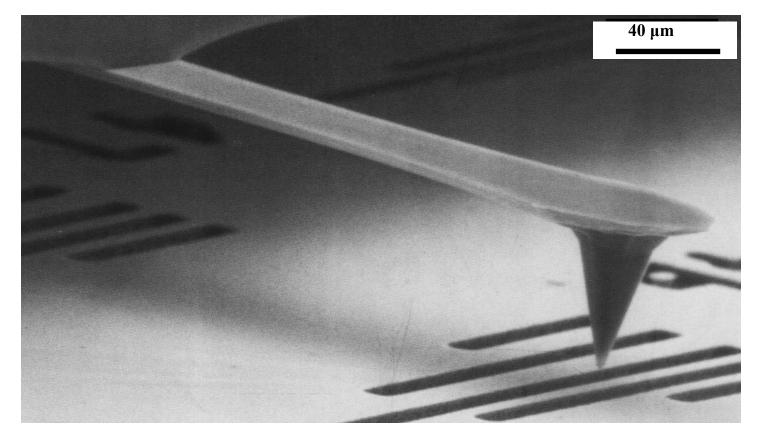
The vertical difference signal provides the perpendicular deflection.

The horizontal difference signal provides the torsional bending of the cantilever.

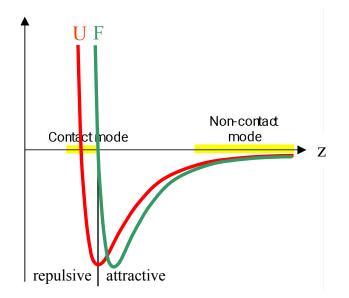
The two deflections determine perpendicular and lateral forces simultaneously.

AFM Cantilever and Tip

To obtain an extra sharp AFM tip one can attach a carbon nanotube to a regular, micromachined silicon tip.



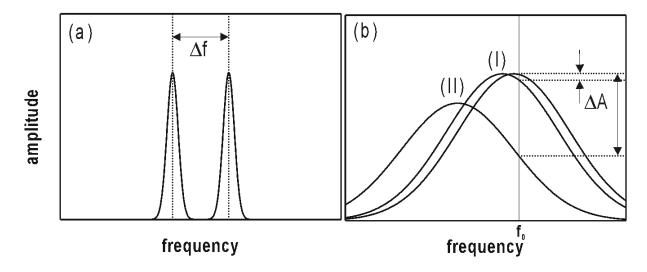
Principle of AFM



Energy U and **force F** between tip and sample as a function of their distance z. The force is the derivative (= slope) of the energy. It is attractive at large distances (van der Waals force, non-contact mode), but it becomes highly repulsive when the electron clouds of tip and sample overlap (Pauli repulsion, contact mode).

In AFM the force is kept constant, while in STM the current is kept constant.

Dynamic Force Detection



The cantilever oscillates like a tuning fork at resonance. Frequency shift and amplitude change are measured for detecting the force.

(a) High Q-factor = low damping (in vacuum):

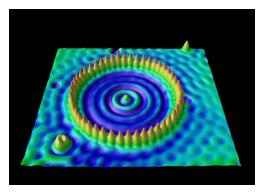
Sharp resonance, detect frequency change, non-contact mode

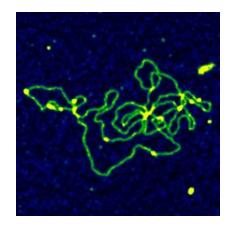
(b) Low Q-factor = high damping (in air, liquid):Amplitude response, detect amplitude change, tapping mode

STM versus AFM

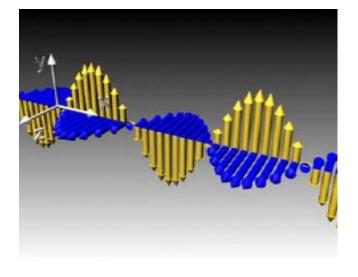
STM is particularly useful for probing electrons at surfaces, for example the electron waves in quantum corrals or the energy levels of the electrons in dangling bonds and surface molecules.

AFM is needed for insulating samples. Since most polymers and biomolecules are insulating, the probe of choice for soft matter is often AFM. This image shows DNA on mica, an insulator.





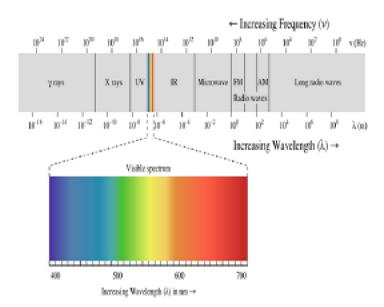
Electromagnetic Waves

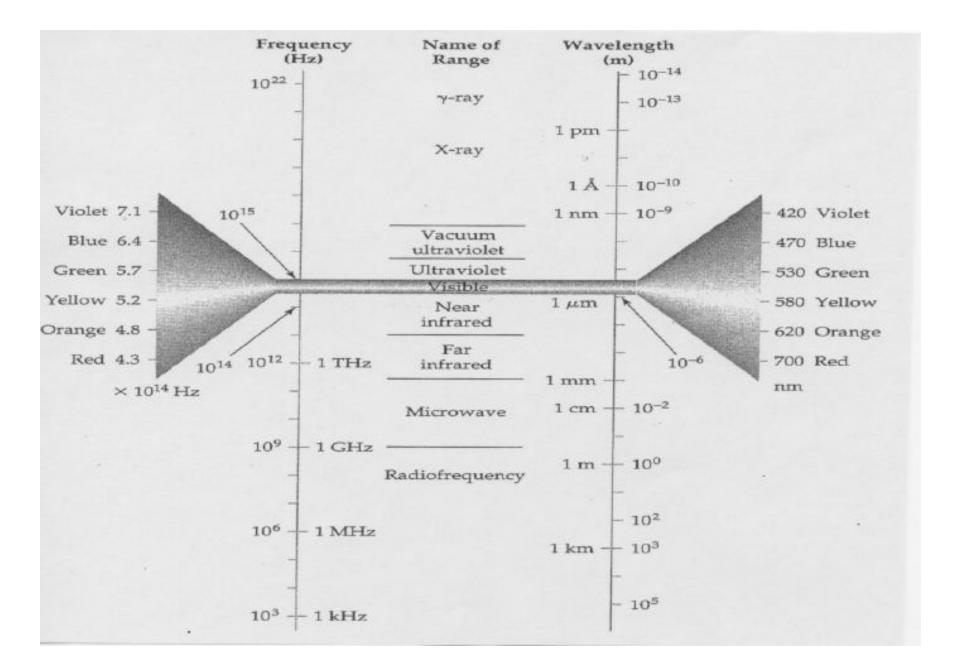


Maxwell's equations

$$\nabla \cdot \mathbf{E} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{B}$$
$$\nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{B} = \mu_0 \epsilon_0 \frac{\partial}{\partial t} \mathbf{E}$$

CLASS	FREQUENCY	WAVELENGTH	ENERGY
Ŷ	300 EHz	1 pm	1.24 MeV
н́х —	30 EHz	10 pm	124 keV
	3 EHz	100 pm	12.4 keV
sx —	300 PHz	1 nm	1.24 keV
	30 PHz	10 nm	124 eV
EUV_	3 PHz	100 nm	12.4 eV
NIR	300 THz	1 µm	1.24 eV
MIR	30 THz	10 µm	124 meV
FIR	3 THz	100 µm	12.4 meV
EHE	300 GHz	1 mm	1.24 meV
	30 GHz	1 cm	124 µeV
SHF	3 GHz	1 dm	12.4 µeV
	300 MHz	1 m	1.24 µeV
VHF_	30 MHz	1 dam	124 neV
HF	3 MHz	1 hm	12.4 neV
MF	300 kHz	1 km	1.24 neV
	30 kHz	10 km	124 peV
VLF	3 kHz	100 km	12.4 peV
VF	300 Hz	1 Mm	1.24 peV
ELF	30 Hz	10 Mm	124 feV

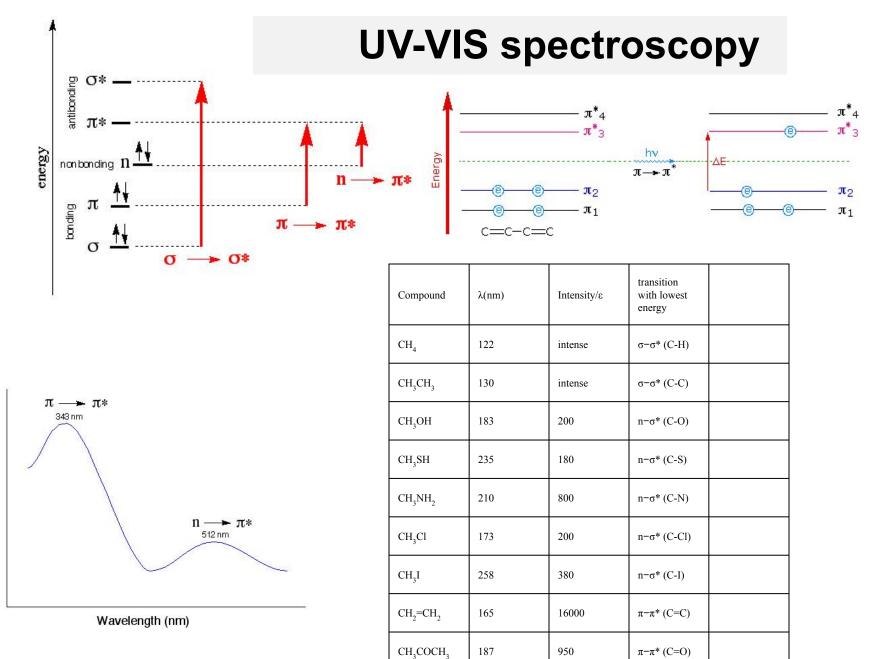




Type Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm ⁻¹	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	_	Nuclear
X-Ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	-	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 µm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–3.75 mm	13-27	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^{3}	Spin of nuclei in a magnetic field

Energy Units for EM waves

- The Energy of EM waves is measured in several different units in the literature.
- $E = hv = hc/\lambda$
- $1 eV = 8065.5 cm^{-1} = 2.418 \times 10^{14} Hz = 11,600 K.$
- $1 eV = 1.2398 \mu m$
- $1 \ cm^{-1} = 0.12398 \ meV = 3X10^{10} \ Hz.$



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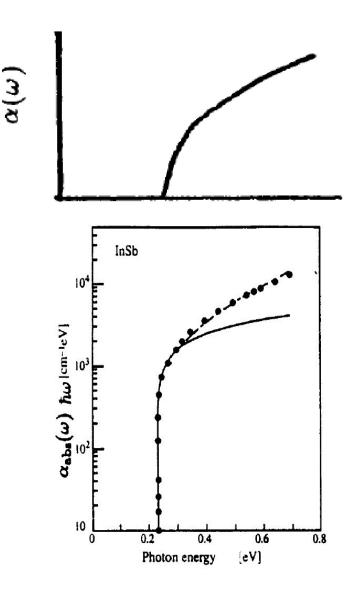
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n-π* (C=O)

Absorbance

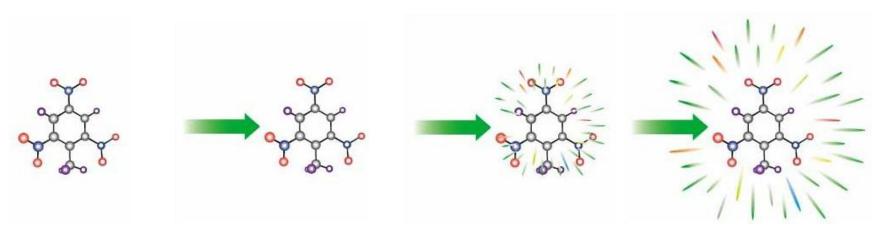
Linear spectroscopy Absorption Coefficient

- 1. Free carrier absorption
 - (a) typical semiconductor $\alpha_{\rm abs}(\omega) \sim \omega^{-2}$
 - (b) metals at low frequencies $\alpha_{abs}(\omega) \sim \omega^{\frac{1}{2}}$
- 2. Direct interband transitions
 - (a) form of absorption coefficient $\alpha_{\rm abs}(\omega) \sim \frac{(\hbar\omega E_g)^{\frac{1}{2}}}{\hbar\omega}$
 - (b) conservation of crystal momentum
 - (c) relation between m^* and momentum matrix element
 - (d) form of $\alpha_{abs}(\omega)$ for direct forbidden transition $\sim \frac{(\hbar\omega E_g)^{\frac{3}{2}}}{\hbar\omega}$
- 3. Indirect interband transitions
 - (a) form of absorption coefficient $\alpha_{\rm abs}(\omega) \sim (\hbar\omega E_g \pm \hbar\omega_q)^2$
 - (b) phonon absorption and emission processes



Raman Spectroscopy Basics

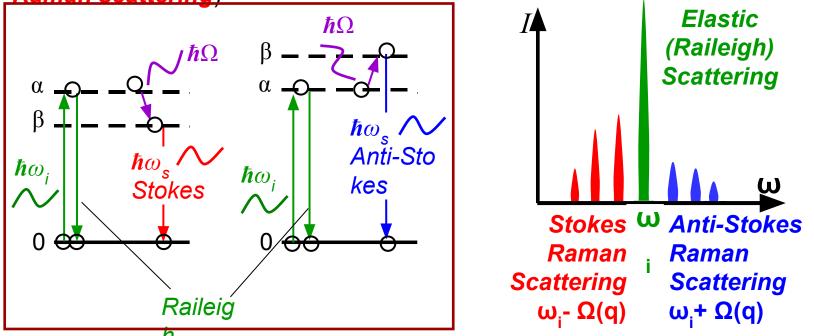
- Basic Physical Realization
 - Illuminate a specimen with laser light (e.g. 532nm)
 - Scattered (no absorbed) Light in two forms
 - Elastic (Rayleigh) $\rightarrow \lambda_{\text{scattered}} = \lambda_{\text{incident}}$
 - Inelastic (Raman) $\rightarrow \lambda_{\text{scattered}} \neq \lambda_{\text{incident}}$
 - Light Experiences a "Raman Shift" in Wavelength



Raman spectroscopy

Inelastic light scattering mediated by the *electronic polarizability* of the medium

- •a material or a molecule scatters irradiant light from a source
- Most of the scattered light is at the same wavelength as the laser source (elastic, or Raileigh scattering)
- •but a small amount of light is scattered at different wavelengths (inelastic, or **Raman scattering**)



Analysis of scattered light energy, polarization, relative intensity provides information on lattice vibrations or other excitations³⁹

Raman scattering in crystalline solids

Not every crystal lattice vibration can be probed by Raman scattering. There are certain *Selection rules*:

1. Energy conservation:

 $\boxtimes \omega_i = \boxtimes \omega_s \pm \boxtimes \Omega;$

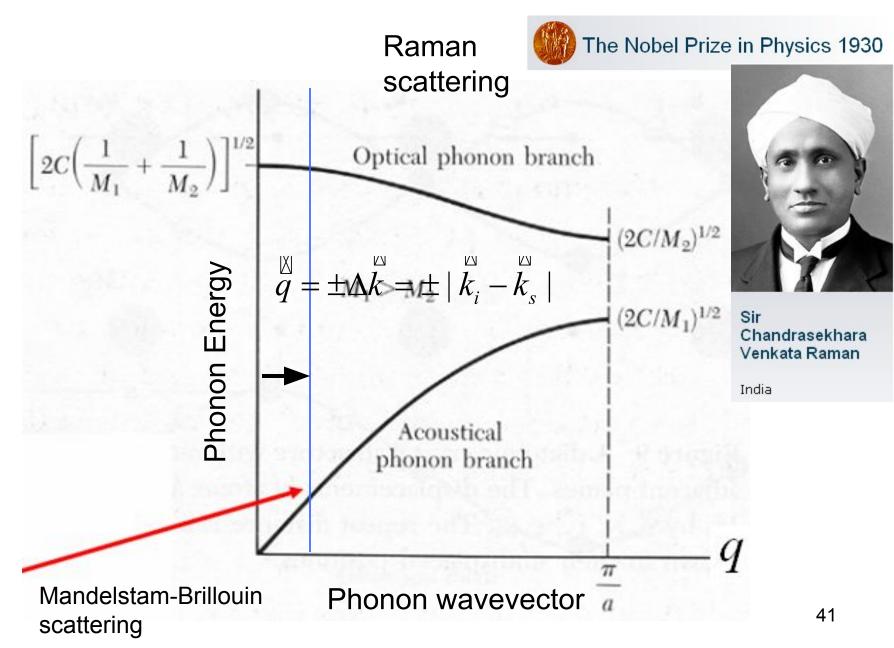
2. Momentum conservation:

$$\mathbf{k}_{i} = \mathbf{k}_{s} \pm \mathbf{q} \implies 0 \le |\mathbf{q}| \le 2|\mathbf{k}| \implies 0 \le |q| \le \frac{4\pi n}{\lambda_{i}} \qquad \overset{\mathbf{k}_{s}}{\Longrightarrow} \mathbf{q} \approx \mathbf{0} \qquad \overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{q} \approx \mathbf{0}$$
$$\overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{q} \approx \mathbf{0} \qquad \overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{q} \approx \mathbf{0} \qquad \overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{q} \approx \mathbf{0} \qquad \overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{q} \approx \mathbf{0}$$
$$\overset{\mathbf{k}_{s}}{\longleftarrow} \mathbf{k}_{i}$$

 \Rightarrow only small wavevector (cloze to BZ center) phonons are seen in the 1st order (single phonon) Raman spectra of bulk crystals

3. Selection rules determined by crystal symmetry

Raman scattering in crystalline solids



Example of Raman scattering in crystalline solids

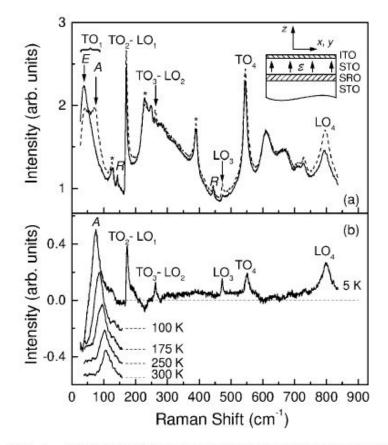
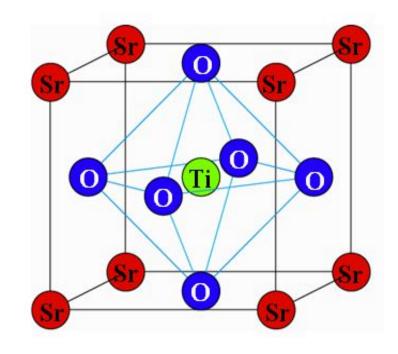


FIG. 1. (a) Solid and dotted lines show the Raman spectra of 1 μ m STO film at T = 5 K without electric field and in the presence of an external electric field of 22×10^4 V/cm directed normal to the film plane, respectively. The soft-mode components are labeled A and E. Structural modes are denoted by R. Optical phonons from the SRO buffer layer are marked with stars. The inset shows the schematics of the investigated trilayer ITO/STO/SRO structure grown on an STO substrate. (b) Electric-field-induced modification of the Raman intensity obtain by subtracting spectrum at $\ell = 22 \times 10^4$ V/cm from that at $\ell = 0$ for different temperatures shown next to the spectra. Spectra are shifted vertically for clarity.



3S = 15 modes 3 acoustic modes 12 optical modes; 3×4 $2 \times TO_1 + LO_1$ $2 \times TO_2 + LO_2$ $2 \times TO_3 + LO_3$ $2 \times TO_4 + LO_4$

IR SPECTROSCOPY

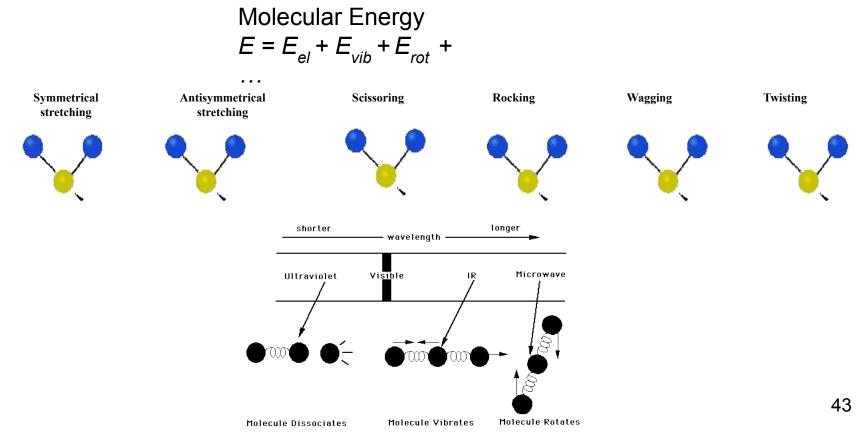
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far- infra

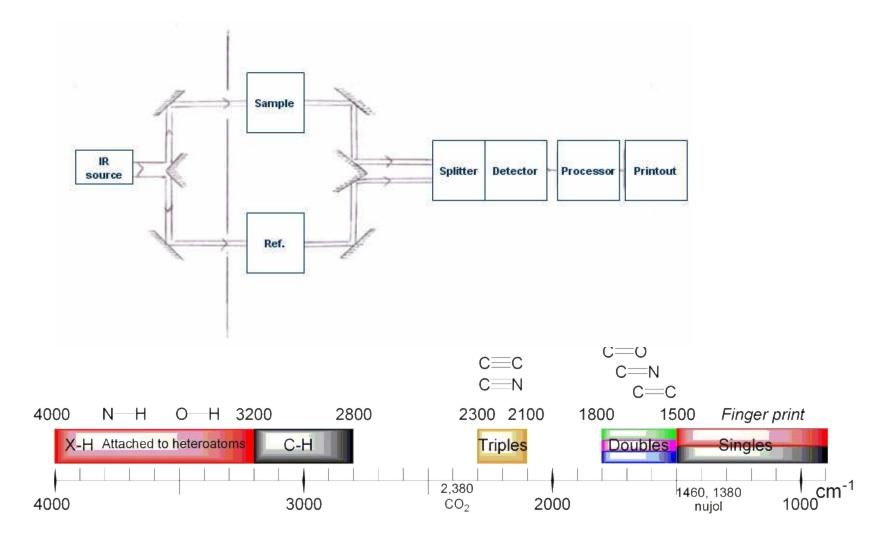
400-10 cm-1 (1000–30 μm), adjacent to the microwave region => rotational-vibrational

mid- IR: 4000-400 cm-1 (30–1.4 µm) => fundamental vibrations & rotational-vibrational

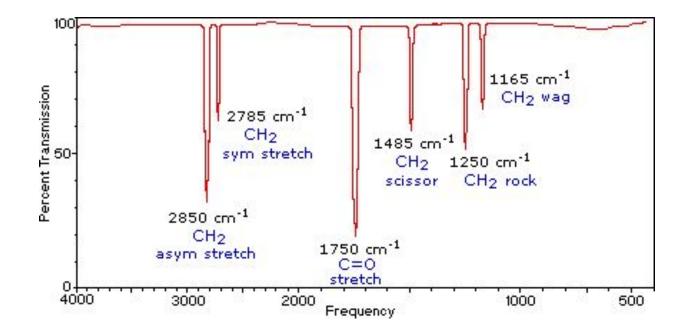
Near IR: 14000-4000 cm-1 (1.4–0.8 μm) can excite <u>overtone</u>: 14000-4000 cm-1 (1.4–0.8 μm) can excite overtone or <u>harmonic</u> vibrations



IR SPECTROSCOPY



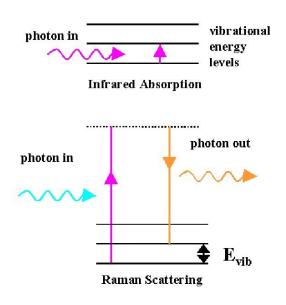
IR vibrational spectrum for Formaldehyde



Raman vs. FTIR

- FTIR
 - Sensitive to functional group vibrations especially OH stretch in water, good for studying the substituents on organic molecules
 - Usually needs some sample prep for transmission
 - Good sensitivity
 - Good microscopic technique

Raman and IR



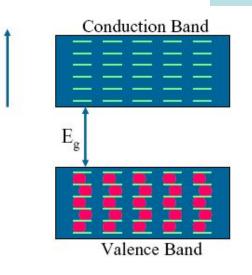
- Raman
 - Sensitive to C=C, C=C
 - Distinguish diamond-C from amorphous-C
 - Studying backbone vibrations of the organic chain
 - Little sample prep
 - Fluorescence Light Can
 Swamp Raman Light
 - Fair sensitivity
 - Good microscopic technique

Luminescence

- •Luminescence : Emission of radiation in excess of the amount emitted in thermal Equilibrium (Non equilibrium phenomenon)
- •Needs to create excess electrons and holes
- •Electron-hole recombination => luminescence
- 1. photoluminescence by optical radiation,
- 2. electroluminescence by electric fields or currents,
- 3. cathodoluminescence by electron beams (or cathode rays),
- 4. radioluminescence by other energetic particles or high energy radiation.

If the emission is fast (<10⁻⁸ sec) – Fluorescent Slow emission process --- Phosphorescent

Photoluminescence in semiconductors



E

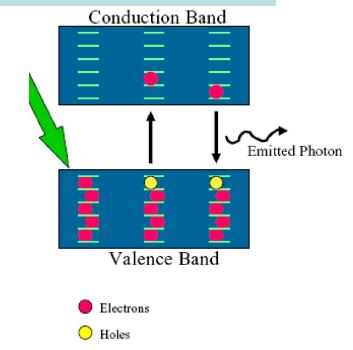
Electrons

Energy Levels

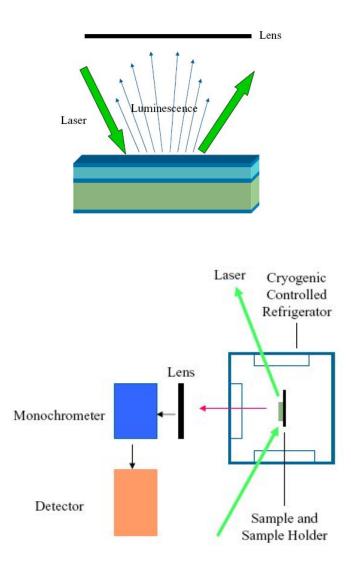
Band-edge luminescence is recombination of excess electrons and holes They are photogenerated by an optical pump, laser

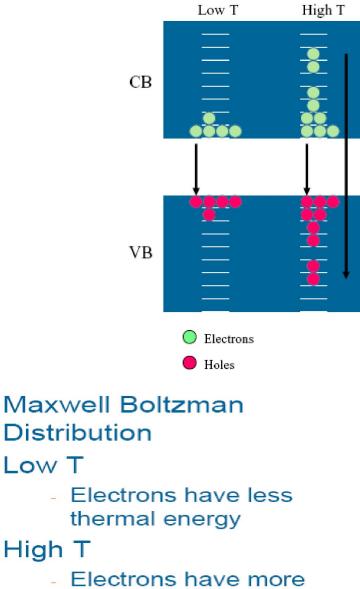
Energy of photon $\approx E_g$

Indirect transition can occur without a phonon



Radiative Recombination – A photon is emitted to conserve energy Band-to-Band recombination – CB electron combines with a VB hole (empty state) Energy of emitted photon is approximately equal to the band gap Emission of a transverse optical (TO) phonon (indirect transition)

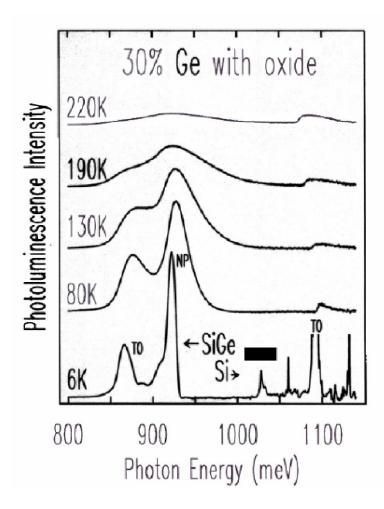




thermal energy

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PL spectrum of a semiconductor



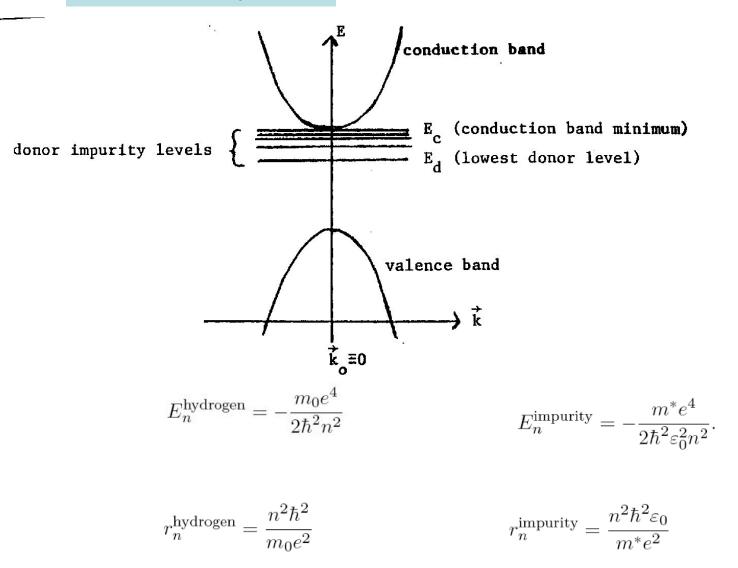
Reduced peak width at low temperature

Photoluminescence intensity is related to Temperature

PL=(E-E_g)²e -(E-Eg)/kT

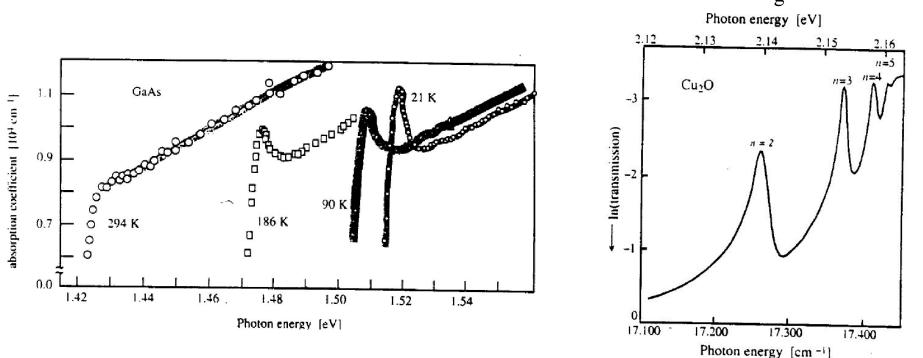
Impurity Levels in semiconductors

Shallow impurity Levels

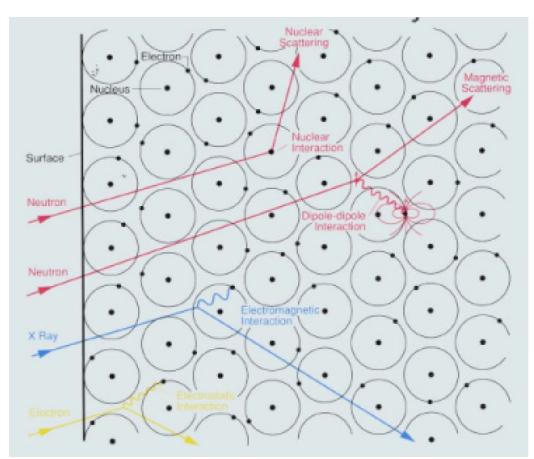


Excitons

- •Electrons and holes bound together by their Coulomb Interaction
- •Important at low temperatures
 - LEDs and semiconductor lasers
- •Created by photons with energy slightly less than E_g



Interaction of Electrons, X-rays, and Neutrons with matter

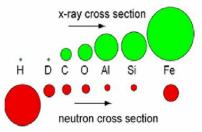


Neutrons vs. x-rays

Whereas neutrons interact primarily by the strong force, xrays interact by scattering from electrons.

The interaction of neutrons with nuclei has the advantage that neutrons can see small atoms (the scattering power for neutrons varies almost randomly for neutrons, as compared to x-rays where it goes like Z²).

Neutrons are therefore wellsuited to study low-Z atomic structures.



This shows how the cross-section, which is related to the size of the Bragg peaks, varies for x-rays (where it increases for increasing size of the atoms, and therefore the number of electrons), compared to neutrons (where it is governed by nuclear interactions – almost random).

X-Ray diffraction

Rotating crystal method – for single crystals, epitaxial films θ-2θ, rocking curve, φ- scan

