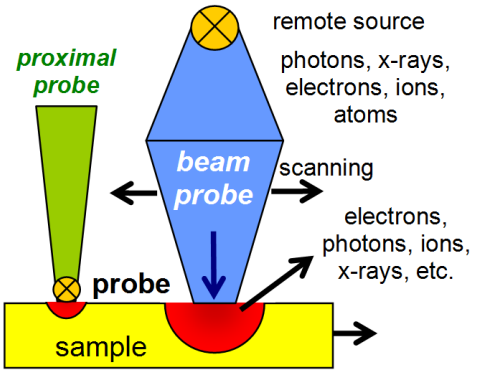
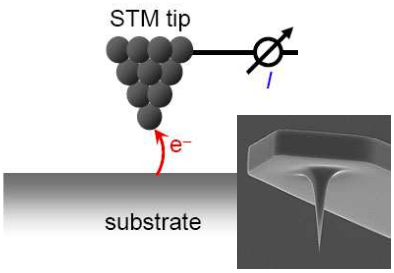
Chapter 2

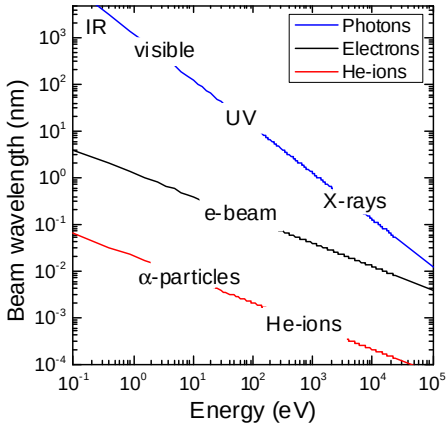
Nanocharcterization: Probes and Probe – Sample Interactions

This chapter is intended to give a brief overview over the different characterization techniques, where photons, electrons, particles and proximal probes are used.

In addition, the different properties and information obtained is described.







Contents - Chapter II

Nanocharcterization: Probes and Probe/Sample Interactions

2.1 Introduction

Nanoscience and technology means:

To make, *measure*, *see*, model and predict materials on the scale of atoms and molecules.

⇨ **Nanocharacterization is an essential building block of NST !**

Why ? We know that the properties of nanomaterials *strongly change* with size, shape, composition, surface and interface structure - in contrast to bulk material, as has been described in detail in chapter I.

⇨ Thus, many different parameters of the nanostructures must be known, such as:

- ⇨ **Structure: Geometry, size, shape, morphology**
- ⇨ **Chemical composition, and distribution of elements**
- ⇨ **Bonding type, properties of surface and interfaces,**
- ⇨ **Electronic properties: Band structure & energy levels**
- ⇨ **Transport and optical properties: Absorption/emission, ..**
- ⇨ **Magnetic properties, mechanical properties,**
- ⇨ **Chemical & biological functionality, ..**

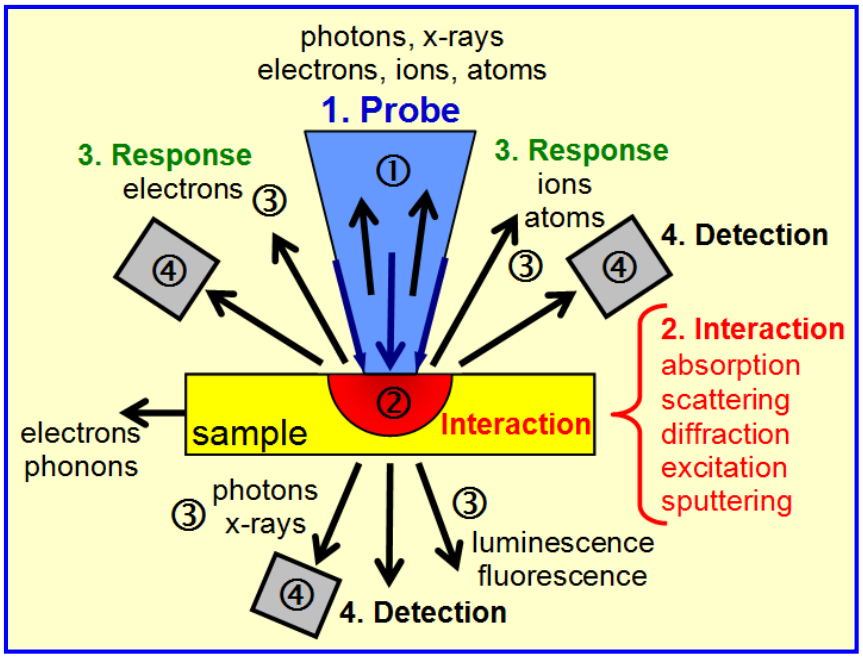
⇨ Many different *complementary* experimental techniques must be employed in order to gain a *comprehensive* understanding of the complex behavior of nanostructures.

2.2 How to Measure Properties of Nanomaterials ?

Generic approach: To obtain information on a sample property, we need to

- ❖ ***excite or illuminate*** it with a ***probe*** consisting of photons, electrons, etc. that
- ❖ ***interacts*** elastically or inelastically with the sample, which
- ❖ leads to a ***response signal*** emitted and that is measured by some kind of detector.

⇨This yields information on the local sample properties within the ***interaction volume***.



1. Probes
Photons (IR, visible, UV) x-rays, electrons, ions, electric & magnetic fields, probe tips

2. Interactions
elastic & inelastic interactions, scattering, diffraction, absorption, excitation of secondary particles,

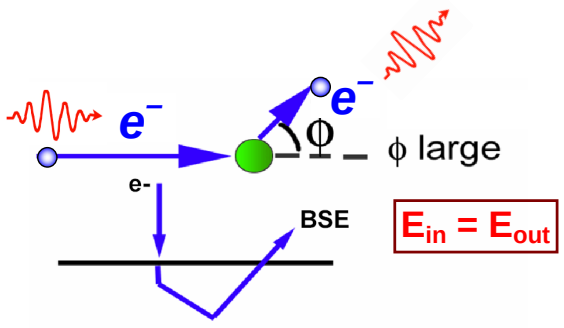
3. Response
photons (IR,VIS,UV), x-rays, electrons, ions, atoms, current, forces, ..

4. Detection:
Spatial or angular distribution, Spectroscopy: Energy or time dep., mass spectroscopy, ..

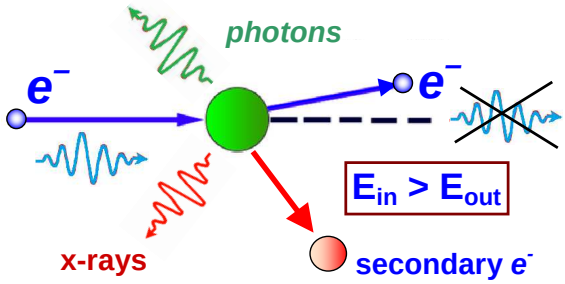
2.2.1 Elastic versus Inelastic Interactions

Many different probe-sample interactions can occur:

Elastic Scattering



Inelastic Scattering & Generation of Secondary Signals



➢ **Energy conserved but momentum transfer**

❖ ***Changes the direction*** of photons / particles due to refraction, reflection, Rutherford or diffuse scattering, ***diffraction***…

⇨ Elastic scattering is determined by atom density, *Z*- number, atom arrangement, lattice structure as well as total number of atoms, i.e., the sample size & shape,

⇨ Sensitive to **structure** and **morphology**,

➢ **Energy transfer to the sample** but (usually) only small momentum transfer, (*small change* of trajectories)

❖ Excitation of vibrations, electronic transitions, core level electrons, generation of many secondary signals such as **secondary photons, electrons, ion,** etc.. .

⇨ Sensitive to atomic species, chemical composition, bonding, electronic structure, vibrations, magnetic structure, …

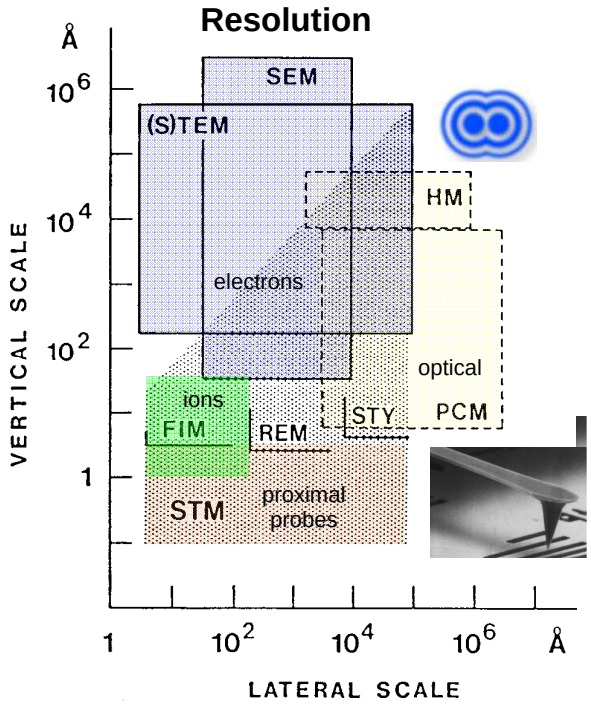
2.2.2. Characterization Techniques and Information Obtained Depends on …

① Which *kind of probe* is used to excite the sample, ② What *kind of interaction* occurs,
③ Which *secondary signal* is generated, and ④ How the secondary *signal is detected*.

Probe	Interaction	Response	Resulting Characterization Method
Photons **NC-I**	**reflection**	**photons**	= optical spectroscopy, ellipsometry, FTIR
	absorption	**photons**	= microscopy, scanning near field microscopy (SNOM)
	excitation	**photons**	= photoluminescence (PL), Raman spectroscopy
		electrons	= photoelectron spectroscopy
		atoms & ions	= laser ablation
Probe tips **NC-I**	**tunneling**	**electrons**	= scanning tunneling microscopy (STM)
	force	**forces**	= atomic force microscopy (AFM)
	magnetic fields		= magnetic force microscopy (MFM)
X-rays **NC-I**	**elastic**	**x-rays**	= x-ray diffraction & scattering (XRD),
	inelastic	**x-rays**	= x-ray fluorescence (XRF)
	excitation	**electrons**	= x-ray photoelectron spectroscopy (XPS)
Electrons **(NC-I)** **NC-II**	**elastic scattering**	**electrons**	= electron diffraction (LEED, RHEED)
		electrons	= electron microscopy (TEM, SEM, LEEM)
		electrons	= electron loss spectroscopy (EELS)
	inelastic scattering	**photons**	= cathodoluminescense (CL)
		x-rays	= microanalysis (EDX,WDX)
	excitation	**electrons**	= Auger electron spectroscopy (AES)
		sample current	= electron beam induced current (EBIC)
α - particles	**scatterning**	**α particles**	= Rutherford backscattering (RBS)
Ions, atoms **NC-II**	**elastic scat.**	**ions, atoms**	= ion & atom (He) diffraction & scattering
	inelastic scat.	**ions, atoms**	= ion scattering spectroscopy (LEIS)
	sputtering	**ions & atoms**	= secondary mass spectroscopy (SIMS)
			= atom probe tomography

2.2.3 Spatial Resolution

⇨ **Limited by size of the probe**: = ½ wavelength λ for photons, = deBroglie wavelength $\lambda = h/\sqrt{2mE}$ for particle beams (<<nm), = physical size of scanning probes (~ nm)

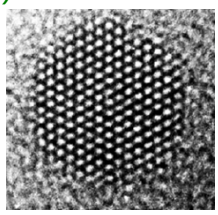


• **Optical microscopy (HM, PCM)**:
Resolution down to λ/2 ~200 nm

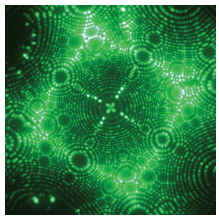
• **Electron microscopy:** (SEM,TEM)
Small wavelengths: λ = 12.25Å /√E[eV]

(a) TEM (100 - 3000 keV): Resolution of single atom rows, limited by lens optics,

(b) SEM (10 - 50 keV): Resolution limited by interaction volume

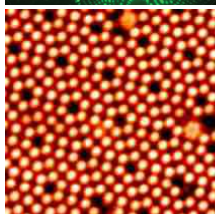


• **Field ion microscopy:** (FIM)
(Müller 1951): Direct imaging of single atoms at surface steps,
requires very high electric fields, thus limited to sharp tips with radius < 100 nm.



• **Scanning probe microscopy**

(Binning&Rohrer,1984)
STM & AFM: Atomic resolution.
Scanning near field optical microscopy (SNOM): ~ 50 nm

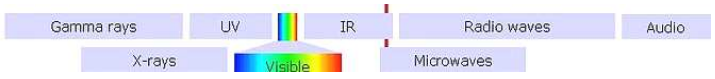


2.3 NanoProbes

Different probes can be used to excite and interact with the sample. They are characterized by their ***nature***, ***energy***, ***wavelength***, ***charge*** and ***mass*** and are distinguished as:

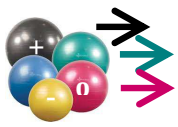
(A) *Beam Probes*: Emission from a *remote source* is focused by optical elements onto the sample. The beam may consist of:

(i) Photons (electromagnetic radiation),

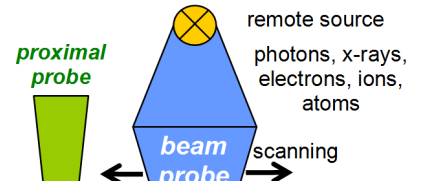


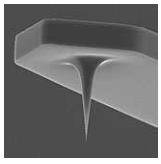
Energies: VIS ~ eV, XR ~keV, depending on wavelength.

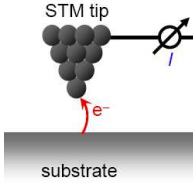
(ii) Particles: *Charged* such as electrons, protons, α-particles, or ions, *or neutral* such as neutrons, atoms or molecules.



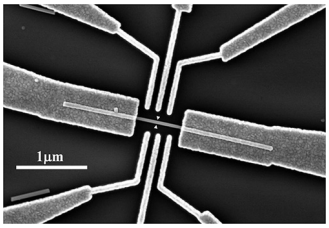
Typical energies: 10 – 200.000eV set by acceleration voltage.
Neutral particles: Thermal beams (atoms) or nuclear reactions.
Wavelengths (de Broglie): λ << 1nm (much smaller than for photons).







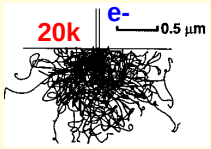
(B) Proximal *Probes*: Optical fibers, STM/AFM probe tips that are scanned in close proximity over the sample surface. Small excitation energies and excitation volume.



(C) Contact Probes: such as electrical contacts produced by electron beam lithography. Measurement of current-voltage characteristics, resistance, capacitance, etc.

2.3.1 Probe Parameters

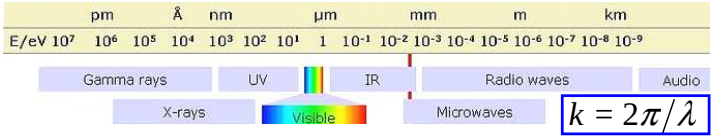
The probe parameters determine many features of used techniques:

Probe Parameter:	Determines….
Energy ***E*** 	• **Possible sample excitations:** High energy versus low energy excitations. • **Interaction strength** and **interaction volume:** **Penetration depth**, surface sensitivity & spatial resolution. • **Wavelength** due to E(*k*) dispersion.
Charge ***Q*** photons, charged particles neutral particles	• **Interaction strength:** Relatively weak for neutral particles and photons, very strong for charged particles due to Coulomb interaction. • **Penetration depth** related to interaction strength • **Instrumentation:** Required beam sources, optical elements, detectors, etc.. Drastically differs for photons, electrons, neutrons, ions, ...
Wavelength λ **momentum** $k \sim 1/\lambda$	• **Probe size and spatial resolution:** Resolution limit for perfect optical systems $s_{min} \sim \lambda/2$ • **Excitation processes** due to selection rules and momentum transfer
Mass ***M*** (particles)	• **De Broglie wavelength** & resolution limits • **Environmental conditions**: Vacuum required for particles.

2.3.2 Energy versus Momentum *E*(*k*)

Photons: Energy: $E\,[eV] = h \cdot \upsilon = 1240\ /\lambda\,[nm]$

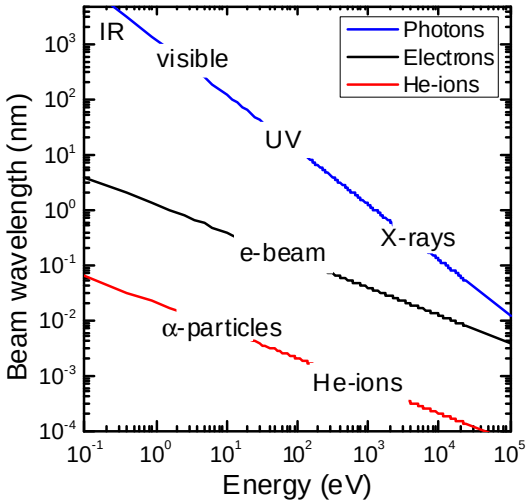
Wavelength: $\lambda\,[nm] = c\ /\upsilon = 1240\,/E\,[eV]$



Visible: E_{ph} ~ 1.8 – 3 eV, λ ~ 700-400 nm, k ~ 10^{-2} nm^{-1}

UV: E_{ph} ~ 5 – 200 eV, λ ~ 200 – 5 nm, k ~ 0.1 – 1 nm^{-1}

XRD: E_{ph} ~ 0.5 – 50keV, λ ~ 3 – 0.03 nm, k ~ 2 – 200 nm^{-1}



Particle waves: Electrons, neutrons, protons, ions, …

Energy: $E = \tfrac{1}{2} m v^2 = q \cdot U$ de Broglie wavelength: $\lambda = h\,/\,p = h\,/\sqrt{2mE} = \lambda_{el}\sqrt{m_e\,/\,m_{particle}}$

Electrons: $\lambda_e\,[nm] = 1.225\,/\sqrt{E\,[eV]}$ Neutrons/protons: $\lambda_{n,p}\,[nm] = 0.02853\,/\sqrt{E\,[eV]}$

α - particles: $\lambda_\alpha\,[nm] = \lambda_{p,n}(E)/2$ Ions: $\lambda_{ion}\,[nm] = \lambda_{p,n}\,/\sqrt{M_A} = 0.02853/\sqrt{E(eV)/M_A}$

$m_p = 1836 \cdot m_e$, $m_n = 1838 \cdot m_e$, $m_\alpha = 7294 \cdot m_e$, $m_{ion} = M_A \cdot m_p$

⇨ For a given energy, the **wavelength of a particle is *much* shorter than for photons !**

⇨ **This yields much *higher spatial resolution* !**

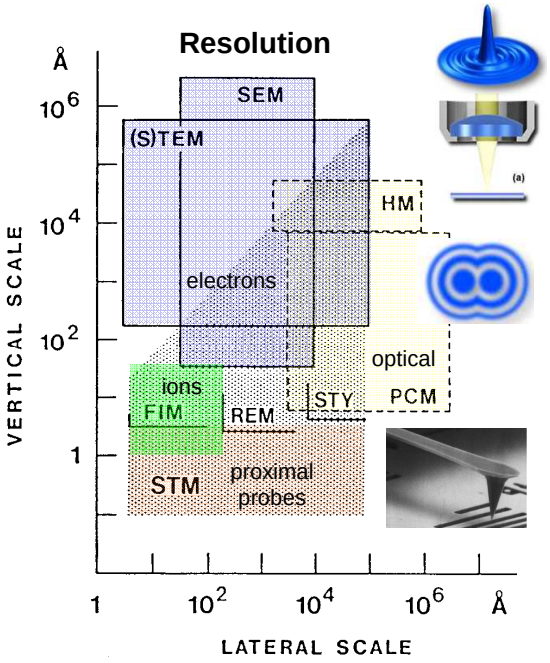
2.3.3 Wavelength, Probe Size and Spatial Resolution

The ***minimal probe size*** is ultimately limited by the Heisenberg uncertainty principle: $\Delta x \cdot \Delta p \sim h$

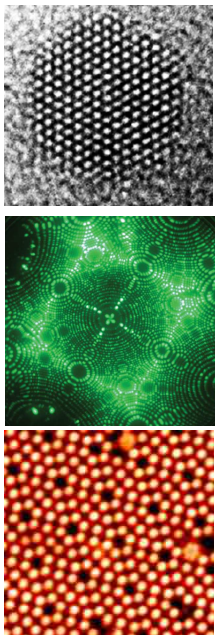
The momentum is given by $p = h/\lambda$, i.e., the resolution is limited by the wavelength as $\Delta x \sim \lambda$.

Photons: » $\Delta x \sim \lambda = 1240\ E^{-1}$ (eV), **Electrons:** » $\Delta x \sim \lambda = 1.225\ E^{-1/2}$ (deBroglie wavelength)

The practical resolution limit is caused by the unavoidable diffraction and imperfections within the optical focusing and imaging system, as well as the size of the interaction volume (see below).
For proximal probes the probe size is the limiting factor.



- **Optical microscopy (HM, PCM)**:
  Resolution down to λ/2 ~200 nm
- **Electron microscopy:** (SEM,TEM)
  Small wavelengths: λ = 12.25Å /√E[eV]
  (a) TEM (100 - 3000 keV): Resolution of single atom rows, limited by lens optics,
  (b) SEM (10 - 50 keV): Resolution is mainly limited by interaction volume
- **Field ion microscopy:** (FIM)
  Direct imaging of individual atoms at surfaces, requires very high electric fields, thus limited to sharp tips with radius < 100 nm.
- **Scanning probe microscopy**
  STM & AFM: Atomic resolution.
  Scanning near field optical microscopy (SNOM): ~ 50 nm



2.3.4 Photons versus Particle Probes

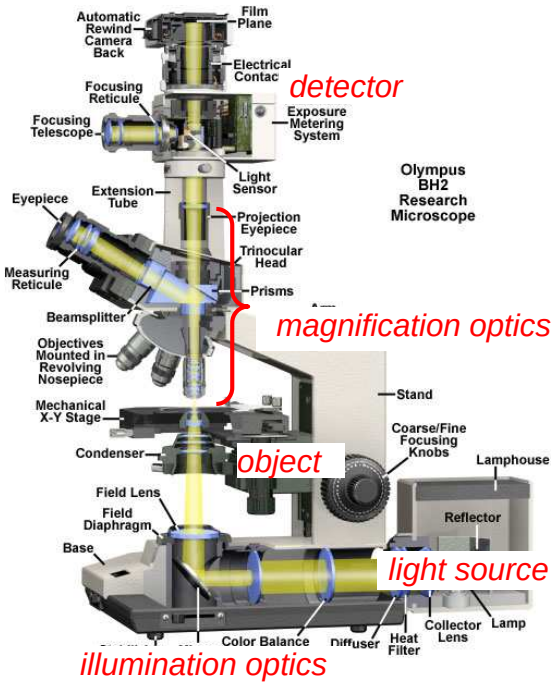
Photon beams differ strongly from particle beams (electrons or ions). This is due to different E(k) relations, different instrumentation and different beam/environment interactions.

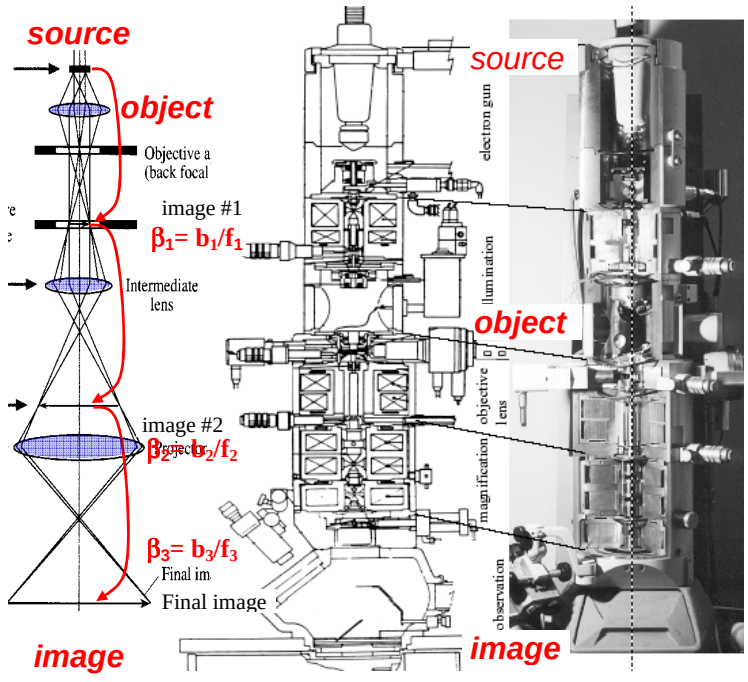
Particle Beams (Electrons/Ions/..)	**Photon Beams** (IR/VIS/X-rays)
1. Very small de Broglie wavelength in the sub nm range. ⇨ **high spatial resolution**	**1. Longer wavelengths** (short only for x-rays) ⇨ **resolutions limited to 100 nm range**
2. Strong beam/sample interactions due to charge, weak only for neutrons. ⇨ **many multiple scattering events** in which particle itself is conserved ⇨ **high vacuum required** ($<10^{-6}$mbar) to avoid scattering (except for neutrons)	**2. Weaker interactions** ⇨ **single step absorption** ⇨ **no vacuum required** (except for UVU/EUV)
3. Electric and magnetic fields used for focusing elements, energy filters and spectrometers	**3. Optical elements:** Lenses, mirrors, prisms, gratings, diffractive optics and diffractive spectrometers
4. Beam sources: Thermionic, field emitters, plasmas/gases (ions), radioactive substances and reactors (*n*, α-particles, ..)	**4. Beam sources:** thermal emitters, gas discharge, LEDs, coherent laser sources, plasmas, ….

Example: Instrumentation for Optical versus Electron Microscopy

Different beam sources, optical elements, detectors, environmental conditions, etc. are required.

Optical Microscope ***versus*** **Transmission Electron Microscope**





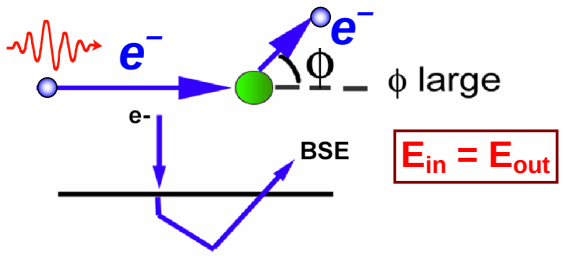
Elements: (1) Beam source, (2) Illumination optics, (3) Magnification optics, (4) Contrast modification elements (apertures, etc.), (5) Detector/image plate.

2.4 Probe – Sample Interactions

To understand the kind of information is obtained, the probe-sample interactions must be known.

Usually, ***many different kinds of elastic and inelastic interactions*** & ***scattering process*** occur simultaneously, and in these processes a wider range of **energy transfers** ΔE_s to the sample is possible. The strength of the interactions also determine the size of the interaction volume.

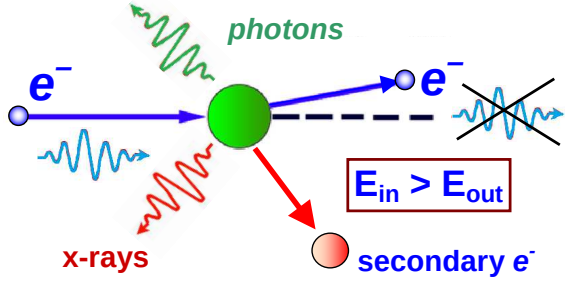
Elastic Scattering



- **Energy conserved but large momentum transfer**
  - ***Changes the direction*** of photons / particles due to refraction, reflection, Rutherford or diffuse scattering, ***diffraction***…
  - ⇨ Elastic scattering is determined by atom density, *Z*- number, atom arrangement, lattice structure as well as total number of atoms, i.e., the sample size & shape,

⇨Sensitive to **structure** and **morphology**,

Inelastic Scattering / Excitation



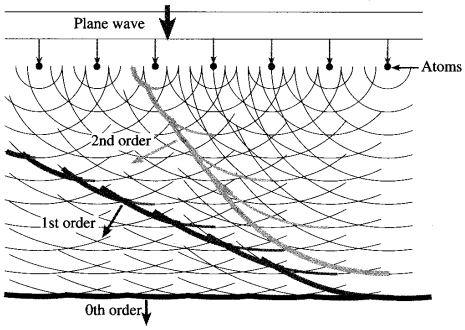
- **Energy transfer to the sample** but (usually) only small momentum transfer, (*small change* of trajectories)
- Excitation of vibrations, electronic transitions, core level electrons, generation of many secondary signals such as **secondary photons electrons, ion,** etc.. .

⇨ Sensitive to atomic species, chemical composition, bonding, electronic structure, vibrations, magnetic structure, …

2.4.1 Elastic Scattering – Diffraction

Diffraction arises from the wave nature of the probe beam and is caused by the interference of the excited secondary waves in the sample.

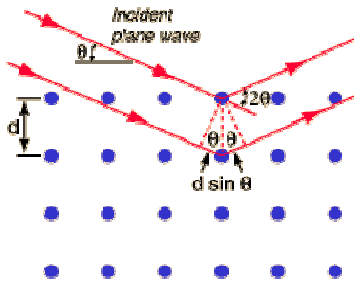
This leads to a preferred scattering (i.e. constructive interference only in certain discreet angular directions = "diffraction pattern" of intensity maxima.



Maxima positions are described by the **Bragg condition**:

Bragg´s law

Path difference: $s = 2d \sin\theta$



Constructive interference when

$n\lambda = 2d \sin\theta$

Bragg's Law

Alternative description: ***Laue condition***

$\Delta k_{beam} = g_{hkl}$ (=reciprocal lattice vector)

Graphical representation: ***» Ewald construction*** based on $|k_{in}| = |k_{out}|$

Lattice plane spacing (cubic):

$$\frac{1}{d_{(h,k,l)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

The resulting angular intensity distribution contains precise information on the interatomic distances on the 0.002 Å scale ! (XRD)

Note: Because for constructive interference the phase differences $s \sim 2d$ from neighboring atoms must be equal to the wavelength λ. Thus, λ must be comparable or smaller than the atomic distances (~1 Å) in the sampe, i.e.

$\lambda < 2d_{hkl}$ » $\lambda <$ 10 Å

This is fulfilled for **photons** with $h\nu > 1$ keV and **particles** with $E_{kin} > 1$ eV.

Laue Condition and Ewald Contstruction

When the detector is sufficiently far away from the sample (= Fraunhofer diffraction) and multiple scattering in the sample is neglected, constructive interference of the excited spherical waves and thus, maximum diffraction intensity is observed at scattering angles given by the

Braggs law: $2d_{hkl} \sin\theta = \lambda$ where d_{hkl} is the lattice plane spacing of the (*hkl*) lattice planes.

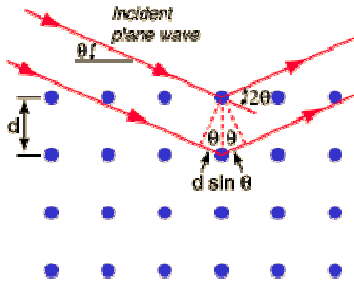
Alternatively, constructive interference can be also represented by the

Laue condition: $\Delta\vec{k} = \vec{k}_i - \vec{k}_0 = \vec{G}_{hkl}$ where $|\vec{k}_0| = 2\pi/\lambda$ and $\vec{G}_{hkl}$ is a reciprocal lattice vector, meaning that the scattering vector Δk must be equal to a reciprocal lattice vector

The diffraction process can be represented and visualized by the ***Ewald construction***:

Bragg´s law

Path difference: $\Delta x = 2d \sin\theta$



Constructive interference when

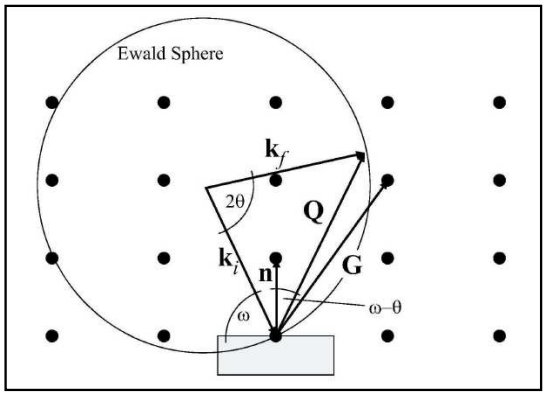
$n\lambda = 2d \sin\theta$

Bragg's Law

Lattice plane spacing:

$$\frac{1}{d_{(h,k,l)}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Laue-Bedingung: $\Delta\vec{k} = \vec{k} - \vec{k}_0 = \vec{G}$



Graphic representation by Ewald construction

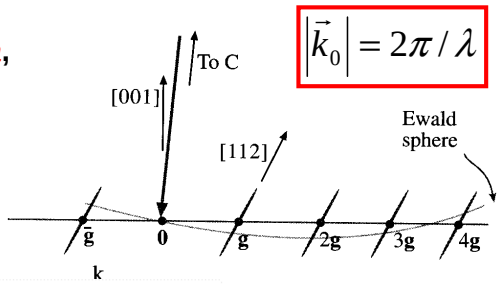
X-Ray versus Electron Scattering

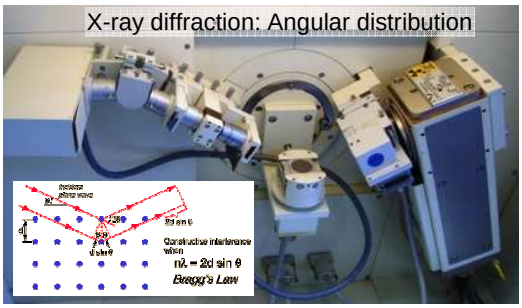
X-Rays: The **photon wavelength λ ~ Å** is comparable to the atom distances *d* in the sample

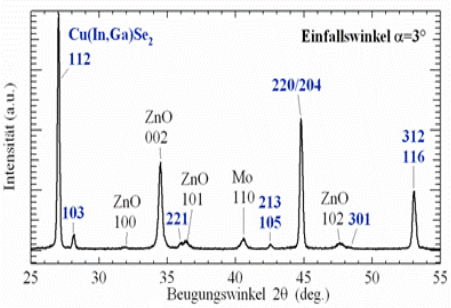
Thus: $k_{XR} = 2\pi / \lambda_{XR} \sim g_{hkl}$, i.e., the angular distance between the diffraction maxima is large !

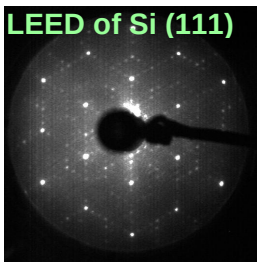
Electrons: **de Broglie wavelength λ_e ~ 0.1 Å** @10keV **<< *a*,**

» Thus, $k_{el} >> g_{hkl}$ and many diffraction spots appear simultaneously at small scattering angles. The resulting diffraction pattern nearly represents a cross-section of the reciprocal lattice.









Obtained Information: The position and intensities of diffraction maxima yields information on:

Lattice structure, symmetries and orientation, lattice constants, strains, structural phases, etc. ..

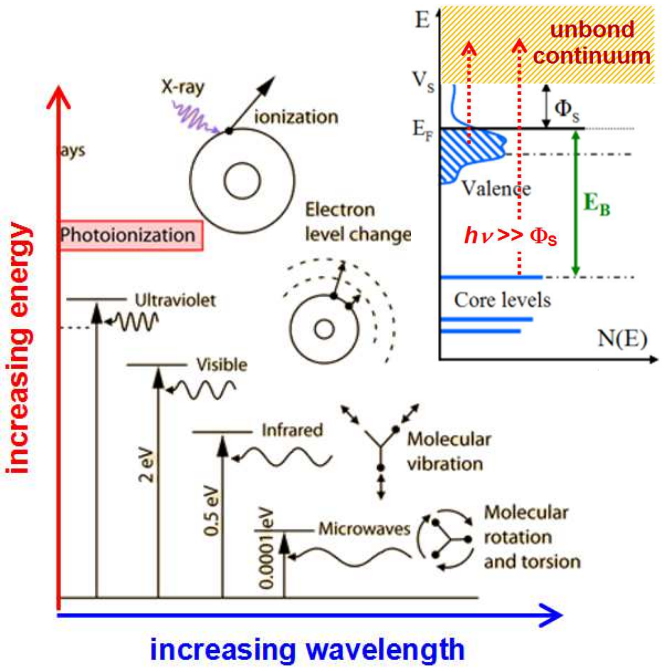
Further aspect: Particle waves induce a much stronger excitation of individual atoms than x-rays.

As a result, for electrons a much high diffraction intensity is obtained already from small sample volumes. This allows *micro-diffraction experiments*. Contrary, x-ray diffraction needs larger ensembles of nanostructures for sufficient intensity and thus, yields only averaged structure information.

2.4.2 Inelastic Excitations

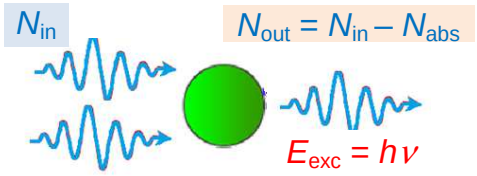
A wider range of **energy transfers** ΔE_s to the sample (excitation) from meV to MeV is possible in inelastic scattering processes.

ΔE_s =	
1-50 meV	❖ Excitation of **phonons** (lattice-vibrations, heat), **low energy**
10 - 200 meV	❖ Intra- or intersubband excitations
0.2-8eV	❖ Interband excitation, generation of electron-hole pairs,
1-10eV	❖ Excitation of **plasmons** (collective electron vibrations)
1-50eV	❖ Generation of **secondary electrons** by ionization of atoms, **medium energy**
>50eV	❖ Atom removal by sputtering, **energy**
1-20keV	❖ **Inner core-shell ionization** of sample atoms, **high energy**
>10keV	❖ **Bremsstrahlung** (emission of x-rays),
>100Me	❖ Momentum transfer to nuclei by elastic **knock-on scattering**, amorphization, sample damaging



2.4.2.1 Excitation by Absorption of Photons

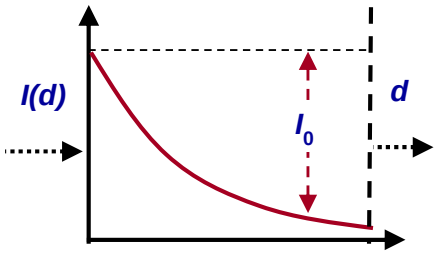
Photons are absorbed in a *one-step process* in which the *whole photon energy hν* is transferred *at once* to the sample, i.e., the *photon is annihilated*.



This means that only excitations are possible in which $E_{final} - E_{initial} = h\nu$. (Exceptions: Raman and Compton scattering)

For a photon beam, this leads to an *exponential decay of the number* of photons with travel length according to the Beer-Lamberts law.

$$I_{ph}(l) = I_0 e^{-\alpha l}$$



The ***excitation*** (i.e., absorption) **probability** s given by

the **absorption coefficient**

$$\alpha(h\nu) = -\frac{1}{N_{ph}}\frac{dN_{ph}}{dl}$$

Depending on the matrix elements of the excitation process, the absorption coefficient can vary over a very wide range from $\alpha = 0 \ldots. 10^7$ cm^{-1}.

The inverse value yields the **penetration depth** $\lambda = 1/\alpha$

which accordingly can vary from λ = infinity ($\alpha = 0$) to a few nanometers ($\alpha = 10^7$ cm^{-1}).

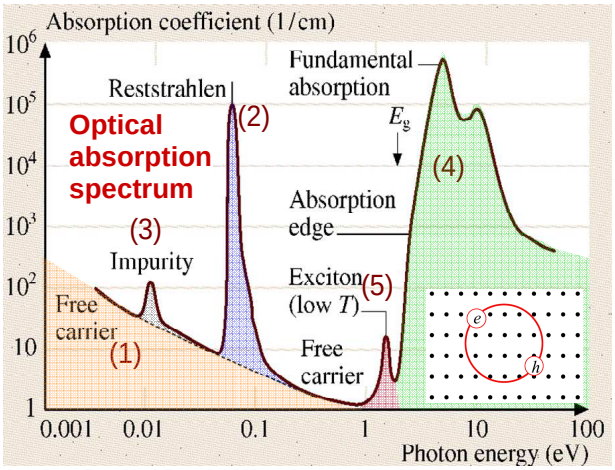
Example: Optical absorption spectrum

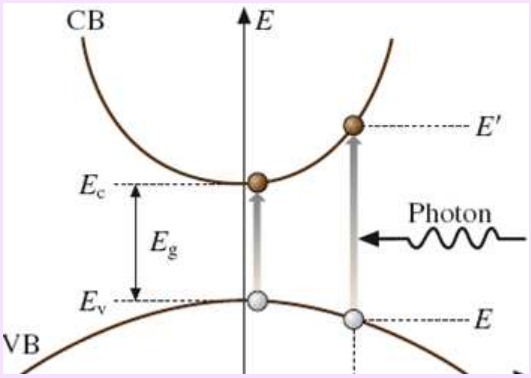
Different ***excitation processes*** lead to photon absorption such as:

1. Excitation of collective damped **plasma oscillations of free carriers**, characterized by the plasma frequency ω_p,
2. Absorption through ***optical phonons*** (lattice vibrations) = „*Reststrahlenbande*“ (~10 – 100 meV)
3. Excitations of electrons from **defect states** (~0.01 – 1 eV)
4. **Exciton absorption** = Excitation of bound electron-hole pairs (~ eV)
5. **Fundamental absorption** by excitation of electrons from the VB to the CB band (~ eV)

$$\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m_e}}$$

$$\alpha_{abs}(\omega) = \frac{\sqrt{\varepsilon_0}\omega_p^2}{c\omega^2\tau}$$



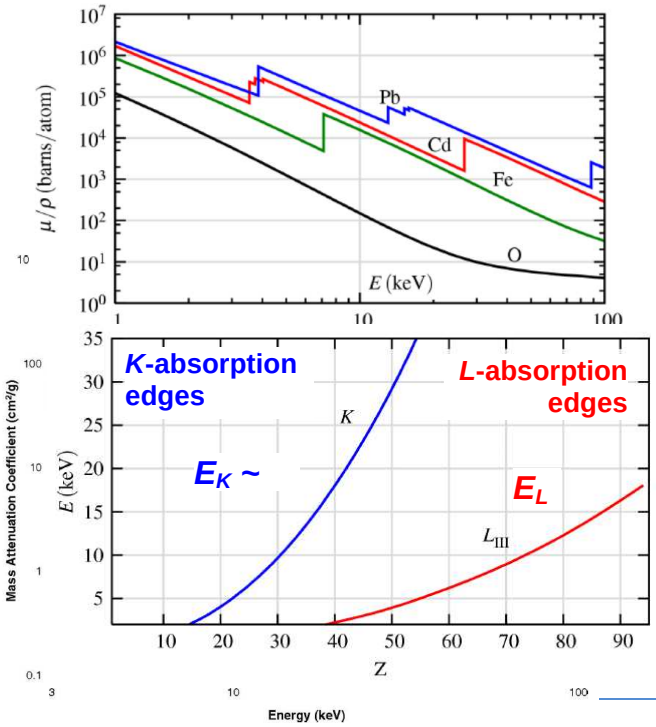


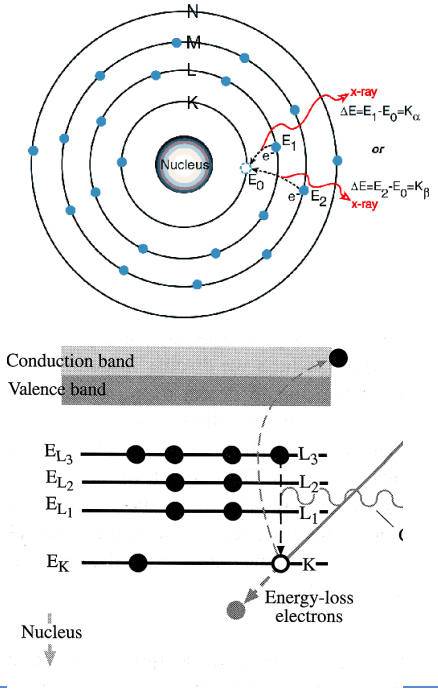
Example: X-ray absorption spectrum

X-ray absorption is due to excitation of strongly bound core electron into unoccupied states.

Thus, the x-ray absorption spectrum is characterized by steps, i.e., *absorption edges* at which the x-ray energy $h\nu > E_{B,core}$ becomes larger than the binding energy of a particular core electron.

The binding energy of core electrons mainly depends on the atomic Z number of the atom.
Thus, the position of the absorption edges *is element specific*.





2.4.2.2 Excitation by Energetic Particles

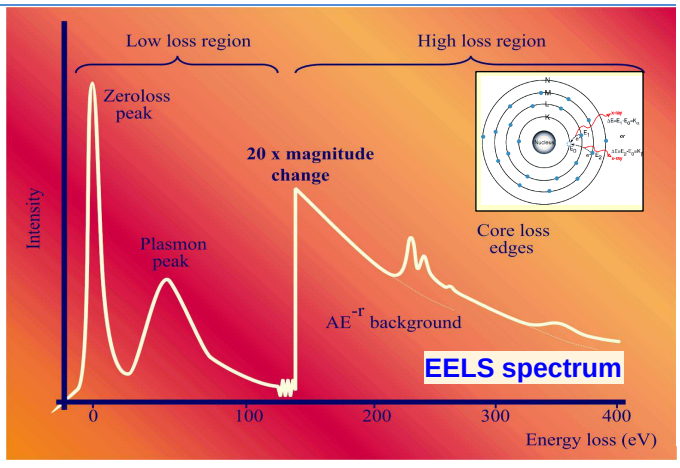
Particles can transfer ***any fraction*** of their kinetic energy in each single excitation event,

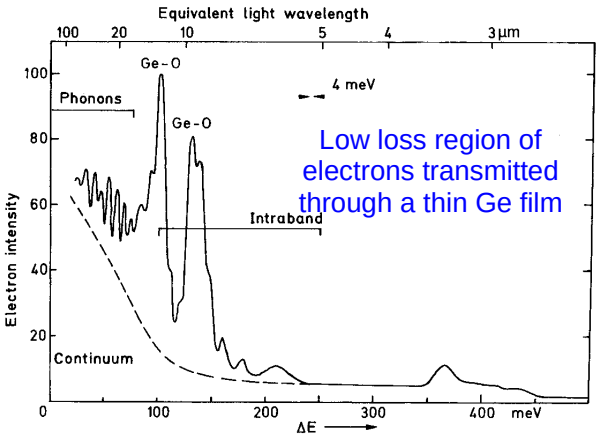
i.e., $E_{exc} < E_{probe}$, after which the particle *continues* its travel however with a reduced energy.

Thus, each particle can induce many consecutive excitation events until the particle energy is completely consumed and it comes to a rest.

The probability for a particular excitation process is defined by the excitation cross section that depends on the particle energy that continuously changes while the particle travels through the sample. Thus, the excitation probability changes continuously along the travel path, which leads to a nonuniform sample excitation.

Example: Electron energy loss spectrum





Low loss region of electrons transmitted through a thin Ge film

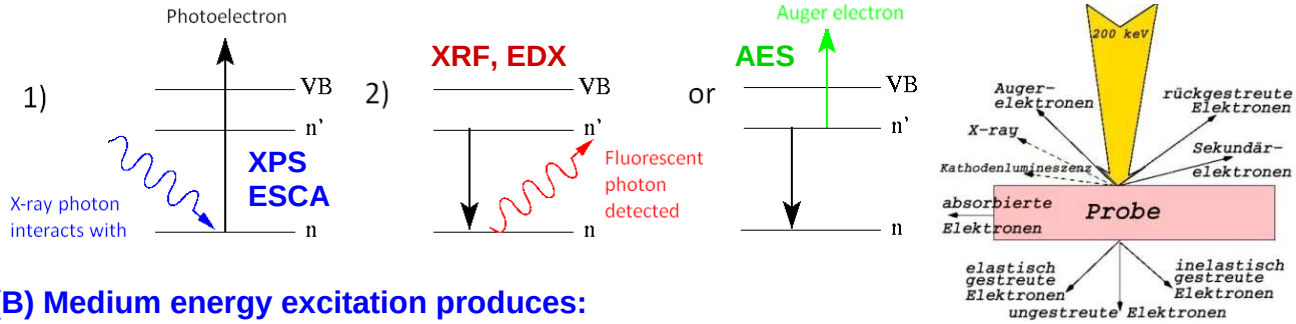
Fig. 5.7. Energy-loss spectrum of an evaporated Ge film due to phonc

2.4.4 Generation of Secondary Signals

Sample excitation eventually leads to generation of various **secondary signals:**

(A) Core-shell excitations generate:

- ⇨ ***Characteristic Photo- or Auger-electrons*** (= AES, XPS) by energy transfer
- ⇨ ***Characteristic X-ray fluorescence*** (= EDX, XRF) by recombination of core shell excitations



(B) Medium energy excitation produces:

- ⇨ ***Secondary electrons*** knocked out be electrons (SEM)
- ⇨ ***Photoelectrons*** excited from valence band (UPS)

(C) Low energy interband and intraband excitation:

- ⇨ ***Cathodoluminescence*** induced by electron irradiation
- ⇨ ***Photoluminescence, fluorescence*** due to photons

(D) Heavy mass particle irradiation leads to:

- ⇨ emission of ***Ions & atoms*** by sputtering and atom removal

❖ Secondary signals carry ***very*** **useful information** on the local sample properties !

2.4.4 Type Information Obtained

1-50 meV	❖ Excitation of **phonons** (lattice-vibrations, heat),	⇨ **FTIR, Raman, IR spectroscopy:** Bond strength and bond configurations
10 - 200 meV	❖ Intra- or intersubband excitations	
0.2-8eV	❖ Interband excitation, generation of **electron-hole pairs,** luminescence emission	⇨ **Optical spectroscopy, luminescence, photoelectron spectroscopy:** Conduction and valence band structure Quantization effects in nanostructures Optical constants and properties
ΔE_s = 1-10eV	❖ Excitation of **plasmons** (collective electron vibrations)	
1-50eV	❖ Generation of **secondary electrons** by ionization of atoms,	⇨ **Photoelectron spectroscopy (UPS)** Electronic band structure Structure and Morphology
>50eV	❖ Atom removal by sputtering,	⇨ **Secondary ion mass spectroscopy** Composition, impurities and dopands
1-10keV	❖ **Inner core-shell ionization** of sample atoms: $\Delta E = f(Z_{atom})$	
>10keV	❖ **Bremsstrahlung**, *i.e.,* emission of continuum x-rays,	⇨ **X-ray fluorescence, Photoelectrons spectroscopy (XPS, ESCA), Rutherford Scattering** Chemical composition and bonding
>100eV	❖ Momentum transfer to nuclei	

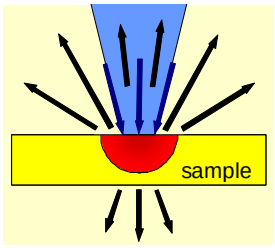
Important: To excite a certain process, the probe energy has to exceed the excitation energy. Thus, **only processes with $\Delta E_s < E_{probe}$ can be excited !**

VIS/IR Photons: $\Delta E << 4$ eV, **X-rays**: $\Delta E \sim$ keV, **Electrons/Ions**: $\Delta E \sim 10 - 100.000$ eV .

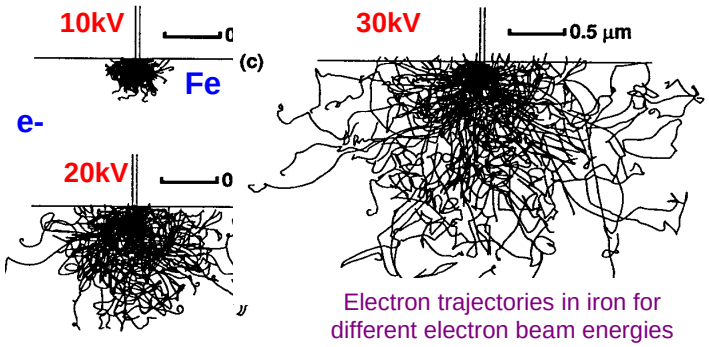
2.4.5 Penetration Depth and Interaction Volume

The **interaction volume** (= size of excited volume in the sample) is **often much larger** than the actual probe size (i.e. diameter). This is because the excitation:

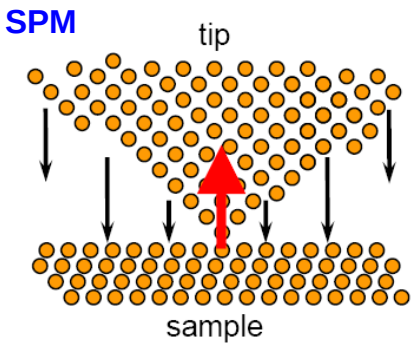
1. Extends vertically into the sample, which is described by the penetration depth λ.
   For photons, λ = 1/α can be very large or small for transparent/opaque media,
   For particles, the penetration depth strongly increase with their energy because it takes much longer until the particle has lost its hole kinetic energy.
2. Due to lateral scattering, the excitation volume also spreads in the lateral direction. This applies particularly for particle beams (see below).
3. The **excitation can also *diffuse* laterally** within the sample before a secondary signal is emitted. (Example: Diffusion of electron-hole pairs and of excitons in PL)



⇨ Overall, the **actual size** of the interaction volume strongly depends on beam parameters, sample composition, interaction mechanism, etc. ...



Electron trajectories in iron for different electron beam energies



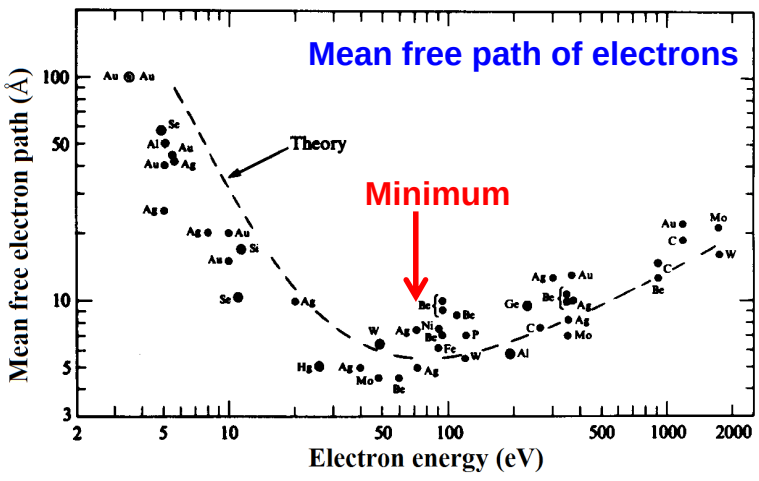
Effect on resolution: Evidently, the size of the sample volume that contributes to the detected signal can much exceed the probe size and thus, the spatial resolution is reduced.

This means that both the probe size and interaction volume must be minimized to achieve the highest resolution. The **theoretical resolution limit** is however, ultimate given by the probe size.

For charged particles, the probe - sample interaction is very strong due to the Coulomb interaction.

As a result, the ***mean free path*** of charged particles between consecutive scattering events is rather small and can be down to less than 1 nm (see figure below). For low particle energies the penetration and escape depth is thus very small and the interaction practically confined to the sample surface.

⇨ For this reason, these techniques can be *very surface sensitive* !



⇨ At low energies, there are only few scattering channels » the mean free path increases. At high energies, the scattering cross sections decrease and the path length increases due to the increasing particle velocity.

2.5 Detection Schemes and Recording Modes

The ***type of information*** obtained from the sample also depends on ***how*** the response signal from the sample is actually recorded and detected: Transmission, absorption, reflection, scattering/diffraction, secondary signals, …..

Recording modes & information obtained:

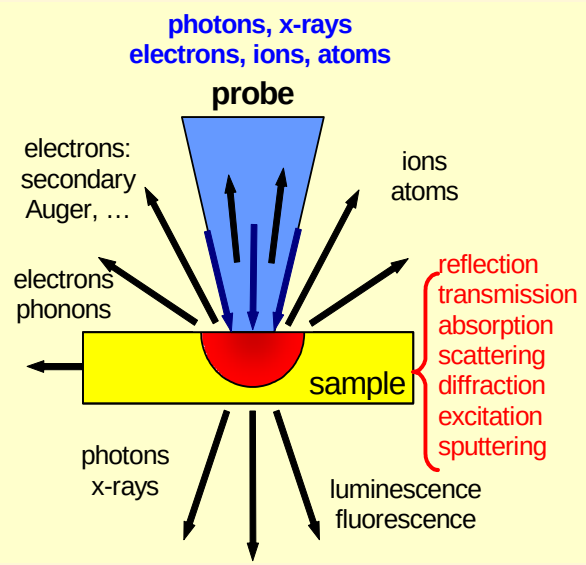
Spatial distribution = *"microscopy"* **NC-I**
structure & morphology

Energy Spectrum = *"spectroscopy"* **NC-II**
fundamental excitations
electronic structure
chemical composition **FK-Spectr**

Angular dependence = *"diffraction"* (spectrum in k-space)
lattice and defect structure **XRD**

Time dependence Carrier/lattice dynamics, dynamics of excitation & relaxation processes

Mass spectroscopy of emitted ions/atoms
Chemical analysis



⇨ The ***combination*** of **probe type, interaction type, recorded response signal** and **detection scheme** defines the name and type of characterization method ……

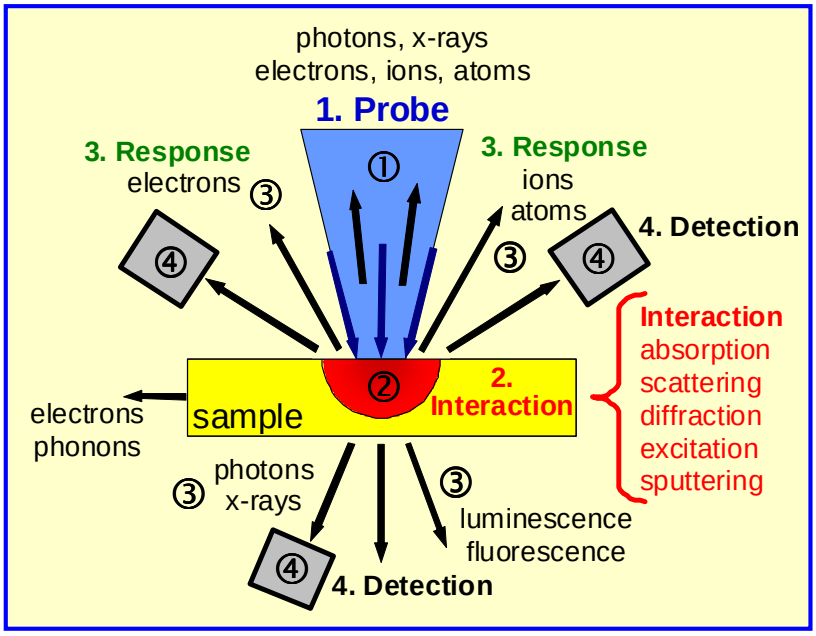
2.6 Characterization Methods

Probe - in	Interaction	Probe - out	⇨ Measurement Method
Photons (optical) ~ meV.. eV	**reflection**	**photons**	Energy spectrum = Optical spectroscopy, ellipsometry, FTIR
	transmission	**photons**	Spatial distribution = Microscopy, SNOM
	absorption	**photons**	Excitation spectrum = Photoluminescence, Raman spec.
	excitation	**electrons**	Energy spectrum = Photocurrent spectroscopy
		atoms & ions	Mass spectroscopy = Laser ablation mass spectroscopy
EUV and X-rays ~ 10 … keV	**elastic**	**x-rays**	Angular distribution = x-ray diffraction & scattering (XRD),
	inelastic	**x-rays**	Energy spectrum = x-ray fluorescence (XRF)
	excitation	**electrons**	Energy Spectrum = Photoelectron spectroscopy (XPS)
Electrons ~ eV .. keV	**elastic**	**electrons**	Angular distribution = electron diffraction (LEED, RHEED)
	scattering	**electrons**	Spatial distribution = electron microscopy (TEM, SEM, LEEM)
		electrons	Energy spectrum = electron loss spectroscopy (EELS)
	inelastic	**photons**	Energy spectrum & spatial distr. = cathodoluminescence (CL)
	scattering	**x-rays**	Energy spectrum & spatial distr = microanalysis (EDX,WDX)
	excitation	**electrons**	Energy spectrum = Auger electron spectroscopy (AES)
		sample current	Spatial distribution = electron beam induced current (EBIC)
Ions, atoms ~ eV .. keV	**elastic**	**ions, atoms**	Angular distribution = ion & atom diffraction and scattering
	inelastic	**ions, atoms**	Energy spectrum = ion scattering spectroscopy (RBS, LEIS)
	sputtering	**ions & atoms**	Mass spectrum = secondary mass spectroscopy (SIMS)
	excitation	**ions & electrons**	Spatial = field electron/ion microscopy (FIM/FEM), Atom Probe
Probe tips ~ meV.. eV	**tunnelling**	**electrons**	= scanning tunnelling microscopy (STM)
	force	**forces**	= atomic force microscopy (AFM) and other SPM methods

2.7 Summary

Many different characterization methods exist, depending on

① *Which* kind of probe is used to excite the sample, ② *What* kind of interaction occurs,
③ *Which* secondary response signal is detected, and ④ *How* the secondary signal is measured.



1. Probes
photons (IR, visible, UV) x-rays, electrons, ions, electric & magnetic fields, proximal probe tips

2. Probe-Sample Interactions
elastic & inelastic, absorption, scattering, diffraction, excitation secondary particles,

3. Emitted Response
photons (IR, VIS, UV) x-rays, electrons, ions, atoms, current, forces,

4. Detection Schemes
spatial and angular distribution, spectroscopy, time dependence, mass spectroscopy.

⇨ The combination of these determines ***what kind of sample information*** is obtained, such as composition, morphology, lattice structure, electronic band structure, quantization effects ...

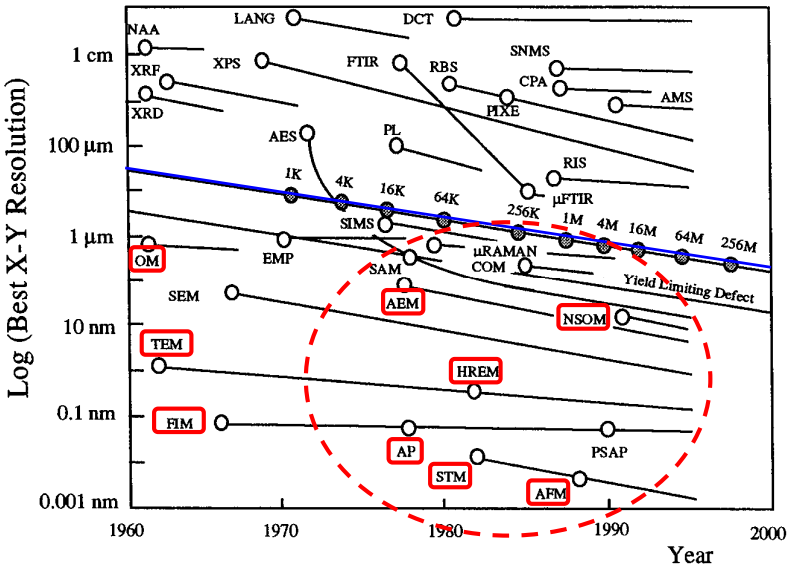
Probes

- One can distinguish between ***beam probes*** that consist either of photons or particles, as well as ***proximal probes*** that closely interact with the sample in a near-field range.
- Beam probes differ by ***energy***, ***wavelength***, ***charge*** and ***mass***, which strongly influences the probe-sample interactions as well as the spatial resolution of the characterization method.
- Due to the much smaller ***de Broglie wavelength*** of particle beams compared to photon beams, ***particle beams*** generally provide a much higher resolution than photon beams.

Probes - Sample Interactions

- **Elastic interactions** mainly lead to an angular scattering of the probes and yield mostly structural information of the sample.
- **Inelastic interactions** range from high-energy core shell excitations to excitations of photo-electrons, electron-hole pairs, phonons, excitons, plasmons. Sample excitation subsequently leads to ***secondary processes*** such as photo- and Auger electrons, characteristic X-ray emissions, cathodoluminescence and photoluminescence, secondary ion emission, etc. .
- **Core-shell transitions** are completely element specific and are therefore used for *chemical analysis*. In addition, they exhibit a distinct *fine structure* that yields information on the local chemical bonding and coordination of the atoms within the sample.
- Information on the **energy level structure** is obtained from optical spectroscopy, tunneling or photoelectron spectroscopy, as well as luminescence measurements.
- Elastic and inelastic scattering determine the **penetration depth** as well as the escape depth of the secondary signal. This determines the *surface sensitivity* and size of the *interaction volume*.

Lateral Resolution



AES	Auger electron spectroscopy (C)
AM	Acoustic microscopy (S)
AMS	Accelerator mass spectrometry
AP	Atom probe (M,C,S)
COM	Confocal optical microscopy (M, OES)
CPA	Charged particle activation analysis
DCT	Double crystal X-ray topography (S,C)
EMP	Electron microprobe (C)
FIM	Field ion microscope (M,S)
FTIR	Fourier transform infrared (C, OES)
HREM	High resolution electron microscopy (M,S,D)
LANG	Scanning Lang X-ray topography (S,D)
NAA	Neutron activation analysis (C)
NSOM	Near field scanning optical microscopy (M, OES)
PL	Photoluminescence spectroscopy (OES,D)
PSAP	Position sensitive atom probe (M,C,S)
RIS	Resonance ionization spectroscopy
RBS	Rutherford backscattering spectrometry (C,D)
SAM	Scanning Auger microprobe (C)
SEM	Scanning electron microscopy (M,S,C)
SIMS	Secondary ion mass spectrometry (C,doping)
SNMS	Sputtered neutral mass spectrometry (C,doping)
STM	Scanning tunneling microscopy (M, Spec)
TEM	Transmission electron microscopy (M,S,C)
XPS	X-ray photoelectron spectroscopy (C)
XRD	X-ray diffraction (S,C)
XRF	X-ray fluorescence (C)
µFTIR	Microspot FTIR (OES,C,S,D)
µRAMAN	Raman microprobe (C,S,D,OES)

Microscopy (M), Chemical Analysis & Bonds (C), Defects (D), Structural Properties (S), Optical & Electronic Structure (OES)

⇨ **High spatial resolution with**

» Electrons, Ions, SPM !

(a) small wavelengths,
(b) small probe size and
(c) small interaction volume

Additional Aspect

❖ Many characterization methods can be also used for nanofabrication & nanomanipulation:

Examples: Electron beam lithography, scanning probe manipulation, focused ion beam etching.

Example: Atom-manipulation using scanning tunnelling microscopy