Università di Pisa
LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem - part 1

Introduction, generalities, diffraction in optics, electron microscopy (as a benchmark)

OUR PROVISIONAL PROGRAMME

Spectroscopy of nanomaterials (12 Cfu)

- Cfu: 12
- Obiettivi formativi: Emission, scattering, absorption properties of confined nano systems; experimental techniques, sources, detectors, spectrometers; Fourier and Raman spectroscopy; magnetic resonance spectroscopy; plasmonics from surface and localized resonances; survey of nano photonics devices; linear and nonlinear optical spectroscopies; optical microscopy beyond the diffraction limit; atomic and electrostatic force microscopy and spectroscopy, scanning tunnelling microscopy.

This will be mostly a container where we will put a variety of issues, matters, topics
(with special emphasis on their "physics" content)

Today's menu:
- Starters (hopefully, appetizers)
- Main course of diffraction and problems
- Dessert (extra): a few words on electron microscopy

WHAT TO DO, AND WHY

Spectroscopy:
an extremely powerful tool to investigate optical properties aiming at several goals, e.g.:

- analytical purposes;

- structural information;

- occurrence of chemical/physical processes;

- functional assessment in optics, optoelectronics, photonics;

- …

Now (our next step):

move towards spectroscopy of <u>nanosized objects</u>

that is

realize spectroscopy with "large enough" <u>spatial resolution</u>

A short list of motivations:
- to get a closest insight into optical properties using spatially-resolved information (e.g., analysis of homogeneity, localization of effects,…);
- to discover effects which can be appreciated only at the small scale (e.g., for reasons of sensitivity, or because their occurrence is due to the small size);
- to access nanoscale investigations (not necessarily restricted to just optical spectroscopy)

(A FEW) WARNINGS

1: a very wide range of topics will be covered
- → *many physical issues are to be considered*
- → *fundamental aspects and technical/experimental details will be frequently mixed*
- → *an often limited variety of examples, arbitrarily chosen, will be presented*

2: the need to "identify" nano-objects will often prevail on their analytical investigation
- → *spectroscopy and microscopy (or **nanoscopy**) will be discussed at once*
- → *reference to optics will be occasionally lost, when needed*
- → *non-optical methods will be mentioned*

3: nanoscopy approaches and tools can be rather specific and innovative
- → *some methods can be used outside the range of spectroscopy*
- → *nano-optics and nano-photonics issues will be eventually presented*

Let's start with defining the relevant size scales and the main problems

SIZE SCALES: WHAT NANO MEANS
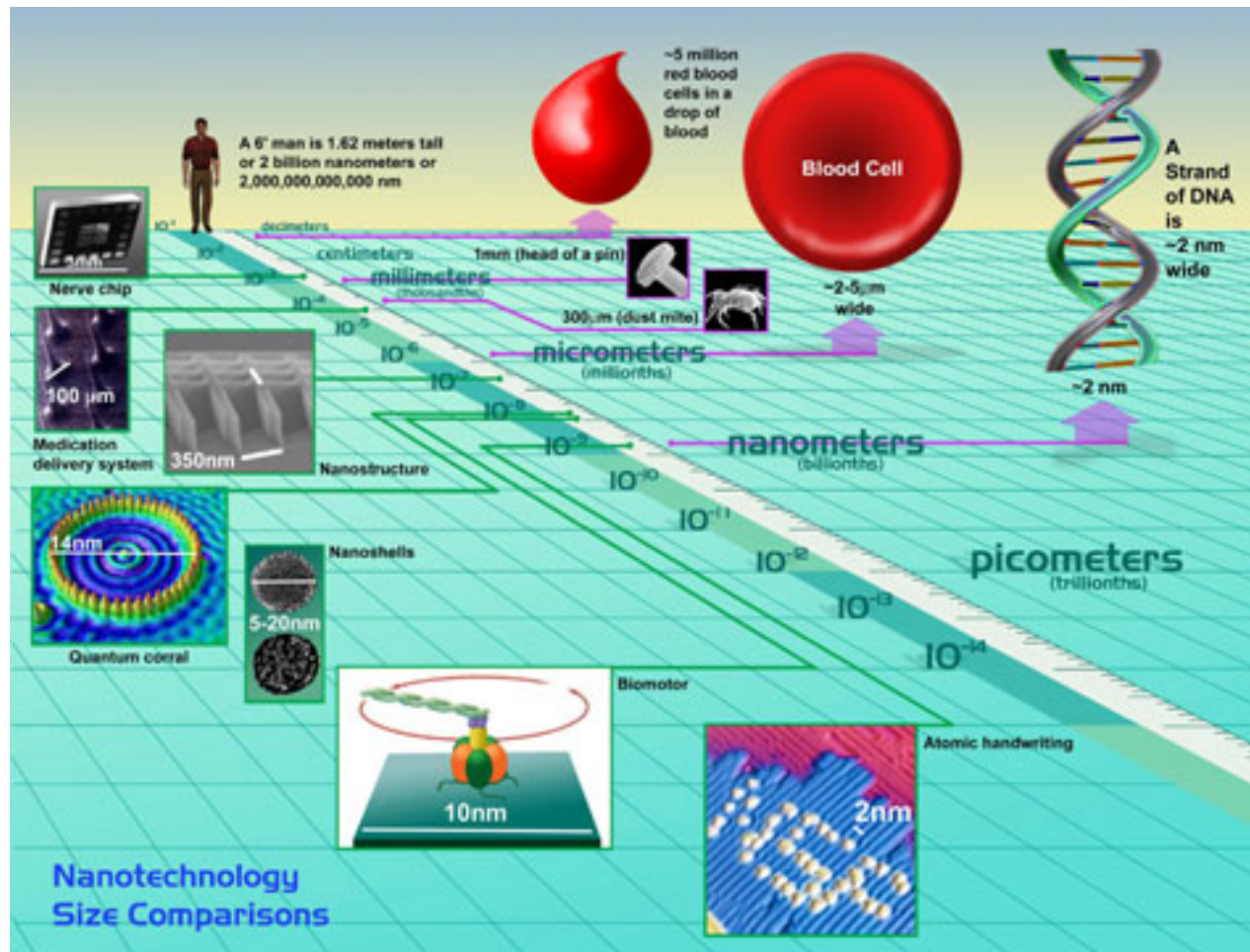
Obviously:

nanosized or nanostructured objects exist in nature (naturally occurring)

but

nanotechnologies have been deployed to produce nanosized, or nanostructured objects

TOP-DOWN ELECTRONIC TECHNOLOGIES (EXAMPLE)

Electronic devices:
they are typically (and *traditionally*) made of "small" structures built through a **top-down** approach
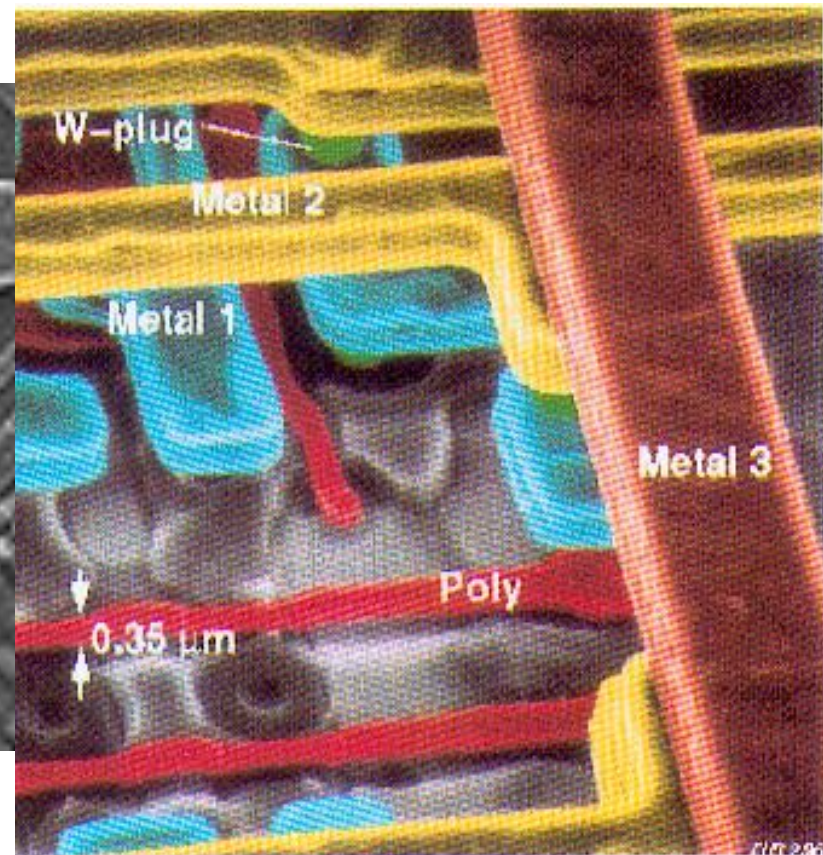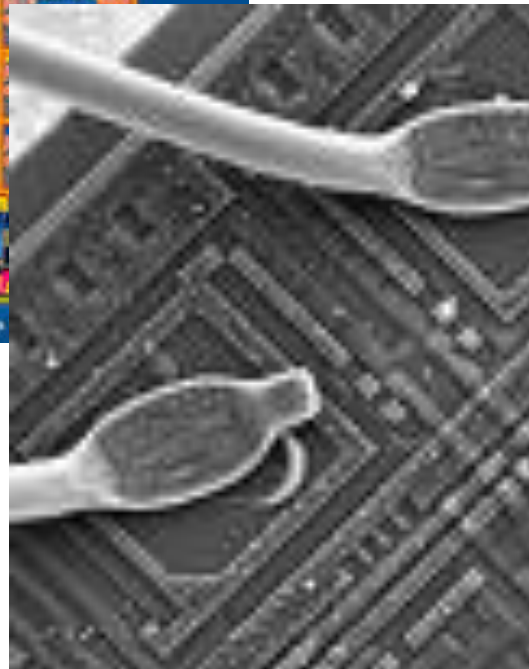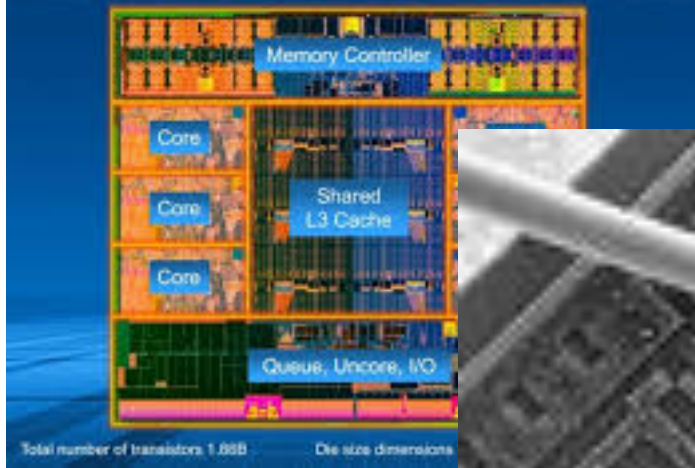
1. Thin films are deposited
2. A pattern is transferred to the multilayered structure
3. The pattern is "fabricated" (material removal or growth) as required

Device components (resistors, capacitors, transistors, …) are hence defined in an *integrated* structure
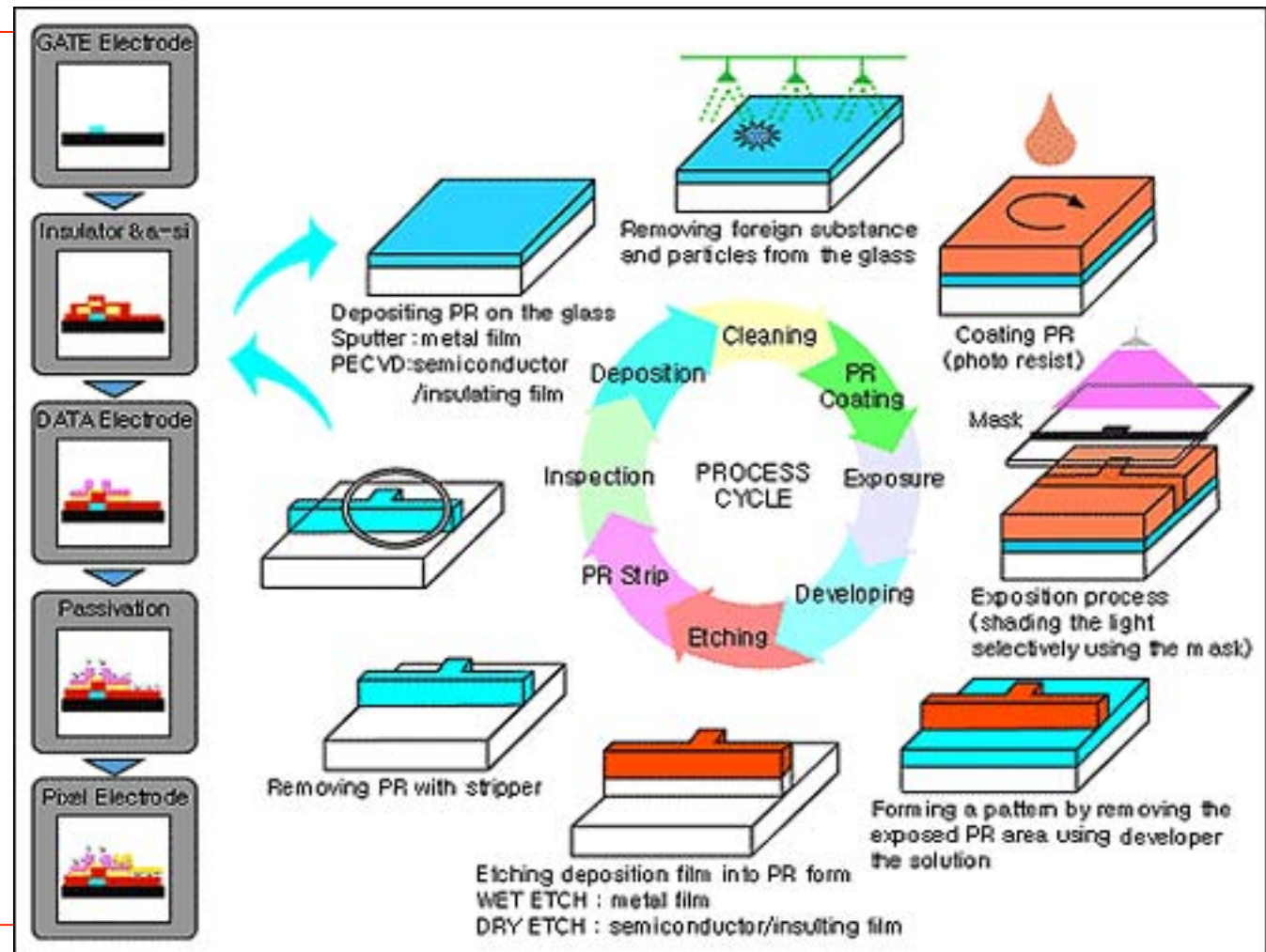
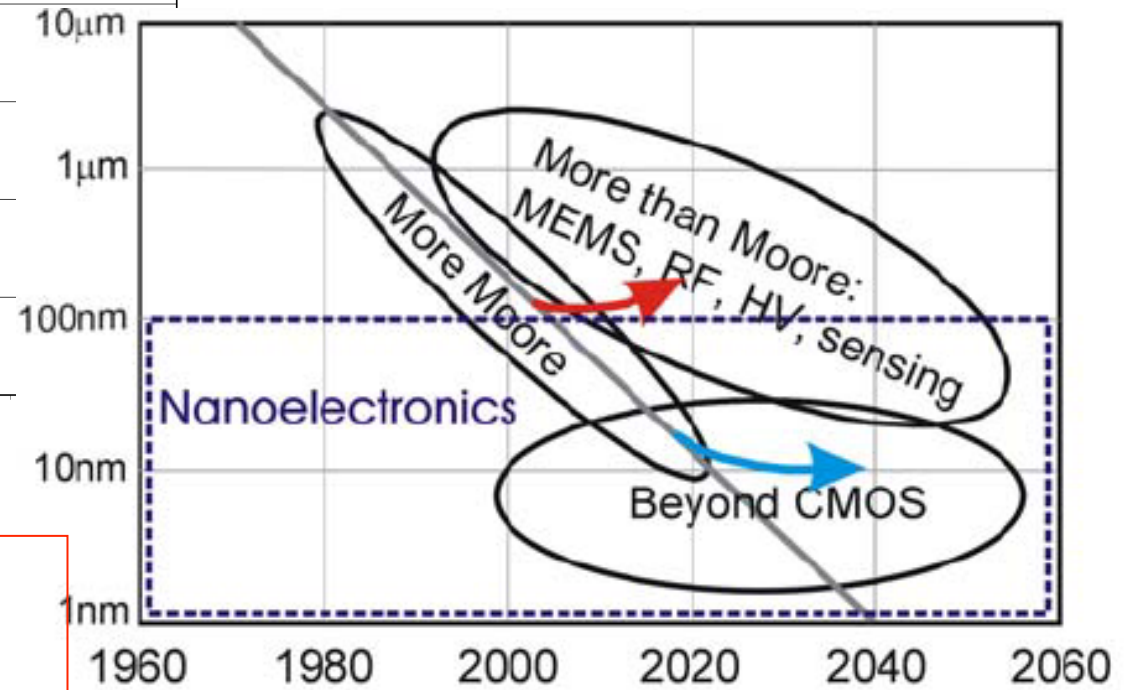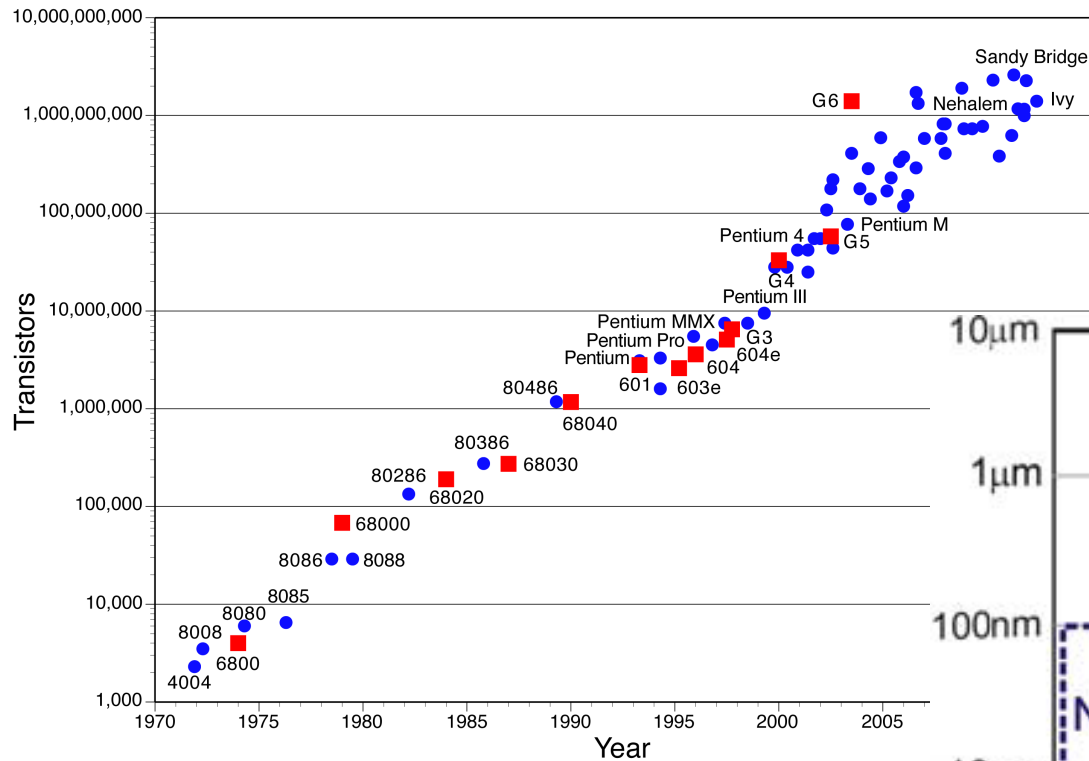# NANOELECTRONICS AS THE MAIN DRIVING FORCE

Feature size
(typ., fwhm of the smaller
device features)

or

Pitch
(typ., the average min distance
between distinct device parts)

TOWARDS NANO IN (CONVENTIONAL) ELECTRONICS

"Moore's law":

the number of integrated individual components grows up by a factor 3-4 every 3 years
(nobody knows whether it will hold valid, or not, in the next decade(s)

FEYNMAN'S VISION (LATE 1959)

There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics

by Richard P. Feynman

This transcript of the classic talk that Richard Feynman gave on December 29th 1959 at the annual meeting of the American Physical Society at the California Institute of Technology (Caltech) was first published in the February 1960 issue of Caltech's *Engineering and Science*, which owns the copyright. It has been made available on the web at http://www.zyvex.com/nanotech/feynman.html with their kind permission.

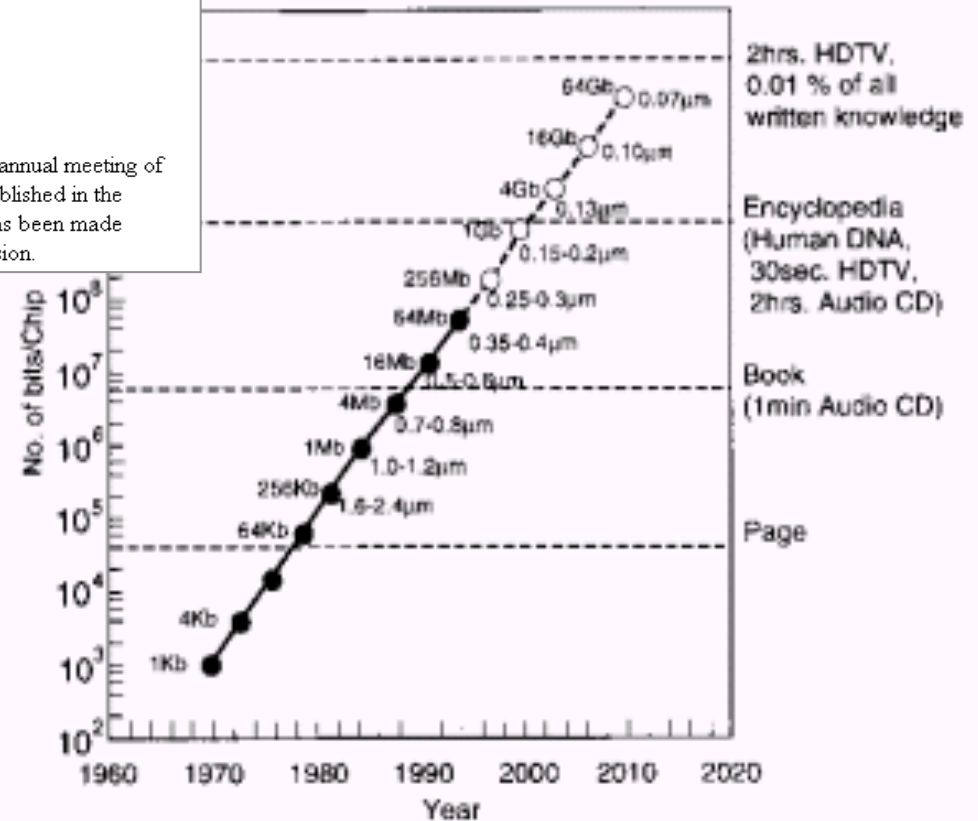*How do we write small?*

Information on a small scale

Miniaturizing the computer

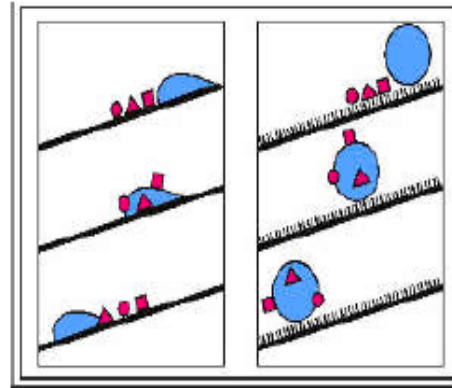*Better electron microscopes*

Atoms in a small world

Rearranging the atoms
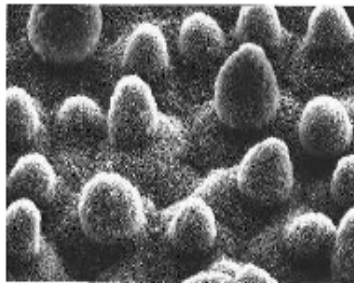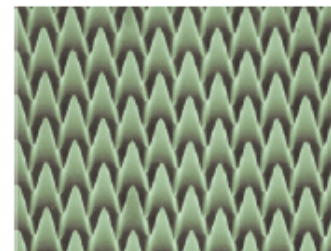
NANO IN THE NATURAL WORLD I

10 mm

W. Barthlott, Univ. of Hamburg

On a smooth surface the contaminating particles are only moved by the water droplet (left). In contrast to that, on a rough surface they stick to the droplet rolling off the leaf thus being washed off (right).

Epicuticular wax

REM recording of a holographically produced self-cleaning surface.
© Fraunhofer ISE

(Source: Metin Sitti, CMU)

A functional property (hydrofobicity) depends on the structural surface arrangement at the nanoscale

NANO IN THE NATURAL WORLD II

beetle

fly

spider
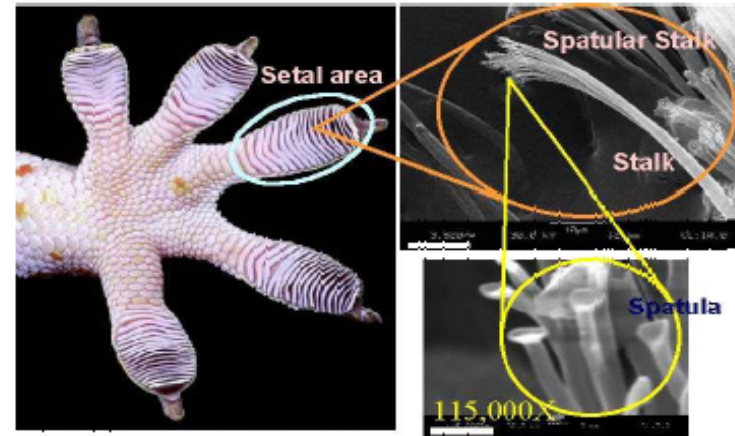
gecko

2 µm

2 µm

2 µm

2 µm

Figure 1: *Tokay* gecko foot-hair images: gecko foot bottom view (left image); zooming into one of the stalks (right upper image, bar indicates 10 µm), and zooming into spatulae and spatular stalks at the end of a stalk under SEM (right lower image, bar indicates 300 nm) (courtesy of Kellar Autumn).
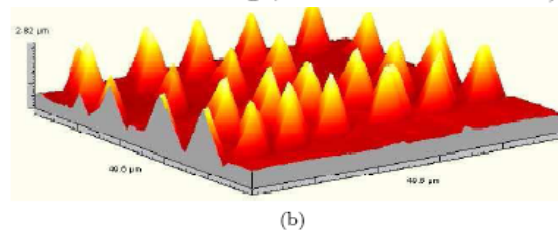
Setal area

Spatular Stalk

Stalk

Spatula

115,000

Figure 3: 3-D AFM tapping mode image of (a) the AFM probe based indented flat wax surface, (b) molded and peeled off silicone rubber nano-hairs.

(b)

Synthetic Gecko Foot-Hair Micro/Nano-Structures for Future Wall-Climbing Robots

Metin Sitti[1] and Ronald S. Fearing[2]
[1] Dept. of Mechanical Engineering and Robotics Institute, Carnegie Mellon University, USA
[2] Dept. of EECS, University of California at Berkeley, USA

A functional/structural property (adhesion) depends on surface nanostructures (their artificial fabrication is under way)

NANO IN THE NATURAL WORLD III

- Heat shock protein (HSP 60) in organisms living at high temperatures ("extremophiles") is of interest in astrobiology

- HSP 60 can be purified from cells as a double-ring structure consisting of 16-18 subunits. The double rings can be induced to self-assemble into nanotubes.
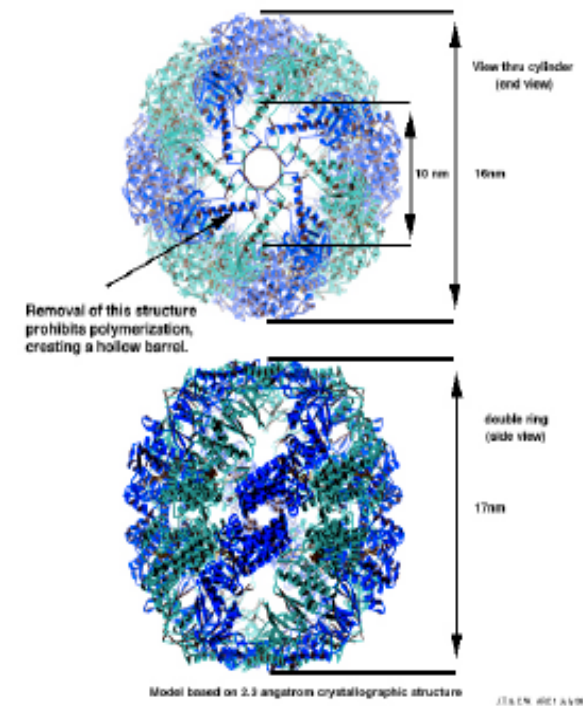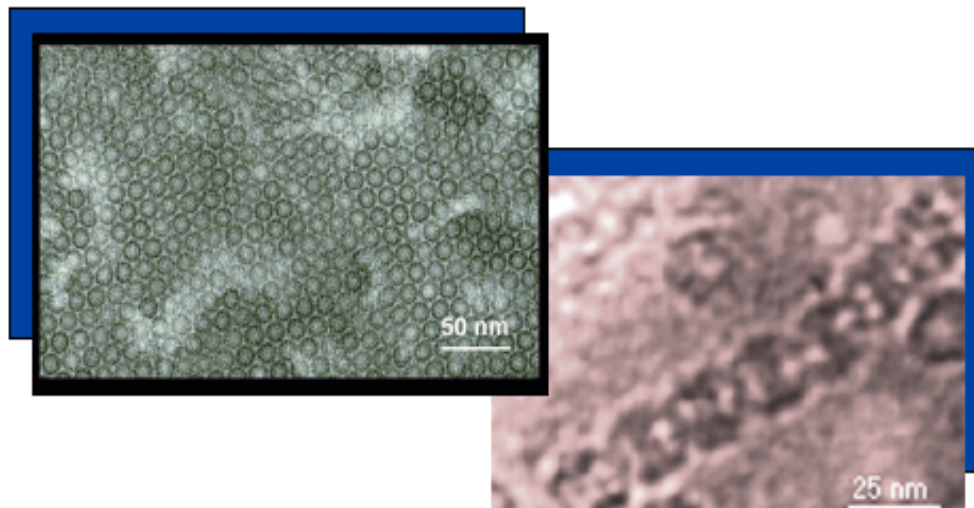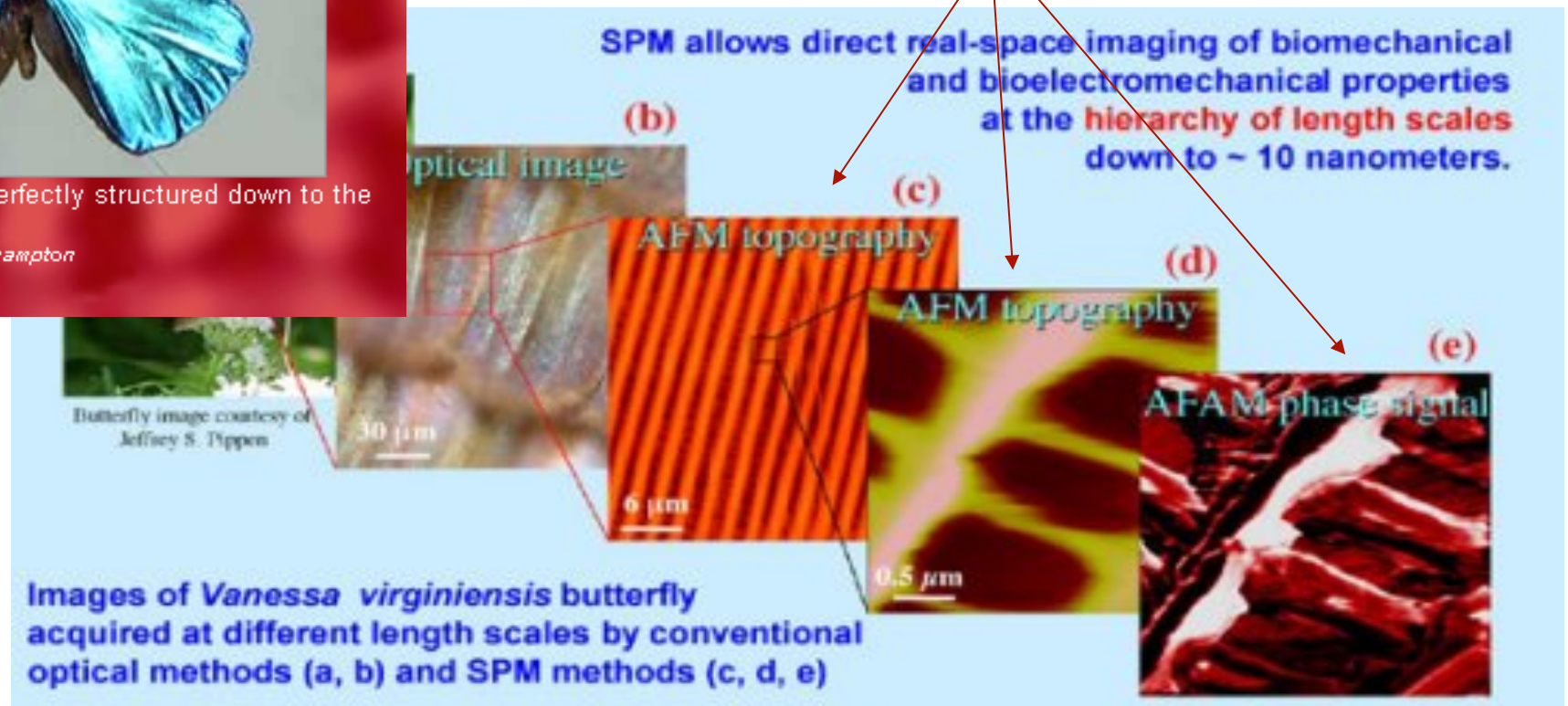

Thermo-mechanical properties are enhanced when specific geometries are attained (at the nanoscale)

NANO IN THE NATURAL WORLD IV

Butterfly wings are perfectly structured down to the nano-scale.
Image: University of Southampton

Observations made possible thanks to the availability of new techniques

SPM allows direct real-space imaging of biomechanical and bioelectromechanical properties at the **hierarchy of length scales** down to ~ 10 nanometers.

(b)
Optical image

(c)
AFM topography

(d)
AFM topography

(e)
AFAM phase signal

Butterfly image courtesy of Jeffrey S. Pippen

30 µm

6 µm

0.5 µm

Images of *Vanessa virginiensis* butterfly acquired at different length scales by conventional optical methods (a, b) and SPM methods (c, d, e)

Very diverse features, including optical properties, can be explained when considering the structure/morphology at the nanoscale

SPECIAL OPTICAL FEATURES OF NANOMATERIALS

Lycurgus Cup in Roman times

Dr. Juen-Kai Wang

The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

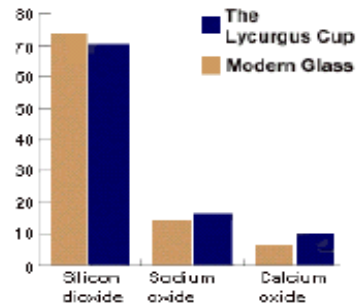Interpretation:
"nanostructured" glass
(i.e., containing gold and silver nanoparticles,
i.e., a "nanomaterial")

The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)
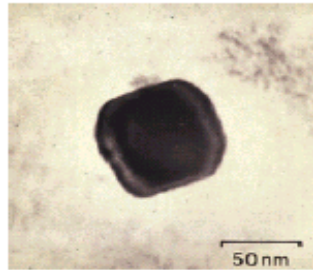F. E. Wagner et al., Nature **407**, 691 (2000).

SIZE-RELATED OPTICAL PROPERTIES

Mysterious red color in Lycurgus Cup

Dr. Juen-Kai Wang

X-ray analysis:
70% Ag + 30% Au

The same composition
as modern glass
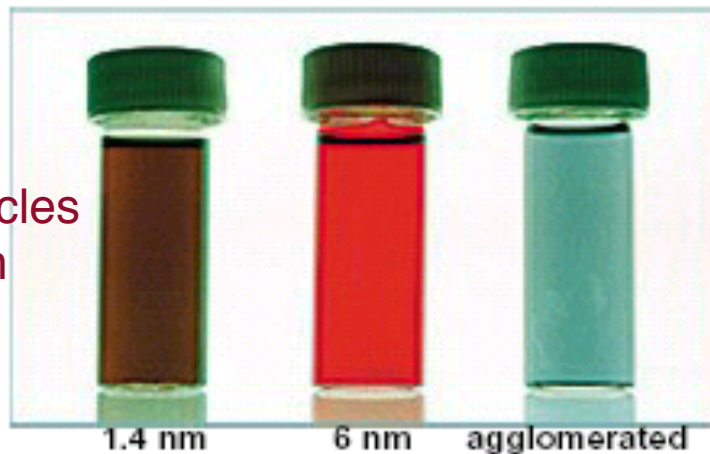
These Ag-Au nanoparticles (~300 ppm) scatter the light, rather in the same way that fine particles in the atmosphere cause a 'red sky at night' effect. They cause the color effects shown by the Cup.

The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)

/~nano/93041702.pdf

Au nanoparticles in solution

1.4 nm   6 nm   agglomerated

Gold Building Blocks

Atoms:
colorless, 1 Å

Gold clusters:
orange, nonmetallic, <1 nm

Gold nanoparticles:
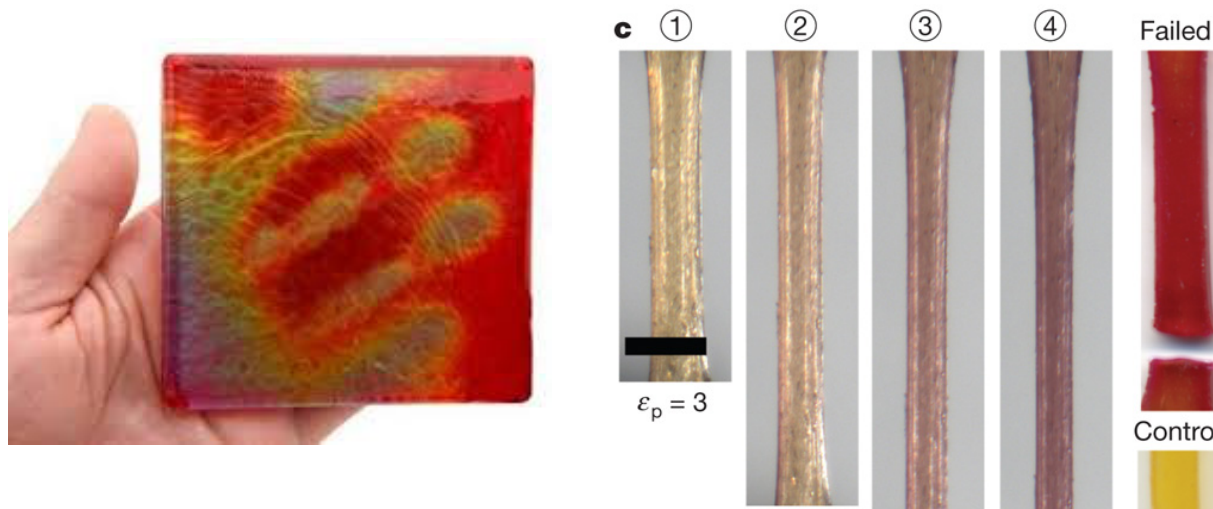3–30 nm, red, metallic, "transparent"

Gold particles:
30–500 nm metallic, turbid, crimson to blue
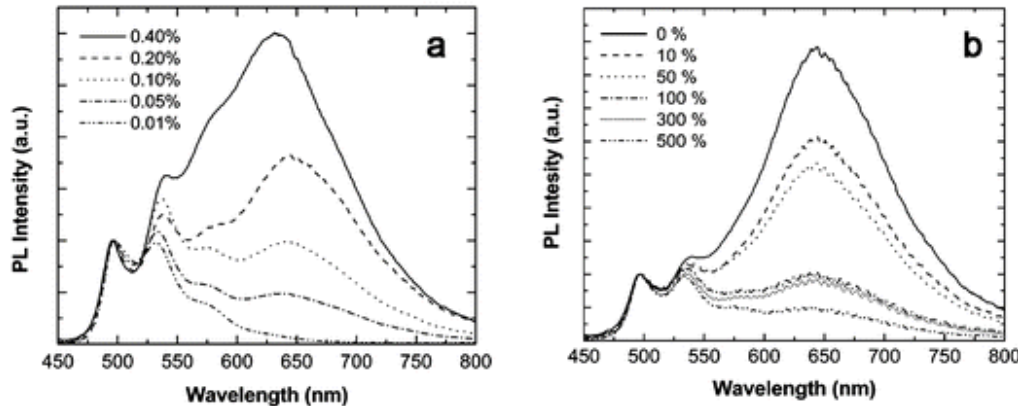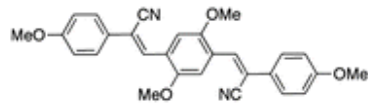
Bulk gold film

Figure 1. Gold building blocks, from the atomic to the mesoscopic, and their changing colors.
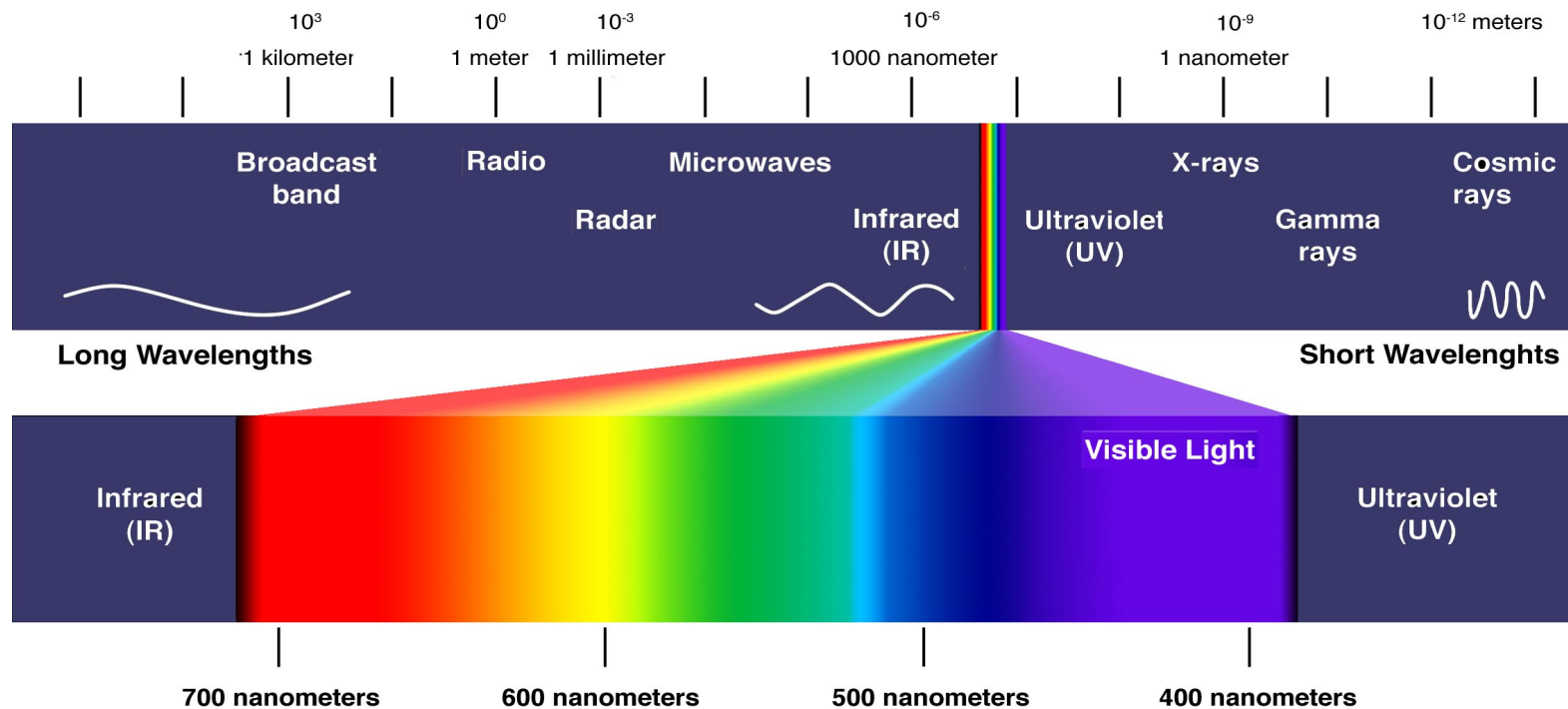
SIZE-RELATED OPTICAL FUNCTIONS

"Smart" functionalities of some polymer blends such as, thermochromism and mechanochromism, can be related to changes in the mutual distance of chromophore components at the nanoscale

In inherently nanosized materials optical properties (emission/fluorescence) turn to depend on distances at the nanoscale

OPTICS vs NANO

Optics entails e.m. radiation with photon energy in the few eV range (i.e., the typical energy scale of electron processes in the matter)

⟹ **the wavelength can be (much) larger than the typical nanomaterial size**

SIZE MATTERS

Suppose you want to couple the emission from an individual nanostructure with a single-mode optical fiber:

Fiber core: typ. dia in the few μm range

Cladding

Outside jacket

Core

An emitting nanostructure: typ. dia in the few tens of nm range

Typical lateral sizes are in the same ratio of a soccer ball and a playground

⟹ few chance to efficiently couple and extract the emission

⟹ no chance to get miniaturization and integration in a device
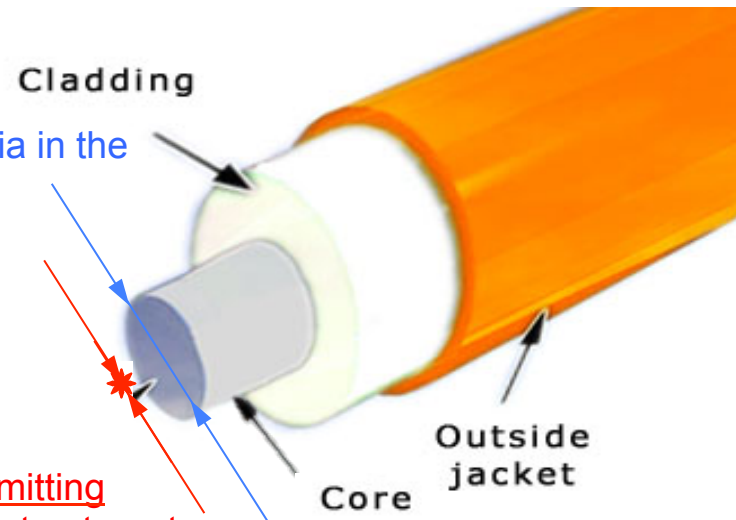
WAVE-LIKE NATURE OF E.M. RADIATION
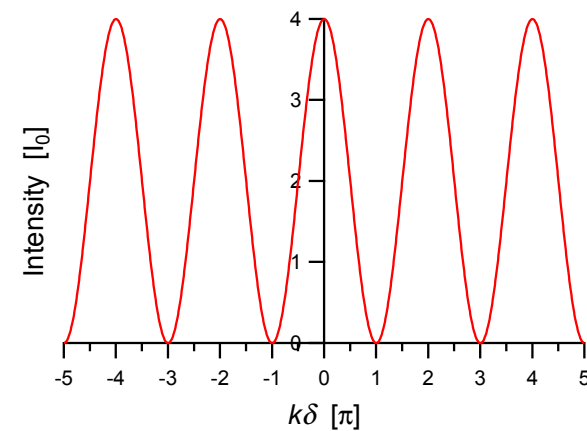
Interference

1, 2: two emitters of plane waves along *z*
(both monochromatic, at the same frequency)

detector

δ
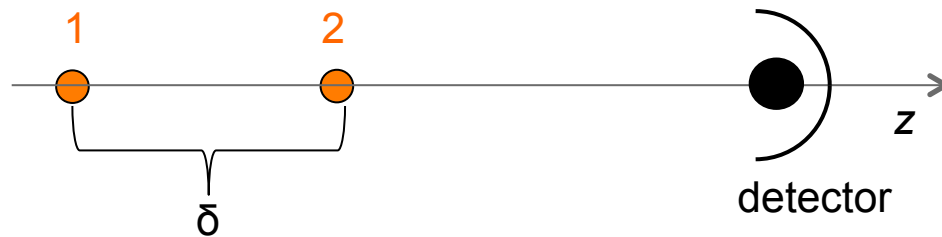
$$\vec{E}_1 = E_{01} \exp[i(kz - \omega t)]\hat{e}_1$$
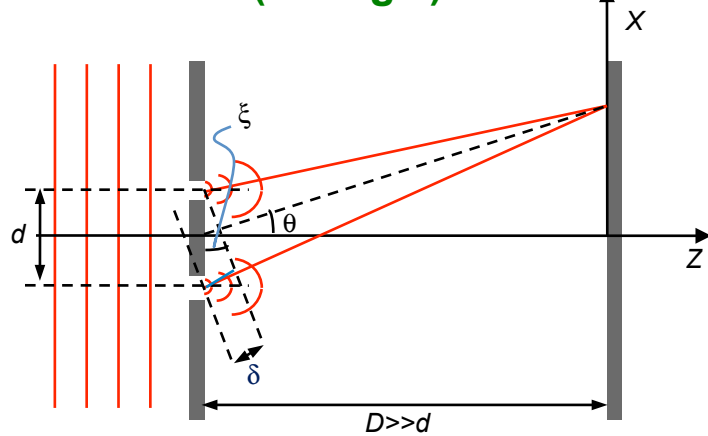$$\vec{E}_2 = E_{02} \exp[i(k(z + \delta) - \omega t)]\hat{e}_2$$

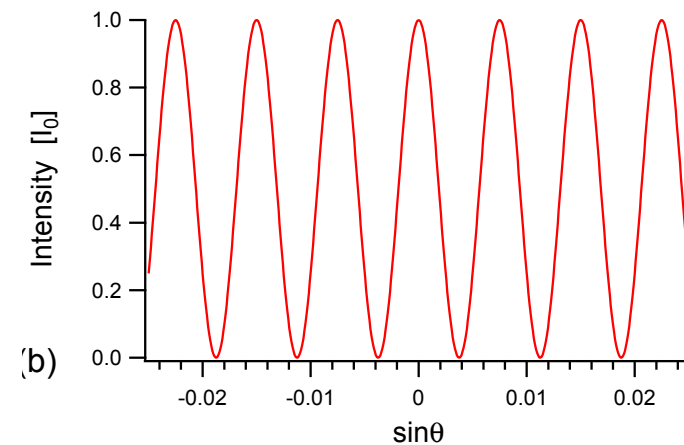$$I = 2I_0(1 + \cos(k\delta)) = 4I_0 \cos^2(k\delta/2)$$

INTERFERENCE/DIFFRACTION

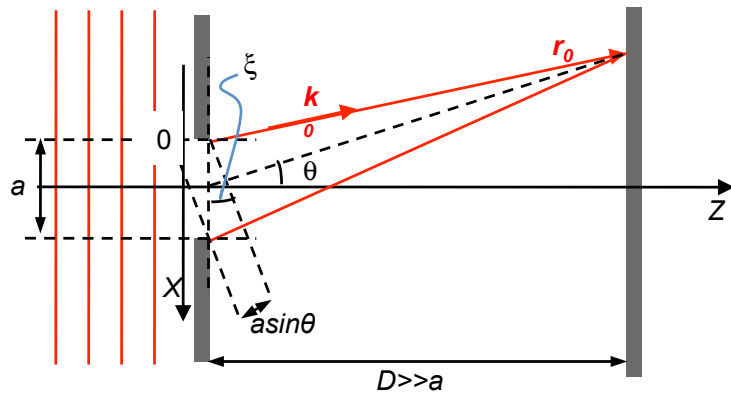**Double slit (Young's) interference**

Huygens (Fresnel) principle:
a "small" aperture behaves like a source of spherical waves

The so-produced wavelets can interfere each other leading to a firnge system of local maxima/ minima in the intensity

(b)

FRAUNHOFER'S DIFFRACTION I

A single "small" slit (aperture)

The aperture is divided into a virtually infinite number of sub-apertures and Young's interference concepts are applied to all produced wavelets

$$E = \int_0^a \frac{E_0}{a} \exp[i(\vec{k} \cdot \vec{r} - \omega t)]dx =$$

$$= E_0 \exp(-i\omega t) \exp(ikr_0) \int_0^a \frac{\exp[ik(r - r_0)]}{a} dx$$

$$\int_0^a \frac{\exp(ik(r - r_0))}{a} dx \equiv \int_0^{a\sin\theta} \frac{\exp(ik\zeta)}{a\sin\theta} d\zeta =$$

$$= \frac{\exp(ika\sin\theta) - 1}{ika\sin\theta} =$$

$$= \exp(ika\sin\theta/2) \times$$

$$\times \frac{\exp(ika\sin\theta/2) - \exp(-ika\sin\theta/2)}{ika\sin\theta}$$

$$I(\theta) \propto \left| \frac{\exp(ika\sin\theta/2) - \exp(-ika\sin\theta/2)}{2ka\sin\theta/2} \right|^2 =$$

$$= \frac{\sin^2(ka\sin\theta/2)}{(ka\sin\theta/2)^2} \ .$$

FRAUNHOFER'S DIFFRACTION II

Circular aperture (cylindrical symmetry)
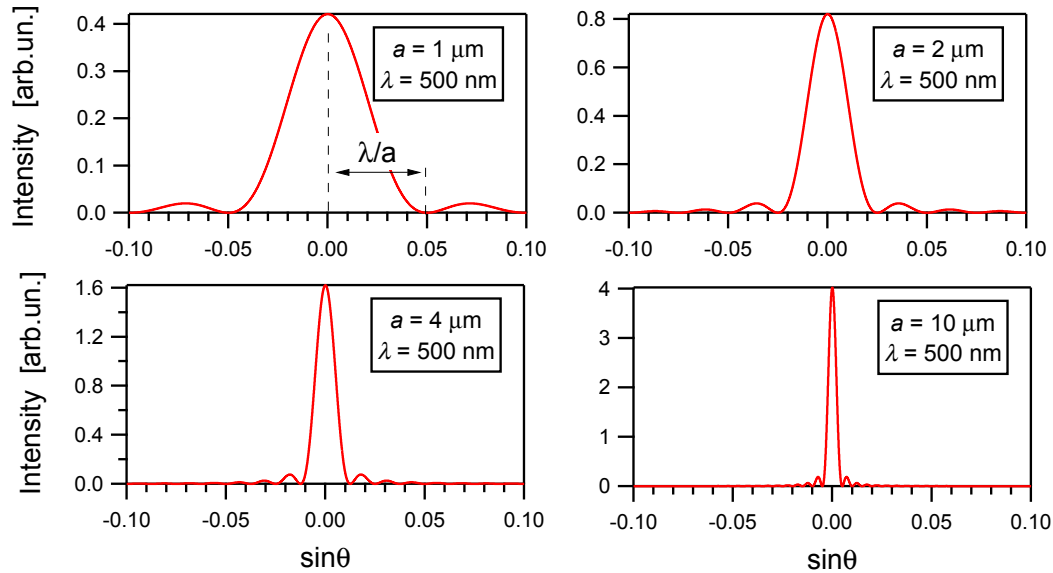
$$I(\theta) = I_0 \frac{J_1^2(\alpha)}{\alpha^2}$$

$$\alpha = \frac{a}{\lambda}\sin\theta ,$$
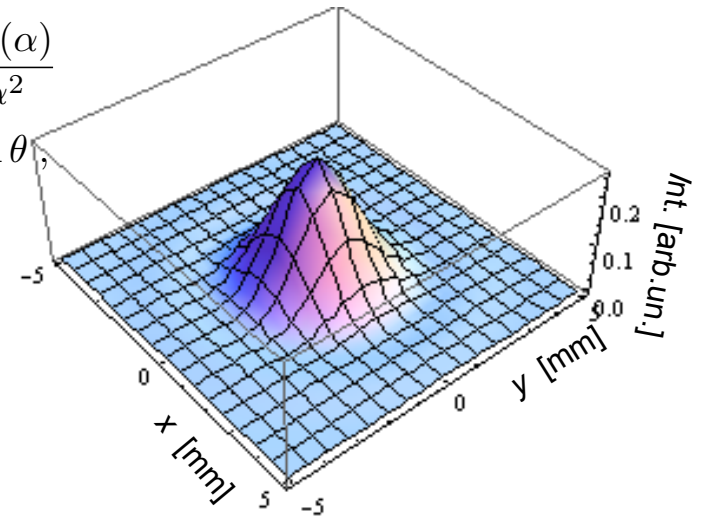
Systems of cylindrical-symmetric interference fringes appear

$\Longrightarrow$ localization of light in a "point" is impossible to achieve

$\Longrightarrow$ spatial-resolved information are smeared out, at some extent

$\Longrightarrow$ diffraction is a **fundamental** limitation

Airy disc diameter
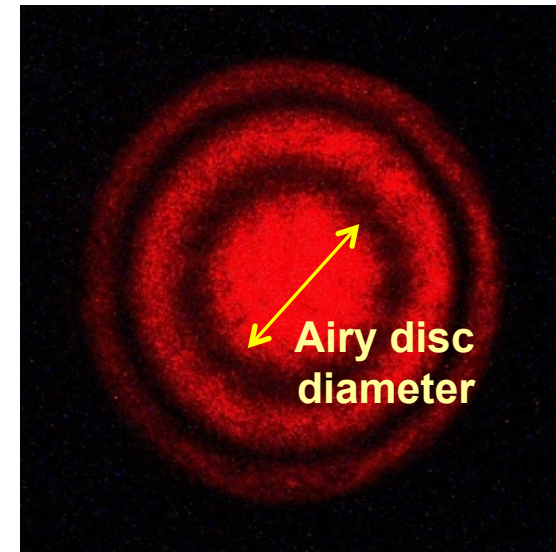
(DIFFRACTION AND QUANTUM MECH)
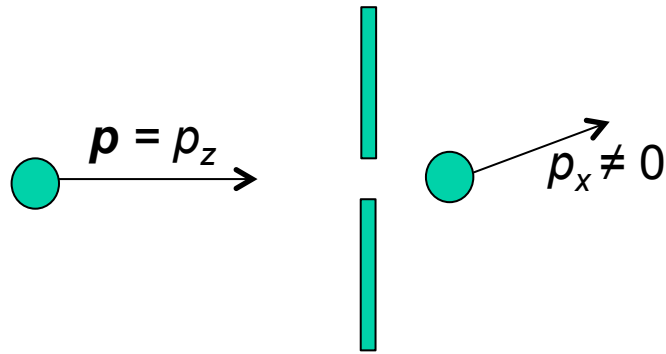
$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

Applying a simple particle model (free particle with impulse along one selected direction passing through an aperture), the uncertainty principle of quantum mechanics leads to impart the particle a momentum component along the aperture plane (analogous to the "diffusion cone" in the diffraction)

"DIFFUSION CONE"

"Diffusion cone":
$\sin\theta \sim \lambda/a$

$a \sim \lambda$

$\operatorname{sen}\theta = \dfrac{2\lambda}{a}$

$\operatorname{sen}\theta = \dfrac{\lambda}{a}$

$\operatorname{sen}\theta = \dfrac{\lambda}{a}$

$\operatorname{sen}\theta = \dfrac{2\lambda}{a}$

Diffraction ripples:
$I \sim I_0 \, (\sin\alpha/\alpha)^2$
with:
$\alpha = \pi a \, \sin\theta \, / \, \lambda$

Resolution Limit

Resolved

Unresolved

Airy Disks

Airy Patterns
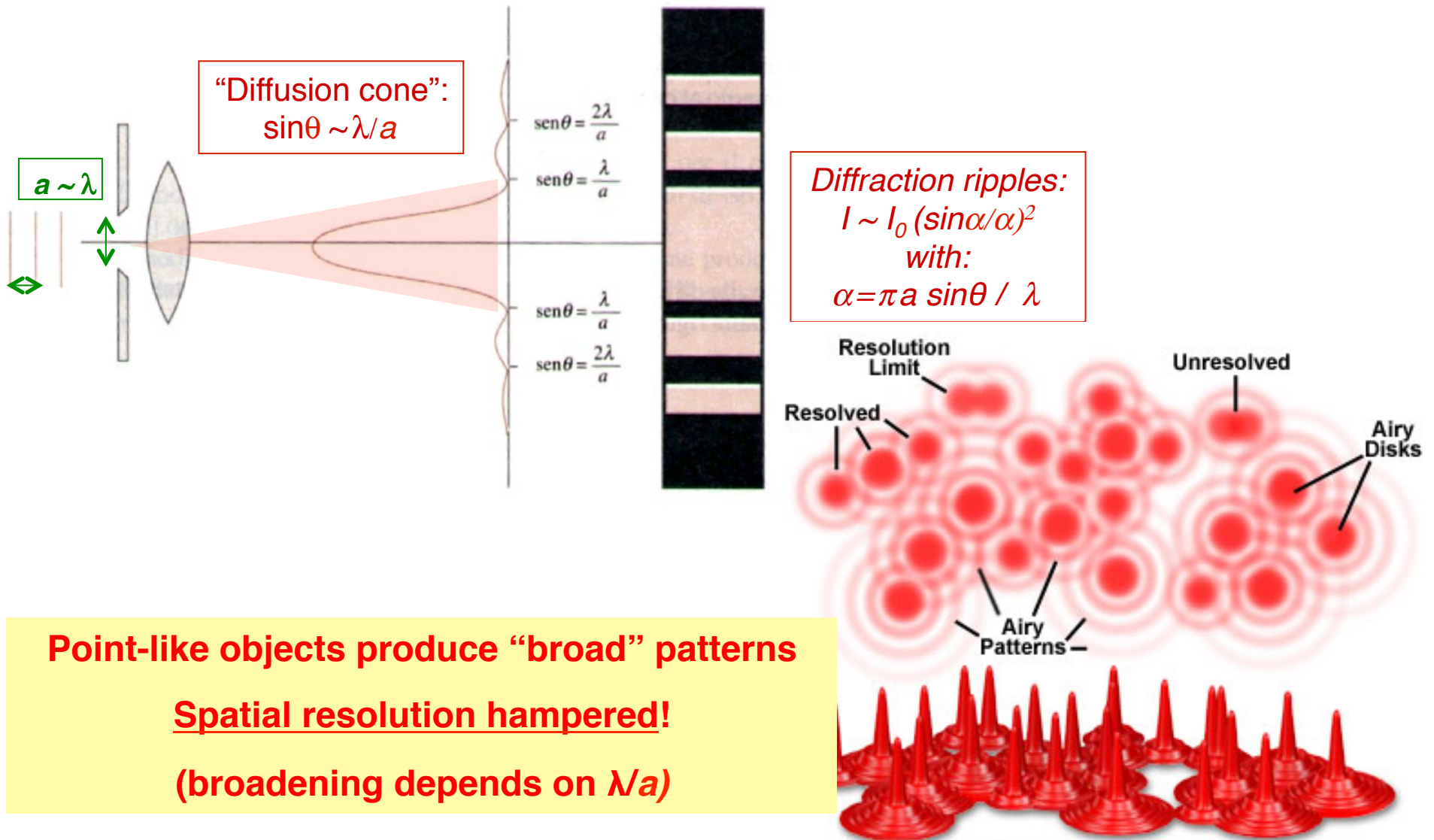
Point-like objects produce "broad" patterns

<u>Spatial resolution hampered</u>!

(broadening depends on λ/a)

(we wiill come back on such aspects later on)

A NON-OPTICAL SOLUTION

Decreasing λ !!

10^{-9}

1 nanometer

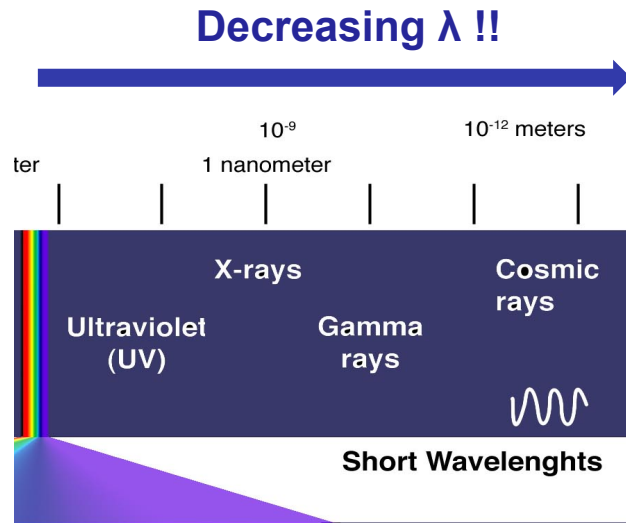10^{-12} meters

ter

X-rays

Cosmic rays

Ultraviolet (UV)

Gamma rays

Short Wavelenghts

Latching on the ideas of EM waves behaving like particles in the photoelectric effect, De Broglie suggested that particles could behave like waves under certain conditions and, therefore, have a wavelength and be subject to wave phenomena like diffraction. He formulated this equation later proven correct by effects like electron diffraction:

Wave-particle duality

$$\lambda = \frac{h}{mv}$$

✓ By increasing *v* , extremely small λ values can be attained

✓ The simplest way to impart speed to a particle is to use electric fields for its acceleration (but the particle must bring a charge!)

✓ The easiest charged particle to be accelerated is the electron, because of its small mass
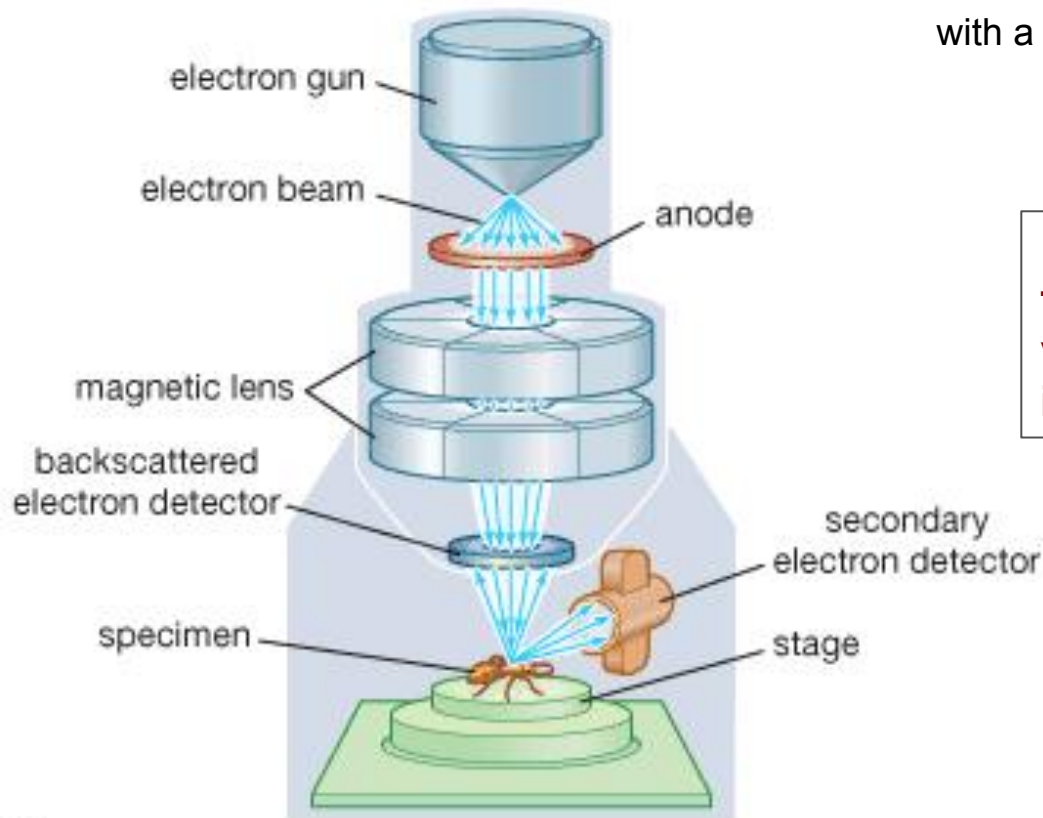
$$h \simeq 6.6 \times 10^{-34} \quad J/s$$

$$m \simeq 9 \times 10^{-31} \quad kg$$
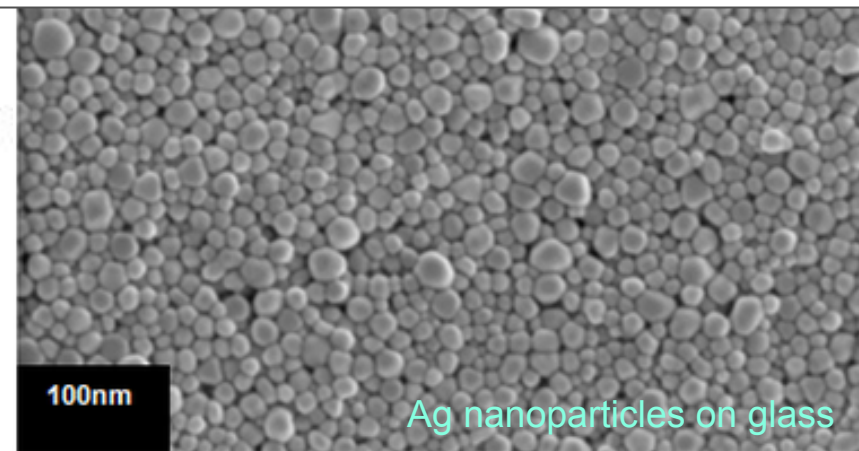
(GREAT IDEA: ELECTRON MICROSCOPE)

The electron microscope is out of our programme, but it is worth of a few words in order to point out some very general aspects

Assuming, e.g., $\Delta V \sim 10$ kV, a velocity $v = (2e\Delta V/m)^{1/2} \sim 6 \times 10^7$ m/s

$$\lambda = \frac{h}{\sqrt{2me\Delta V}} \sim 0.1 \text{ nm}$$

with a relativistic correction: $\lambda = \dfrac{h}{\sqrt{2me\Delta V\left(1+\dfrac{e\Delta V}{2mc^2}\right)}} \sim 0.1 \text{ nm}$

electron gun

electron beam

anode

magnetic lens

backscattered electron detector

secondary electron detector

specimen
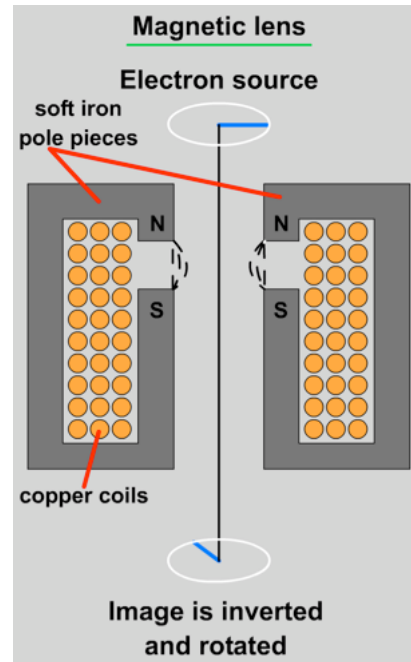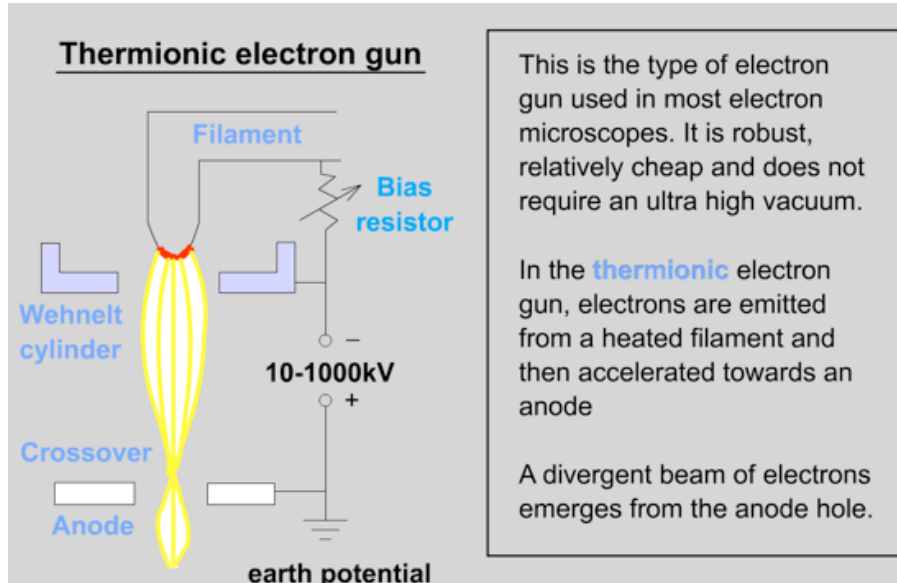
stage

© 2008 Encyclopædia Britannica, Inc.

In the Scanning Electron Microscope (SEM) a **tightly focused** beam of electrons, having a very small de Broglie's wavelength, is used instead of optical radiation
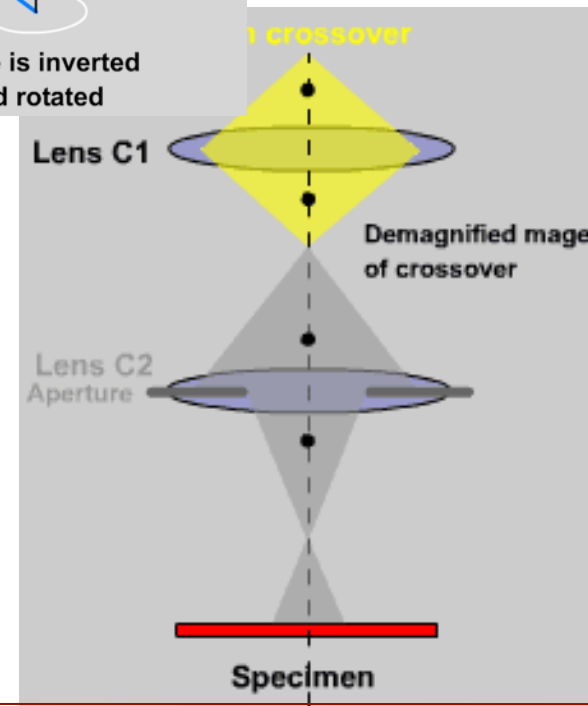

100nm

Ag nanoparticles on glass

SEM COMPONENTS I

Bright electron sources

Thermionic electron gun

Filament

Bias resistor

Wehnelt cylinder

10-1000kV

Crossover

Anode

earth potential

This is the type of electron gun used in most electron microscopes. It is robust, relatively cheap and does not require an ultra high vacuum.

In the thermionic electron gun, electrons are emitted from a heated filament and then accelerated towards an anode

A divergent beam of electrons emerges from the anode hole.

Magnetic lens

Electron source

soft iron pole pieces

N   N

S   S

copper coils

Image is inverted and rotated

Lenses, condensers, etc.

crossover

Lens C1

Demagnified mage of crossover

Lens C2 Aperture
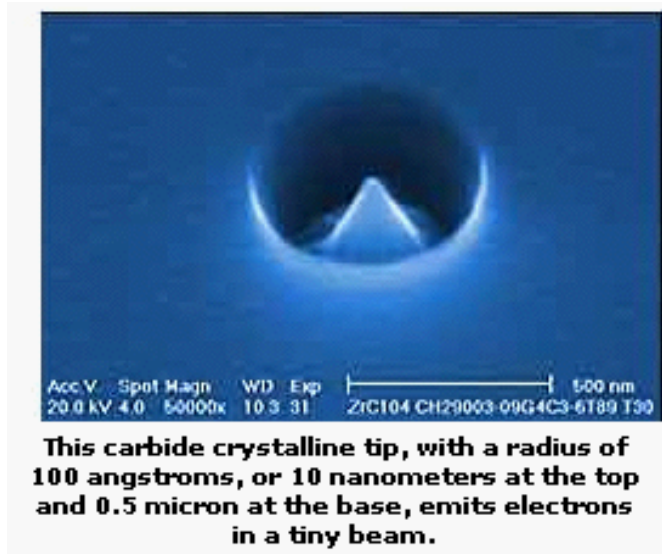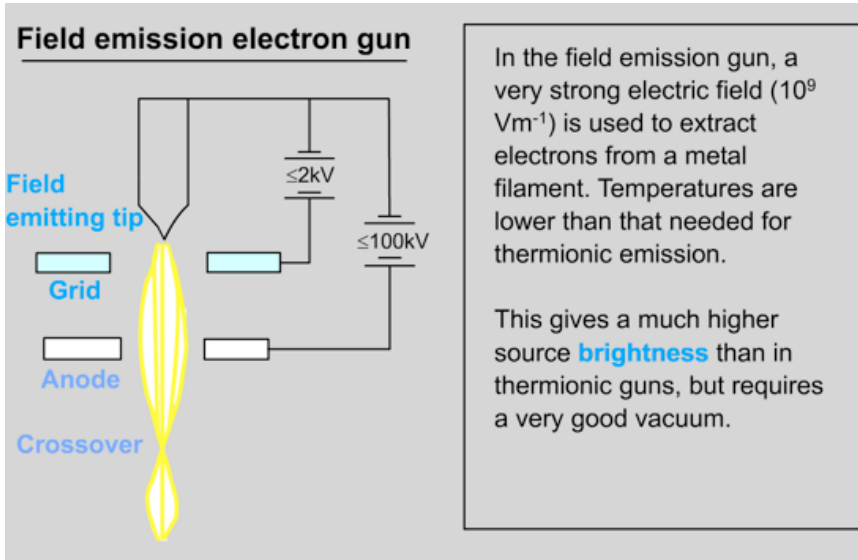
Specimen

In the SEM, the maximum HV is usually ~ 25 kV and its choice is determined by a compromise between penetration (which increases with HV) and beam diameter (which decreases with HV)

Optics is replaced by electron optics (made of magnetic and electric fields)

SEM COMPONENTS II

Field emission electron gun

In the field emission gun, a very strong electric field (10^9 Vm^{-1}) is used to extract electrons from a metal filament. Temperatures are lower than that needed for thermionic emission.

This gives a much higher source **brightness** than in thermionic guns, but requires a very good vacuum.

This carbide crystalline tip, with a radius of 100 angstroms, or 10 nanometers at the top and 0.5 micron at the base, emits electrons in a tiny beam.

Field and thermionic emission and photoemission

(From Lindquist et al., *Research and Development*, June, 91–98, 1990. With permission.)

### Electron emission in a water bucket

THE THREE MECHANISMS used by field emission sources all basically involve emitting electrons and ions from a metal surface under the influence of a strong electric field.

Understanding these mechanisms is where the water bucket comes in.

In this analogy, the water level in a bucket represents the Fermi level—the highest occupied energy level in a cathode material. The work function is the energy required to get the water droplets (electrons) from the top of the liquid out of the bucket. This is the distance equivalent to the potential energy barrier.

In photoemission, photon energy excites electrons at the Fermi level of the cathode material and can impart enough kinetic energy to allow the electrons to escape from the bucket.

In thermionic emission, heat thermally excites the electrons, providing enough energy to boil the electrons off and out of the bucket.

In field emission a high electric field can thin the side of the bucket enough so that the electrons can tunnel through it.
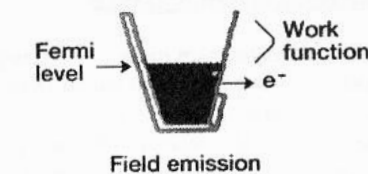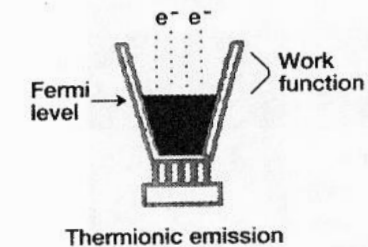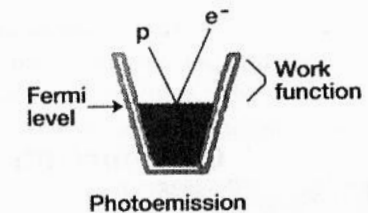
Typically, in a FE-SEM the electron beam current can be as large as 1-10 nA, focused in a few nm spot
→ huge current density

CONTRAST I

1 **General considerations:**

o   Every microscopy requires a contrast mechanism

o   The contrast mechanism is a sort of "spectroscopy", providing with selectivity according to one, or more, local physical properties

o   Spatial resolution is ultimately linked to the size of the probe beam, but also inherently related to the effectiveness of the contrast mechanism, i.e., the "spectroscopy" used to achieve image modifications at the local scale

Because of their kinetic energy, electrons impinging onto a solid surface can (and do) penetrate into the volume

2 **General consideration:**

o   Ideally, a surface is imaged and analyzed, but, at the nanoscale, no investigation tool is truly capable of pure surface interaction
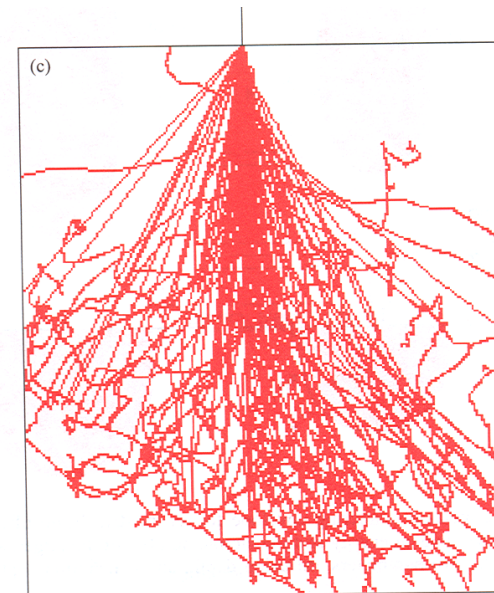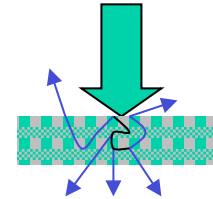
MC simulation of electron trajectories into the material

CONTRAST II

An electron passing through a solid may be scattered
    * not at all
    * once (single scattering)
    * several times (plural scattering), or
   * very many times (multiple scattering)

Each scattering event can be elastic or inelastic. The scattered electron is most likely to be forward scattered but there is a small chance that it will be backscattered

The probability of scattering is described in terms of either an "interaction cross-section" or a mean free path. When the solid specimen is thicker than about twice the mean free path, plural scattering is likely.

The important features are the fraction of electron scattering forward and backward and the volume of the specimen in which most of the interactions (scattering events) take place

Roughly speaking, penetration occurs until electron thermalization with the matter occurs

Incident beam

$E > kT$

$E = kT$
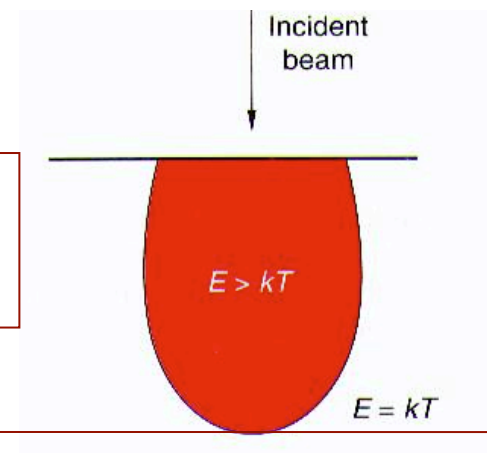
"SPECTROSCOPIES" INSIDE SEM

There are four main processes by which a high energy electron (red here) can lose energy to an atom. These are

1. (The excitation of a plasmon)
2. The excitation of a single electron from the valence band (pale green)
3. The excitation of an inner shell electron (from the K or L shell)
4. (The excitation of a phonon)
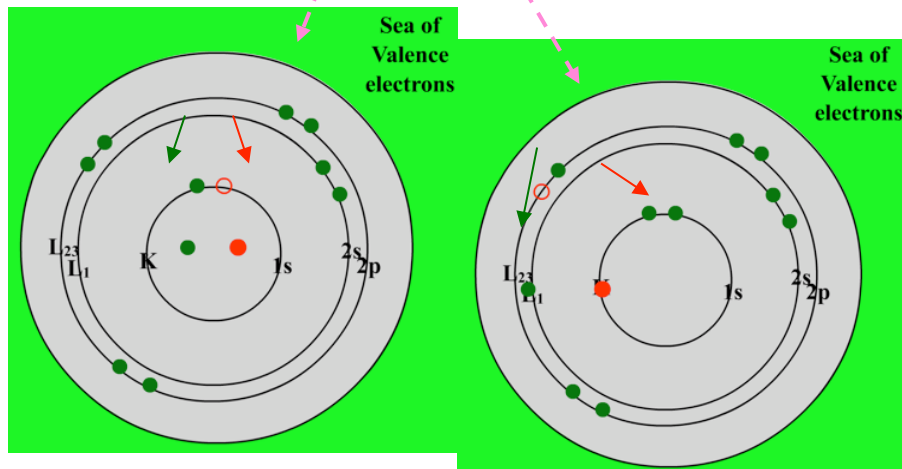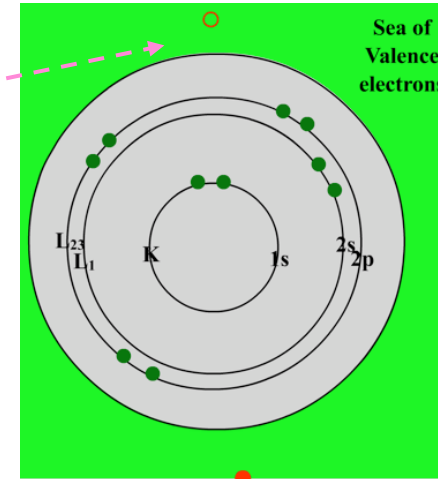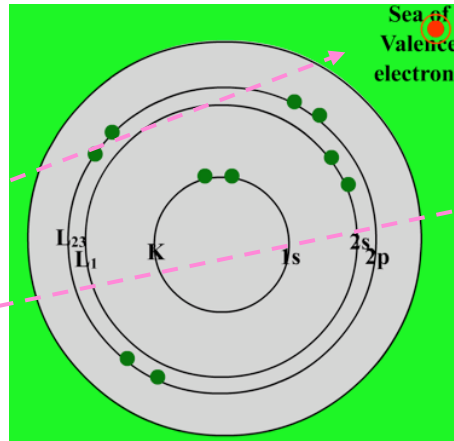
After an inner shell excitation an atom has an energy above its ground state. It can relax and lose some of this energy in several ways, of which two are described here. Both start with an outer electron jumping in to fill the vacancy in the inner shell.
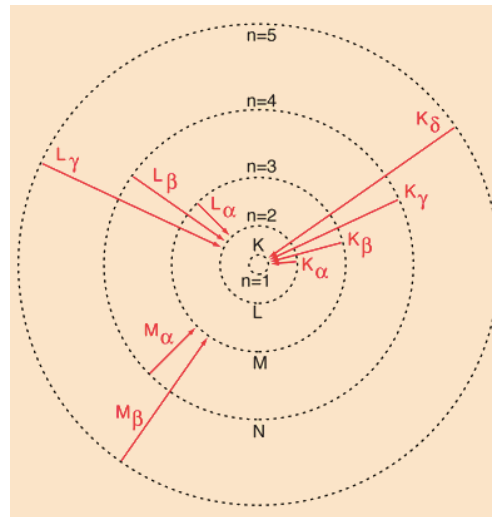
Characteristic X-ray emission. Energy is given off as a single X-ray photon.   **XPS/EDS**

Auger electron emission. Energy is given off by one of the outer electrons leaving the shell. It carries a characteristic kinetic energy.   **AES**

NOMENCLATURE FOR INNER SHELLS
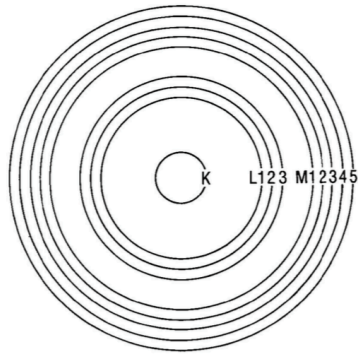
Super-simplified picture of shell-like configuration (atoms): K, L, M, … correspond to n = 1, 2, 3, …

(log scale)
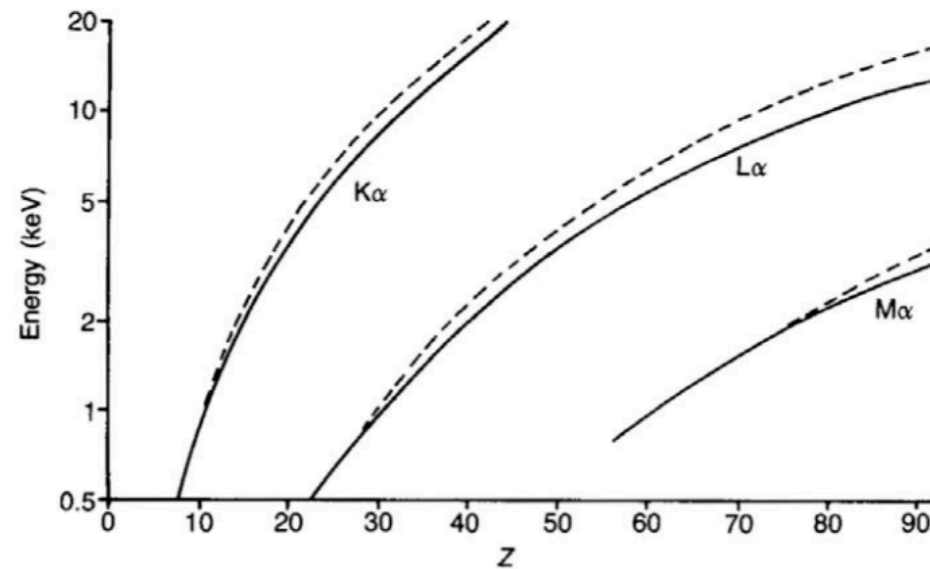
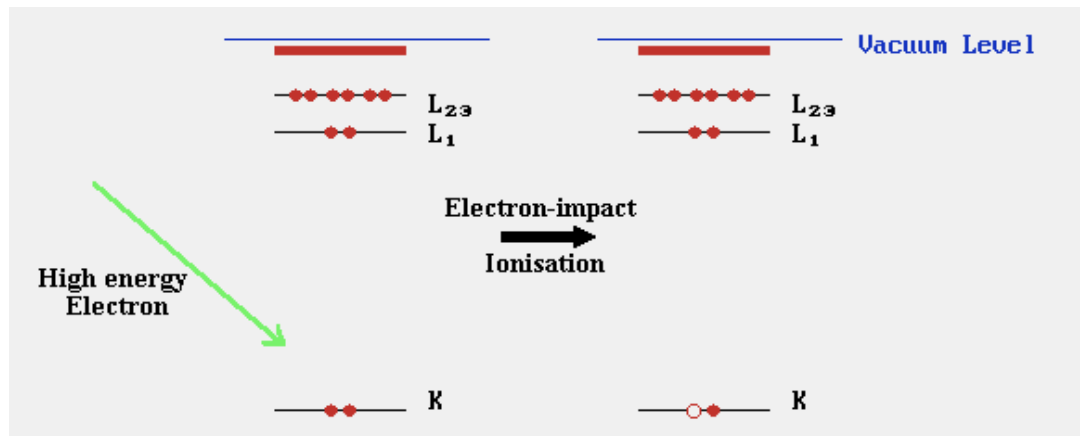Classification and nomenclature of levels and transitions are quite straightforward and hold for virtually all heavy atoms

In a rough approximation, involved energies can be evaluated based on the Bohr model
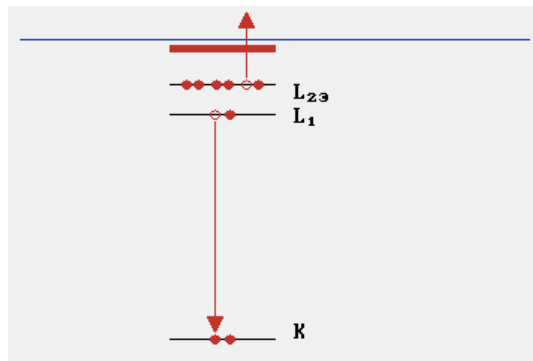
They depend on the atomic number Z

AUGER SPECTROSCOPY (A FEW WORDS)

Impact with high energy electrons (5-10 keV, typically) produces ionization of light elements and vacancies in the inner shell for heavier elements

The so-created metastable state involves multiple rearrangement of electrons and vacancies in the inner shell(s)
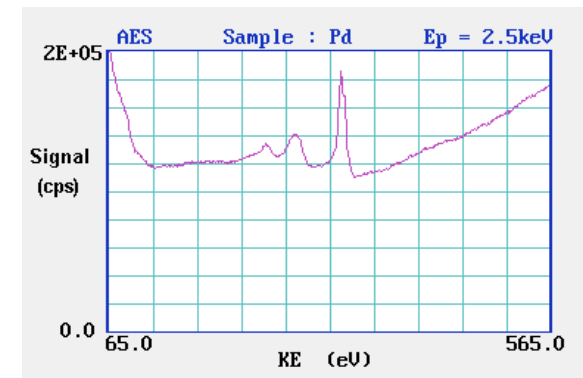

An electron from the outer shell fills the vacancy and <u>simultaneously</u> the energy mismatch is compensated by **emission of an electron** from an outer shell

The kinetic energy of the emitted electron is (approximately):
$$KE = E_K - (E_{L1} - E_{L23}) = E_K - (E_{L1} + E_{L23})$$
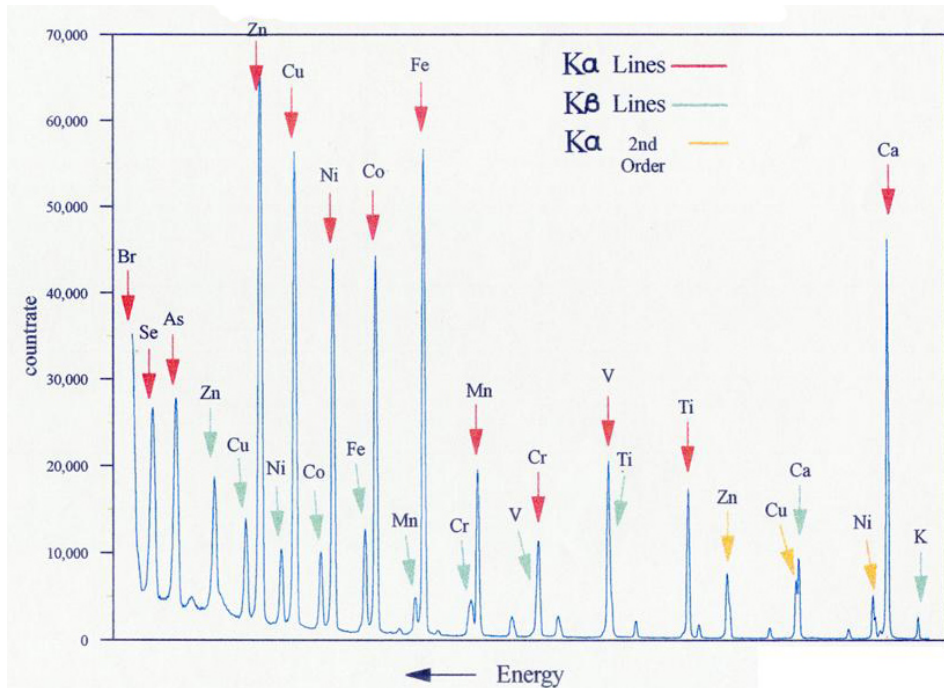hence it is specific of the considered element
→ **selectivity** → **contrast**

ENERGY DISPERSIVE SPECTROSCOPY (A FEW WORDS)

Impact with high energy electrons (5-10 keV, typically) produces vacancies in the inner shell, especially for heavier elements

Vacancies can be filled by an electron coming from an outer shell
→ the energy can be released in the form of X-ray photons
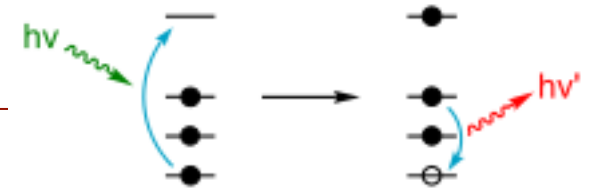
Involved energies can be related to the structure
→ species-selective contrast achieved

By equipping a SEM with an X-ray spectrometer, elemental maps can be built (EDS microanalysis)
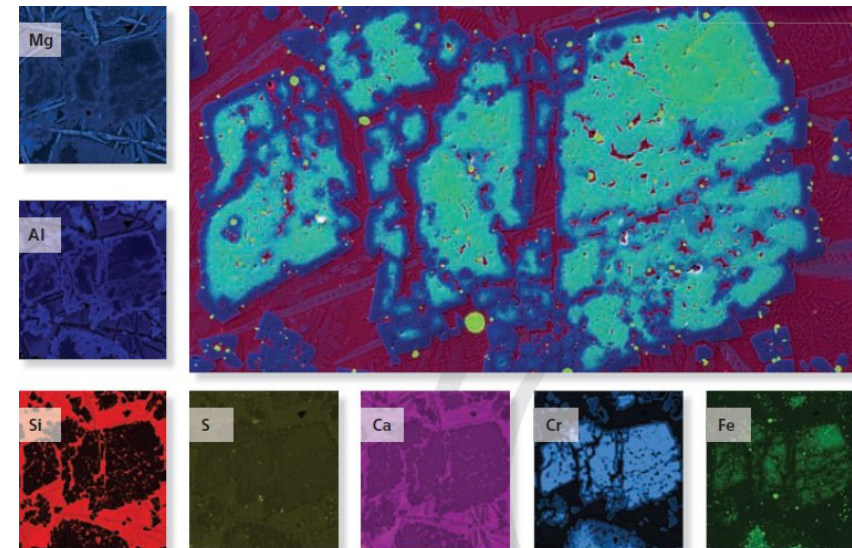
Layered Image gives complete picture of composition and phase distribution. Or view individual X-ray maps for more detailed information.

CONTRAST III

SEM images are built based on **different** measured quantities:

- Backscattered electrons: usually at high energy, usually released in the backward direction, usually strongly depending on the topography (surface steepness and slope, orientation, etc.)

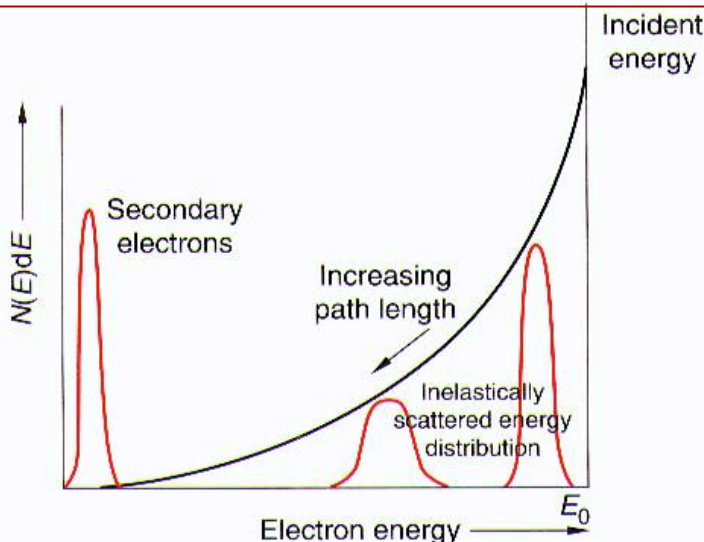- Secondary electrons: usually at low energy (few hundreds of eV), includes a variety of processes, e.g., Auger

Backscattered and secondary can be **selected**

In addition, the relative yield depends on the penetration length, which is a complicated function of the electron beam energy and of the material properties (mostly, the atomic number)

3 **General consideration:**

o At the local scale, it is hard to disentangle different interaction processes

o Contrast mechanisms are usually a combination of various mechanisms

SECONDARY ELECTRONS

4.3.4 Secondary Electron Emission

Most of the electron current generated in a sample due to the impact of a high-energy incident beam is due to the release of *secondary electrons* from the surface. In fact, the *secondary electron emission coefficient*, the number of secondaries released per incident high energy electron, is *always* greater than one and may reach values of several hundred. All of these secondaries have rather similar energies, up to 100 or 200 eV, but typically in the range 10–50 eV, and they are therefore readily deflected by a low-bias voltage and collected with very high efficiency (close to 100 %). Moreover, their low kinetic energy severely restricts their mean free path in the sample, so that the secondaries escaping from the surface are generated very close to the latter, typically within 1–2 nm, and are almost unaffected by beam spreading beneath the surface.

Four factors directly affect *secondary emission* from the surface:

(a) The *work function* of the surface, that is the energy which has to be supplied to an electron in the solid which is at the *Fermi level*, in order to permit it to escape from the surface. Typical work functions are a few eV in magnitude, with the work function depending on both the *composition* and the *atomic packing* (crystal structure) at the surface. The work function is sensitive to both *surface adsorption* and films of *contamination*.

(b) The *beam energy* and *intensity*. As the beam energy is increased, more secondaries might be expected to be created, but a high-energy beam is inelastically scattered further beneath the surface, so that the *proportion* of secondaries escaping from the surface is reduced. On the other hand, the secondary electron current is *directly proportional* to the current in the incident beam.

(c) The *density of the sample* has a relatively limited influence, and is usually masked by the effect of surface films or surface contamination. Since higher atomic-number materials have a smaller diffusion distance, the number of high energy electrons is higher in the surface region for any given beam intensity, thus *increasing* the number of secondaries. This effect is most pronounced at *low* beam energies, when the diffusion distance is comparable to the mean free path of the secondary electrons.

(d) The most pronounced effect is that of *surface topography*, or more precisely, the local *curvature* of the surface. Any region protruding from the surface (*positive* radius of curvature) improves the chances of secondaries escaping, while a
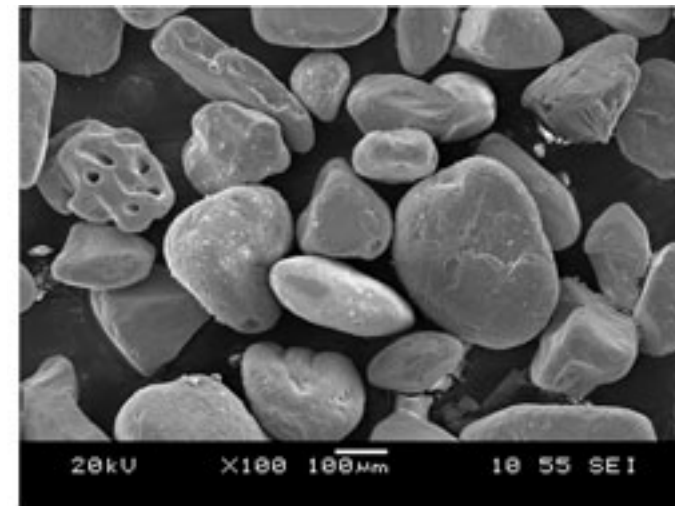
Secondary electron image (SE)
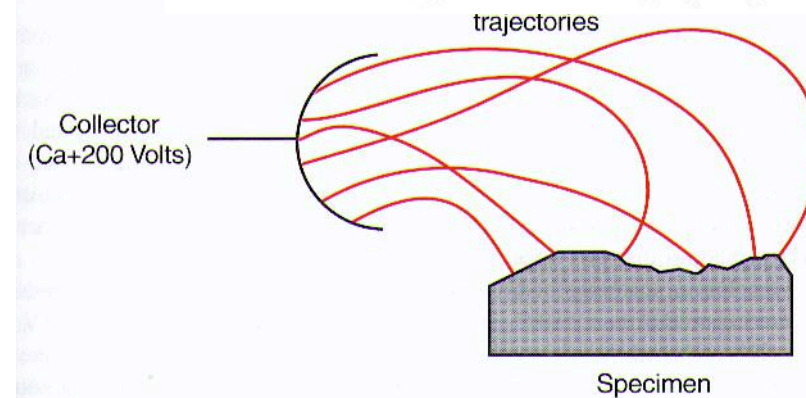
Spatial resolution is virtually limited by the size of the electron beam (typ, a few nm)

4.3.3 Back-Scattered Electrons

A proportion of the incident electrons will be scattered by angles greater than π and may escape from the surface. The proportion of these *back-scattered* electrons, **R**, will depend on the *average atomic number* of the specimen but is almost independent of the incident beam energy. The back-scattered electrons originate in a *surface layer* corresponding to the diffusion distance and come from an area beneath the beam which is also proportional to this distance, but significantly less than the diameter of the envelope of inelastically scattered electrons.

The *average energy* of the back-scattered electrons is of course *less* than that of the primary incident beam, but nevertheless of the same order of magnitude. These electrons are usually detected in an annular region close to the probe lens pole-pieces. The collection efficiency is high, but the back-scattered electron current is only a fraction of the incident beam current.

4.3.3.1 IMAGE CONTRAST IN THE BACK-SCATTERED IMAGE

Contrast in a *back-scattered electron image* may arise from either of the following two sources;

(a) Any region of the specimen surface which is tilted *towards* a back-scattered electron detector will give rise to an *enhanced* signal, while the signal will be *reduced* if the surface is tilted *away* from the detector. A segmented annular detector can therefore be used to obtain a *topographic image* of the surface in which the signals collected from *diametrically opposite detectors* are first subtracted and then amplified, thus enhancing differences in contrast from regions tilted in opposite directions.

(b) On the other hand, collecting a backscattered image from a *conical detector* surrounding the probe lens pole-pieces (or equivalently, *summing* the signals detected from all of the segments) will effectively *decrease* contrast associated with changes in surface topography. Most features detected in the image are then due to *atomic-number* contrast, and reflect variations in the density (usually the composition) of the sample.

The resolution in the *back-scattered electron* (BSE) *image* is typically an order of magnitude better than can be obtained from an *X-ray elemental map*, but not nearly as good as that available in the *secondary electron image* (discussed below). The direct relationship between the BSE image and the *diffusion distance* in the material typically results in a resolution of the order of 10–20 nm when working at 10–20 kV. The BSE image can give very useful information on the *distribution* of the phases present, providing that they differ sufficiently in density (see Fig. 4.36), if the secondary electron image is lacking in contrast.
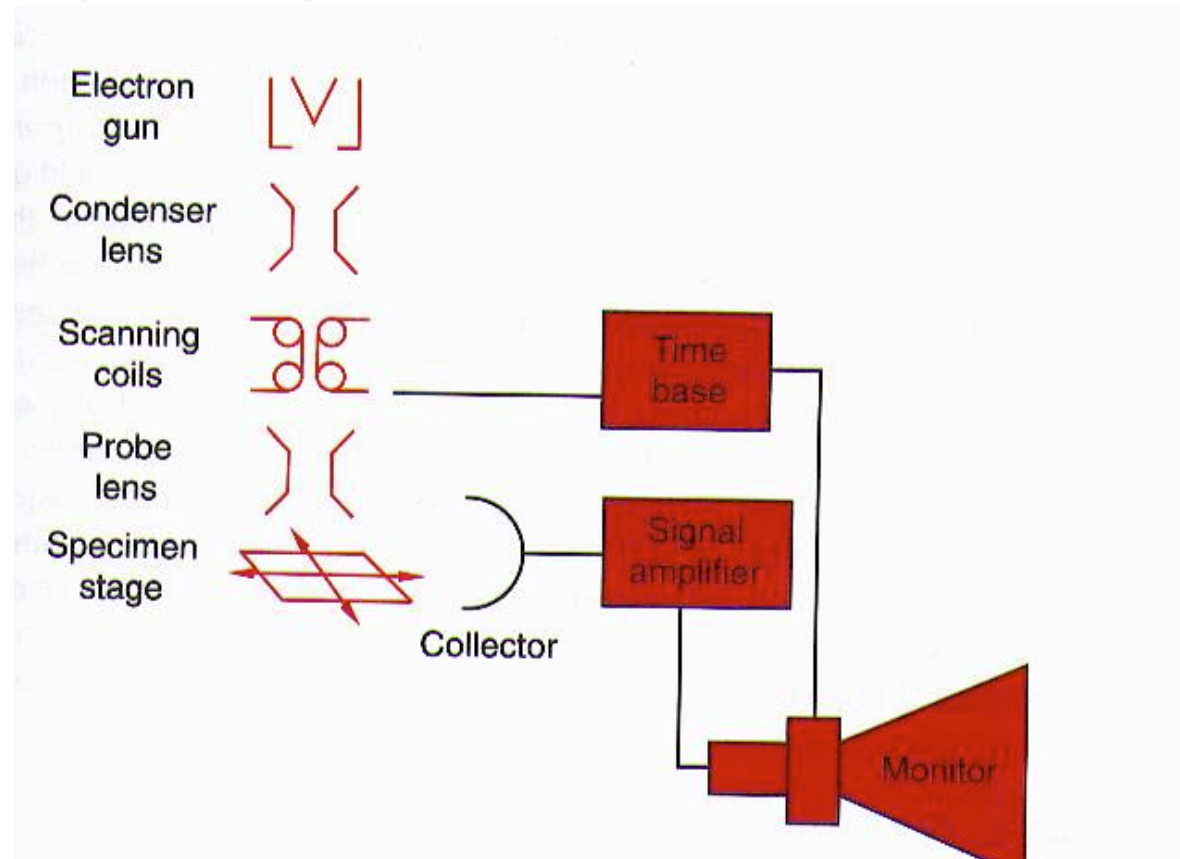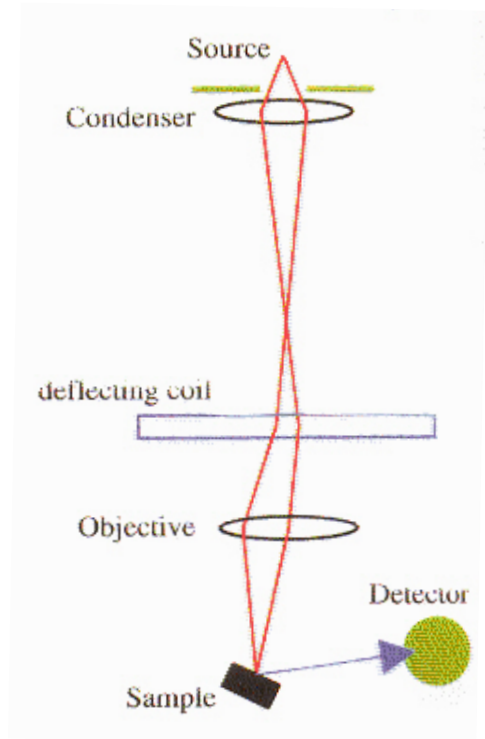
Ti/Si sand
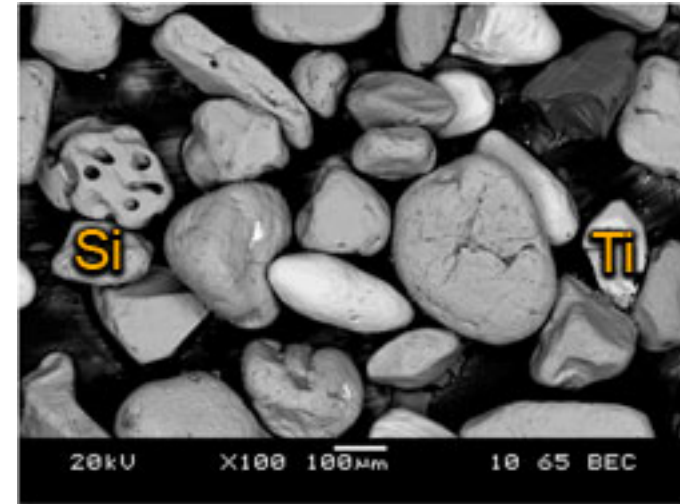
Backscattered electon image (BSE)

4 **General consideration:**

o At the local scale, surface/bulk contributions are mixed together

o Usually, spatial resolution is decreased when bulk contribution is relevant (typ, max ~ 10 nm)
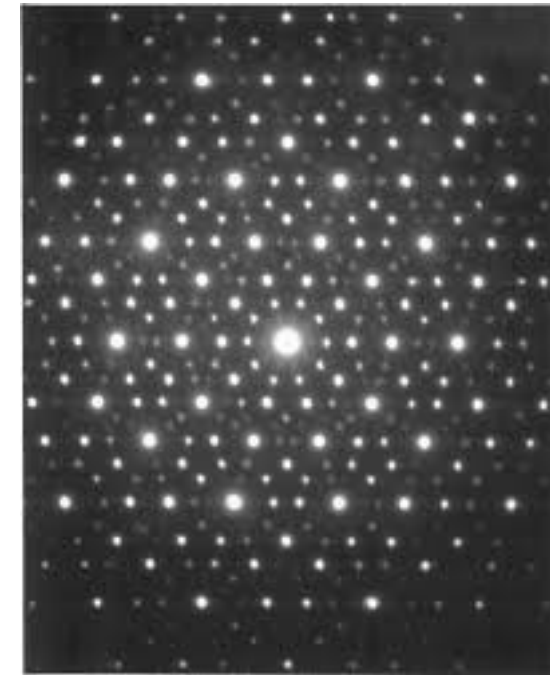
SCANNING (SERIAL) CHARACTER

5 **General consideration:**

o A scanning strategy is deployed, image is reconstructed point by point, as required in order to exploit the contrast mechanism(s)

o Typically, local spectroscopies are based on the comparison between spatially resolved information, acquired on a point to point basis, enabling a reasonable signal-to-noise ratio

BRAGG DIFFRACTION (REMINDERS)

Constructive interference when

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

Bragg's Law
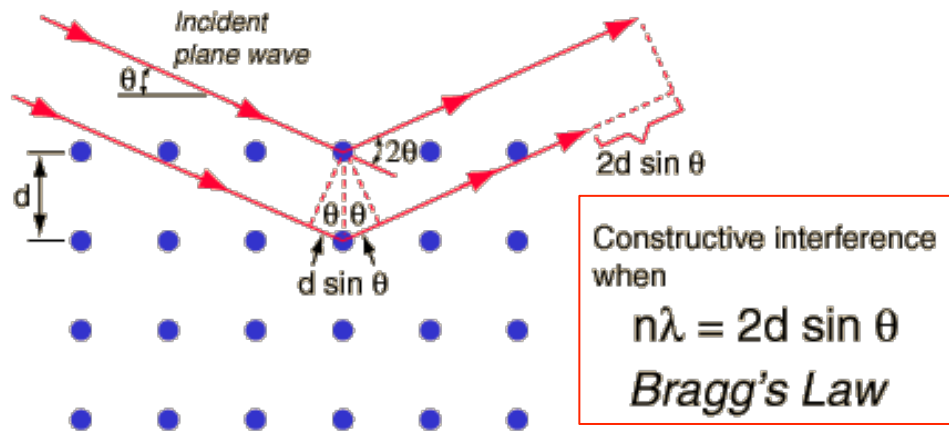
A (plane) wave interacts with dot-like scatterers arranged in a regular structure
→ an interference/diffraction pattern is observed in the image plane

At the basis of X-Ray diffraction (analytical purposes, selcetivity being related to interlattice distance), but similar to diffraction in optical grating and involved in many "optical interference" effects (e.g., iridescence)

X-Ray diffraction pattern of a crystalline material
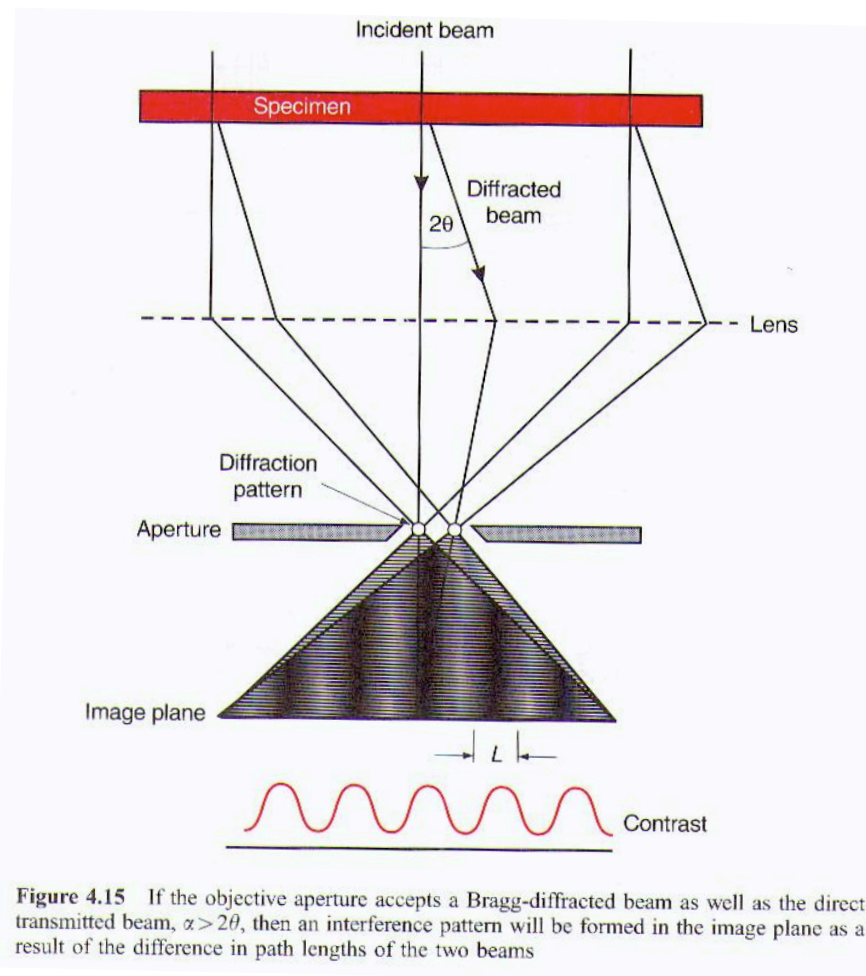
TRANSMISSION ELECTRON MICROSCOPY

Thin specimens (often samples purposely thinned by, e.g., ion milling) can be "transparent" to electrons

In TEM, where elastic interaction is predominant, main contrast mechansims are:

1. **mass thickness** (transmission depends on the amount of mass crossed by the electrons)
2. **diffraction** (in crystalline materials Bragg diffraction plays a role leading to high sensitivity to lattice defects)
3. **phase contrast** (when collection optics has a large numerical aperture, due to mutual interference of many diffracted beams)

6 **General consideration:**

o When accessible, further spatial resolution can be achieved from interference/ diffraction!

Figure 4.15 If the objective aperture accepts a Bragg-diffracted beam as well as the direct transmitted beam, α > 2θ, then an interference pattern will be formed in the image plane as a result of the difference in path lengths of the two beams
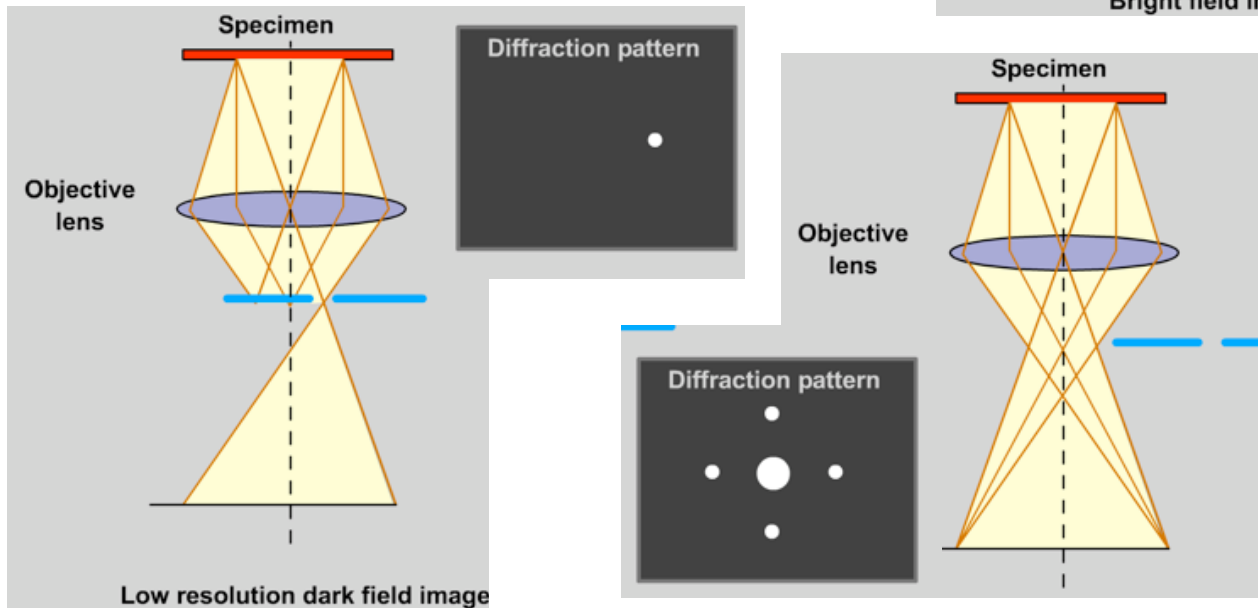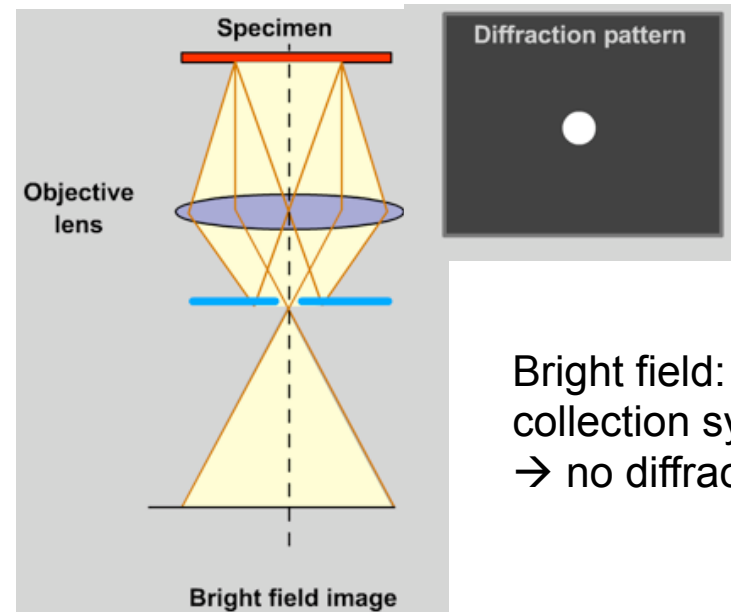
BRIGHT AND DARK FIELD OPERATION

By inserting an aperture or tilting the beam, different types of images can be formed.
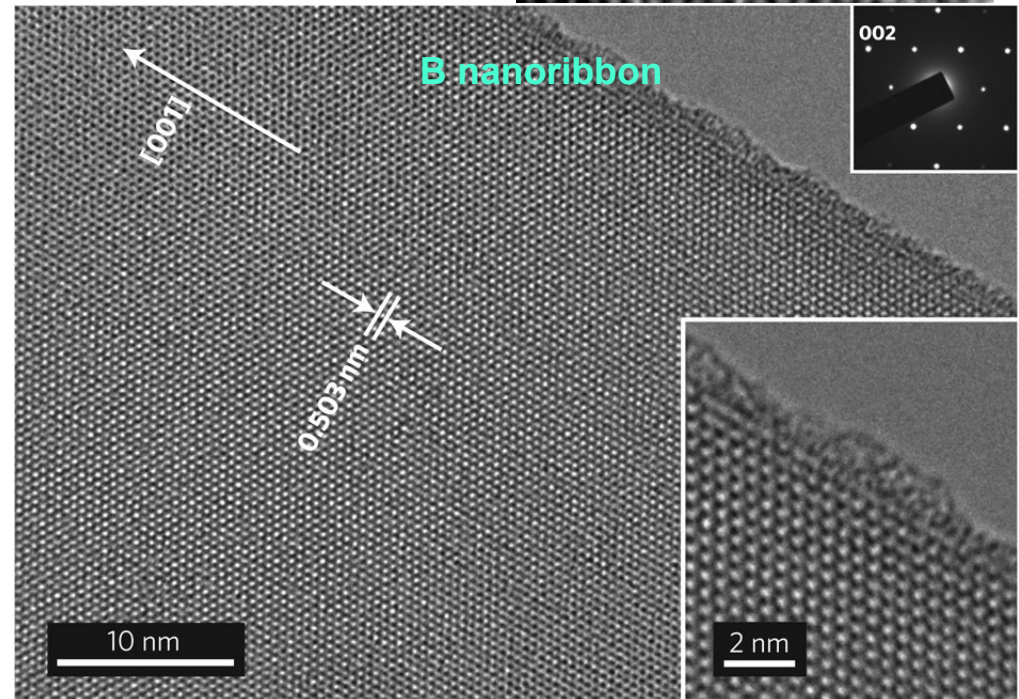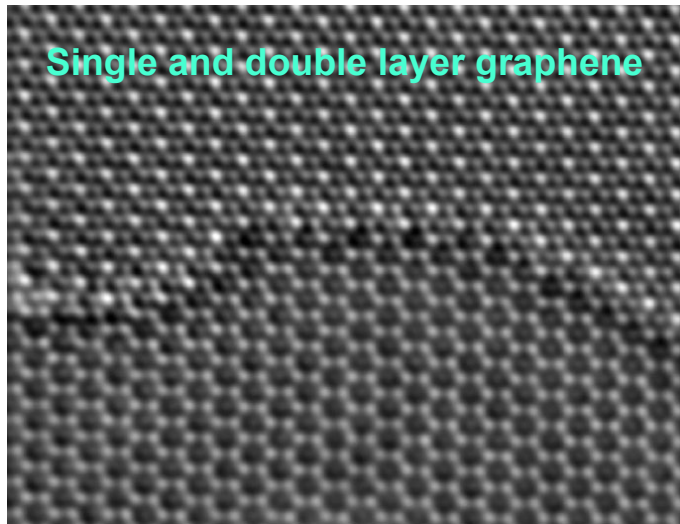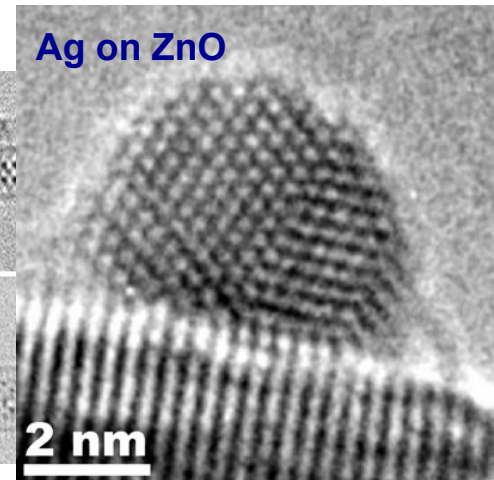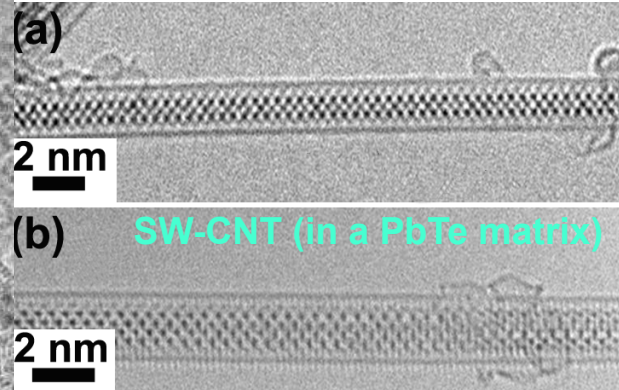The most common conditions are:

- No aperture: the diffraction pattern is centered on the optical axis
- Aperture is centered on the optical axis
  Aperture displaced, selecting a diffracted beam
- Beam is tilted so that the diffracted beam is on the optical axis

Specimen
Diffraction pattern
Objective lens
Bright field image

Bright field:
collection system centered
→ no diffraction (but image)

Specimen
Diffraction pattern
Objective lens
Low resolution dark field image

Specimen
Objective lens
Diffraction pattern

7 **General consideration:**

- Sometimes, spatial resolution can be improved by "suppressing" the main information (which is in the "bright field")

EXAMPLES OF HR-TEM IMAGES

Ce,Zn O nanocrystals

Ag on ZnO

(a)

(b) SW-CNT (in a PbTe matrix)

B nanoribbon

Single and double layer graphene
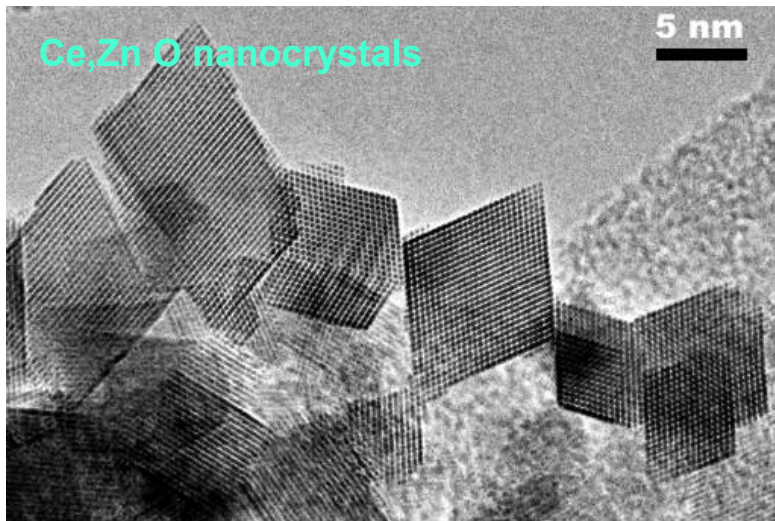
CONCLUSIONS

✓ Adding spatial resolution to spectroscopy opens wonderful perspectives in the "nano" world

✓ Microscopy and spatial-resolved spectroscopy share quite similar problems

✓ Diffraction sets a fundamental limitation to spatial resolution in the "optical" range

✓ Electron microscopy represents a powerful and brilliant shortcut to overcome diffraction: in some sense, it is a benchmark useful for comparison and to unravel some basic aspects

✓ <u>Note that not all glitter is gold</u>: SEM/TEM suffers many limitations such as, e.g.:
  o they require conductive or metalized samples, able to whitstand vacuum, and often prepared in a destructive fashion (thinning in TEM);
  o Imaging results from a convolution of effects, no truly quantitative analysis can be carried out (or it can be accomplished with severe limitations in sensitivity/selectivity);
  o more important: direct analysis of optical properties cannot be accomplished, since no specific sensitivity exixts in any contrast mechanism

Therefore, we will leave electrons and come back to photons soon (next lecture)!

FURTHER READING

For electron microscopy:

D. Brandon, W.D. Kaplan, Microstructural Characterization of Materials, Wiley, New York (1999).

For very general introductory remarks:

M.A. Ratner, D. Ratner, Nano technology: a gentle introduction to the next big idea, Prentice-Hall, Upper Saddle River (2003).

R. Feynman, There is plenty of room at the bottom, 1959 Speech,
https://www.pa.msu.edu/~yang/RFeynman_plentySpace.pdf