Topic 3d - TEM

1.0 Review

- **1.1 Types of Solids**
- **1.2 Basic of Crystallography Concepts**
- **1.3 Crystal Structures**

2.0 Basic Principles

- **2.1 The Microscope Column**
- **2.2 Beam and Specimen Interaction**
- **2.3 Sample Prep**
- **2.4 Sample Holder**

3.0 Imaging and Examples

- **Bright field, Dark field, Phase contrast, e^- diffraction, SAED, EELS, EDS, Mapping, STEM**

4.0 Limitations

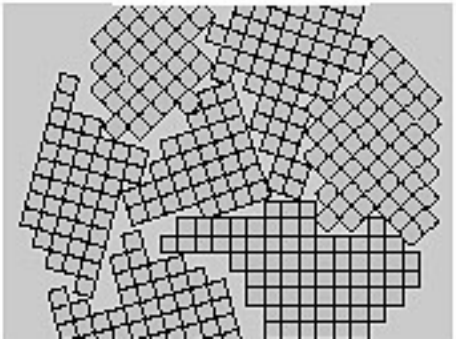
5.0 Summary

1.1 Types of Solids

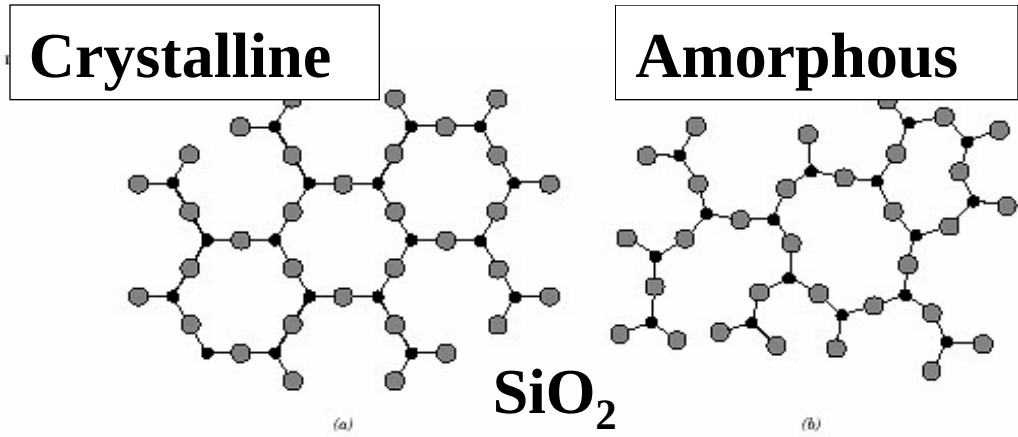
Crystalline material: atoms self-organize in a periodic array

Single crystal: atoms are in a repeating or periodic array over the entire extent of the material

Polycrystalline material: comprised of many small crystals or **grains**



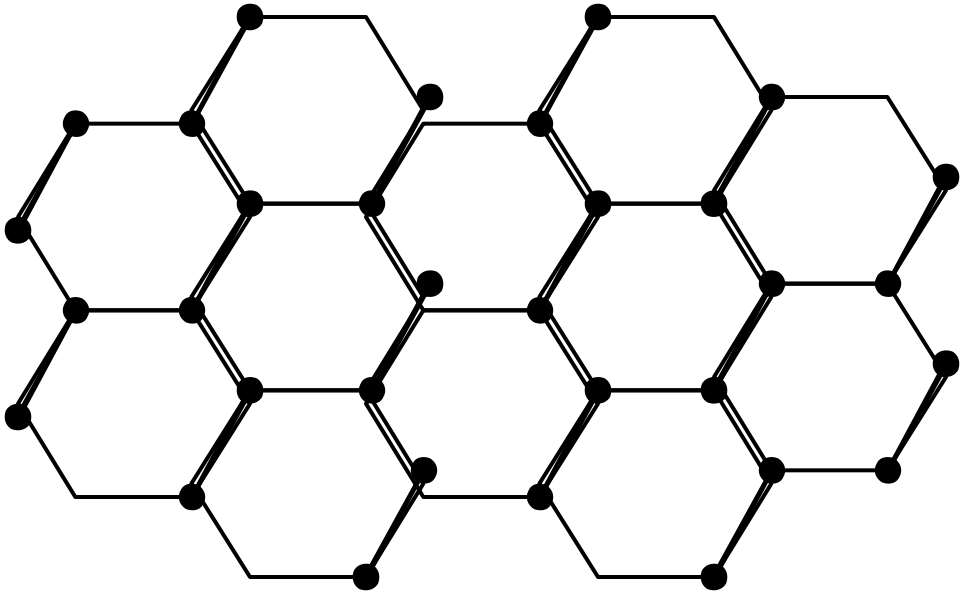
Amorphous: lacks a systematic atomic arrangement



1.1 Unit Cell

The unit cell is the smallest structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal.

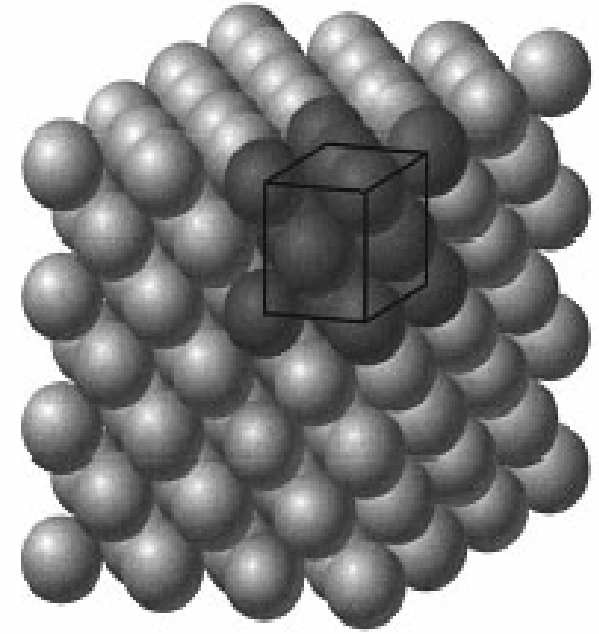
Example: 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure

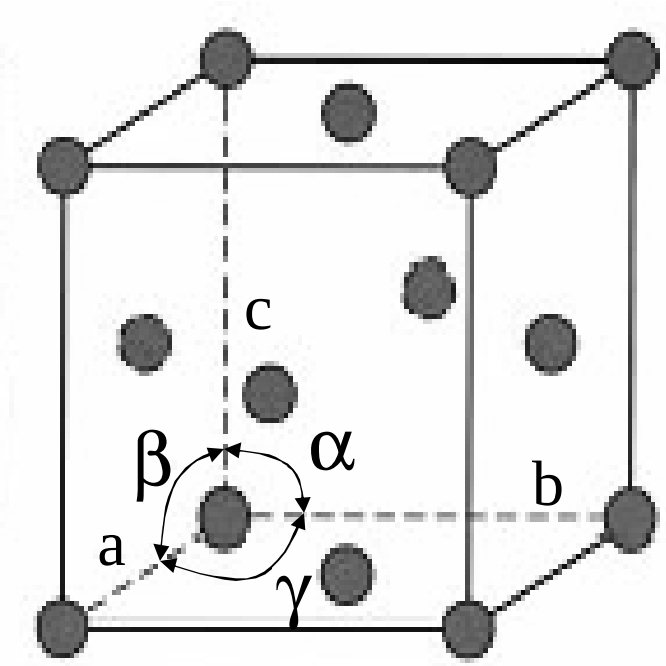


1.1 Crystal structure

To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter.

We can also consider crystalline structure as a lattice of points at atom/sphere centers.

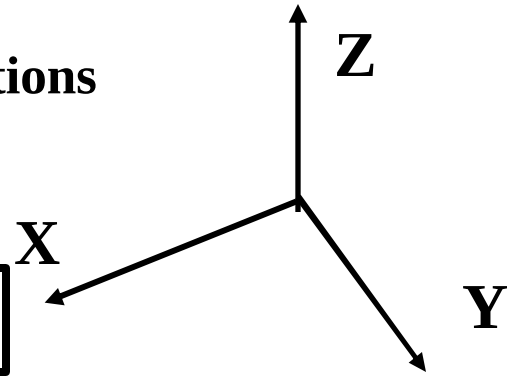




- Think of a crystal as being an array of ***atomic hard spheres***
- Or a ***lattice point :*** a 3D array of points at sphere (atom) centers
- Lattice parameters: edge lengths (a,b,c), angles (α,β,γ) of unit cells.

1.2 Review of Crystallography Concepts

Positions and Directions

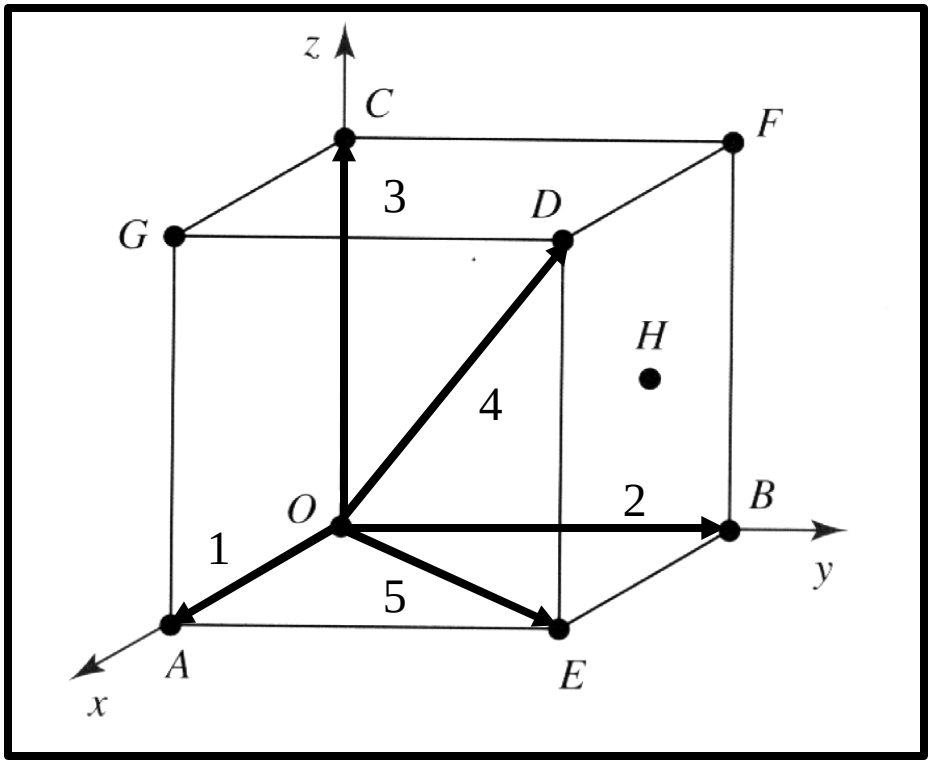


x, y, z ® u, v, w

Lattice Positions and Directions:

1) **Always establish an origin**
2) **Determine the coordinates of the lattice points of interest**
3) **Translate the vector to the origin if required by drawing a parallel line or**
   move the origin.
4) **Subtract the first point from the second: u2-u1,v2-v1,w2-w1**
5) **Clear fractions and reduce to lowest terms**
6) **Write direction with square brackets [uvw]**
7) **Negative directions get a bar over them.**

1.2 Positions and Directions

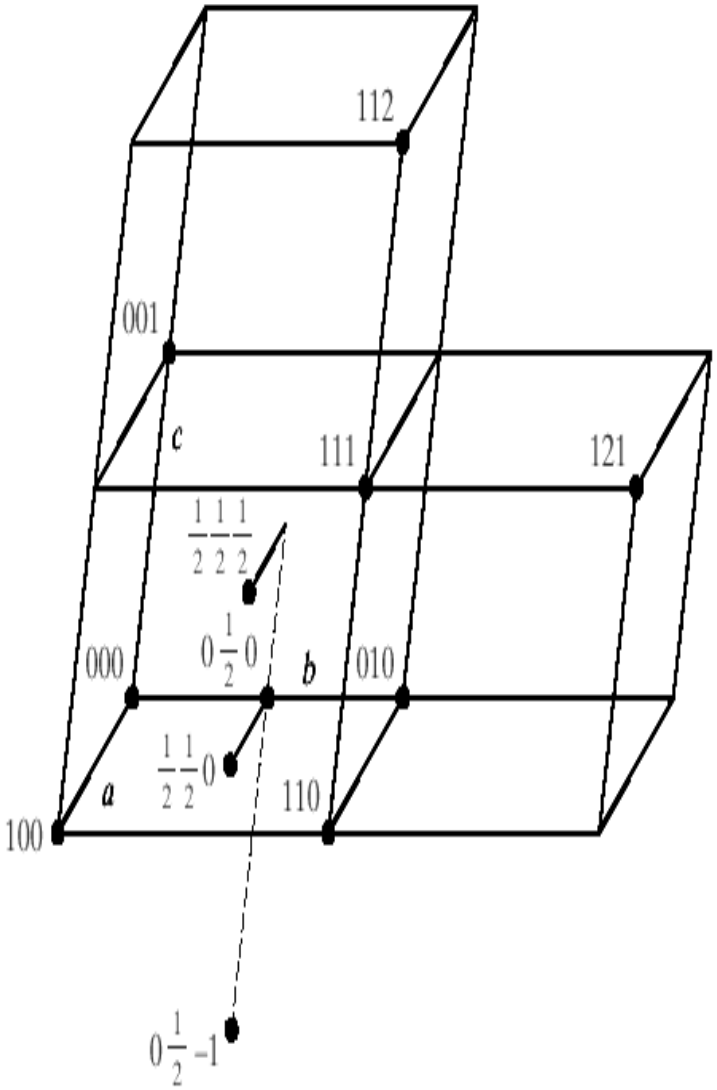


1)
2)
3)
4)
5)

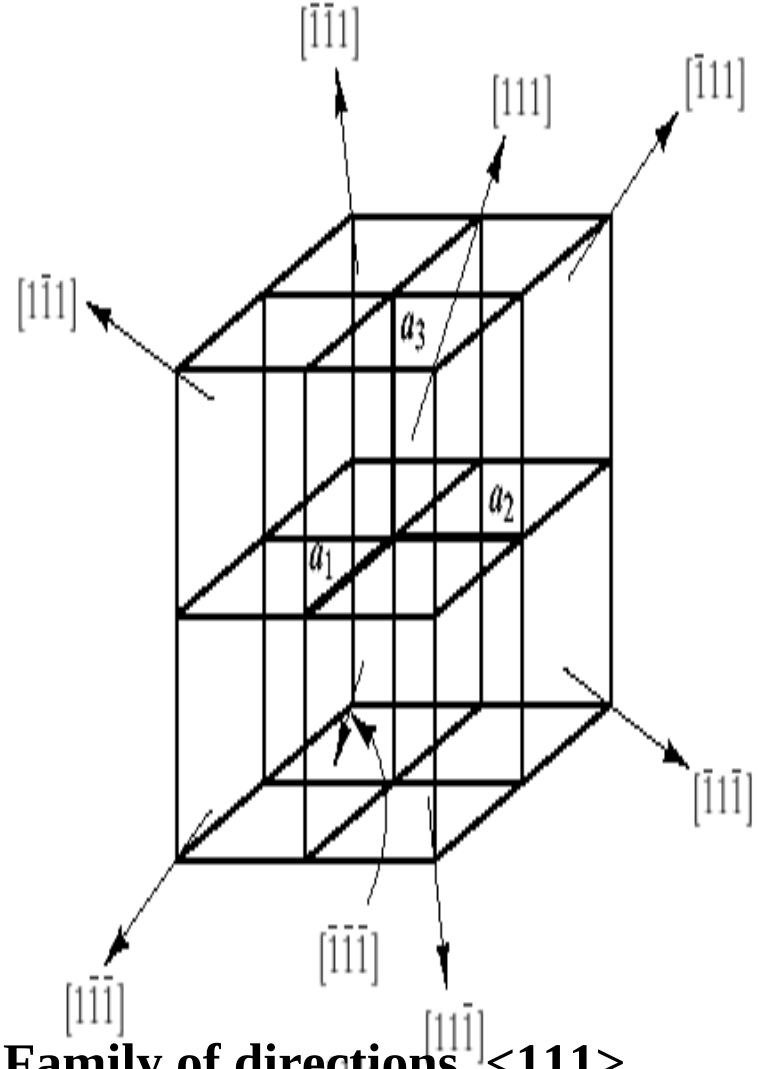
Position	Coordinate
O	0, 0, 0 (Origin)
A	1, 0, 0
B	0, 1, 0
C	0, 0, 1
D	1, 1, 1
E	1, 1, 0
F	0, 1, 1
G	1, 0, 1
H	1/2, 1, 1/2

Miller indices- h,k,l- for naming points in the crystal lattice. The origin has been arbitrarily selected as the bottom left-back corner of the unit cell.

1.2 Positions and Directions



Notation for lattice positions.



Family of directions, <111>, representing all body diagonals for adjacent unit cells in the cubic system.

Miller Indices

Miller indices are a notation for describing directions and labelling planes in lattices and crystals. The basis for determining the index is the unit cell. It is important to be clear about the unit cell being used.

A direction is expressed in terms of its ratio of unit vectors in the form [uvw] where u, v and w are integers. A family of crystallographically equivalent directions is expressed as <uvw>.

A Miller index for a plane is expressed as (hkl), where h, k and l are integers. A family of crystallographically equivalent planes is expressed as {hkl}.

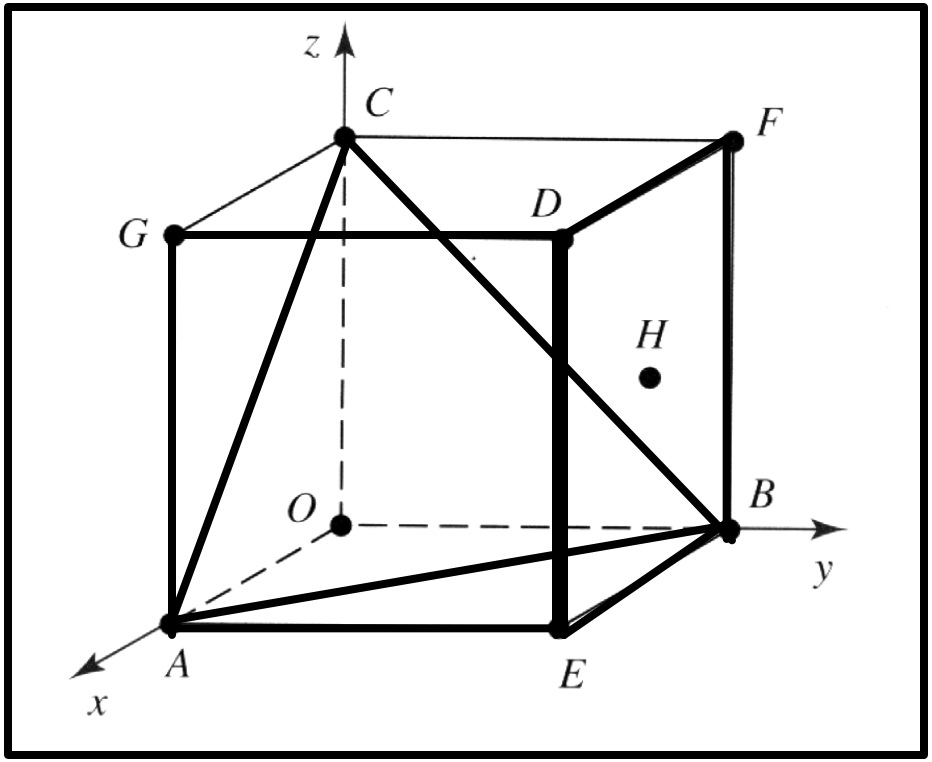
1.2 Planes

1) Identify the locations where the plane intercepts the x, y, z axes as the fractions of the unit cell edge lengths a, b, c.
2) Infinity if the plane is parallel.
3) Take the reciprocal of the intercepts.
4) Clear any fraction but do not reduce to lowest terms.
5) Example: 1/3,1/3,1/3 is (333) not (111)!!!
6) Use parentheses to indicate planes (hkl) again with a hat over the negative indices.
7) Families are indicated by {hkl}

Remember Terminology:
Defined coordinate system: x, y, z
Respective unit cell edge lengths: a, b, c
Direction: Denoted by [uvw]
Family of direction(s): Denoted by: <uvw>
Plane: Denoted by: (hkl)
Family of Plane(s): Denoted by: {hkl}

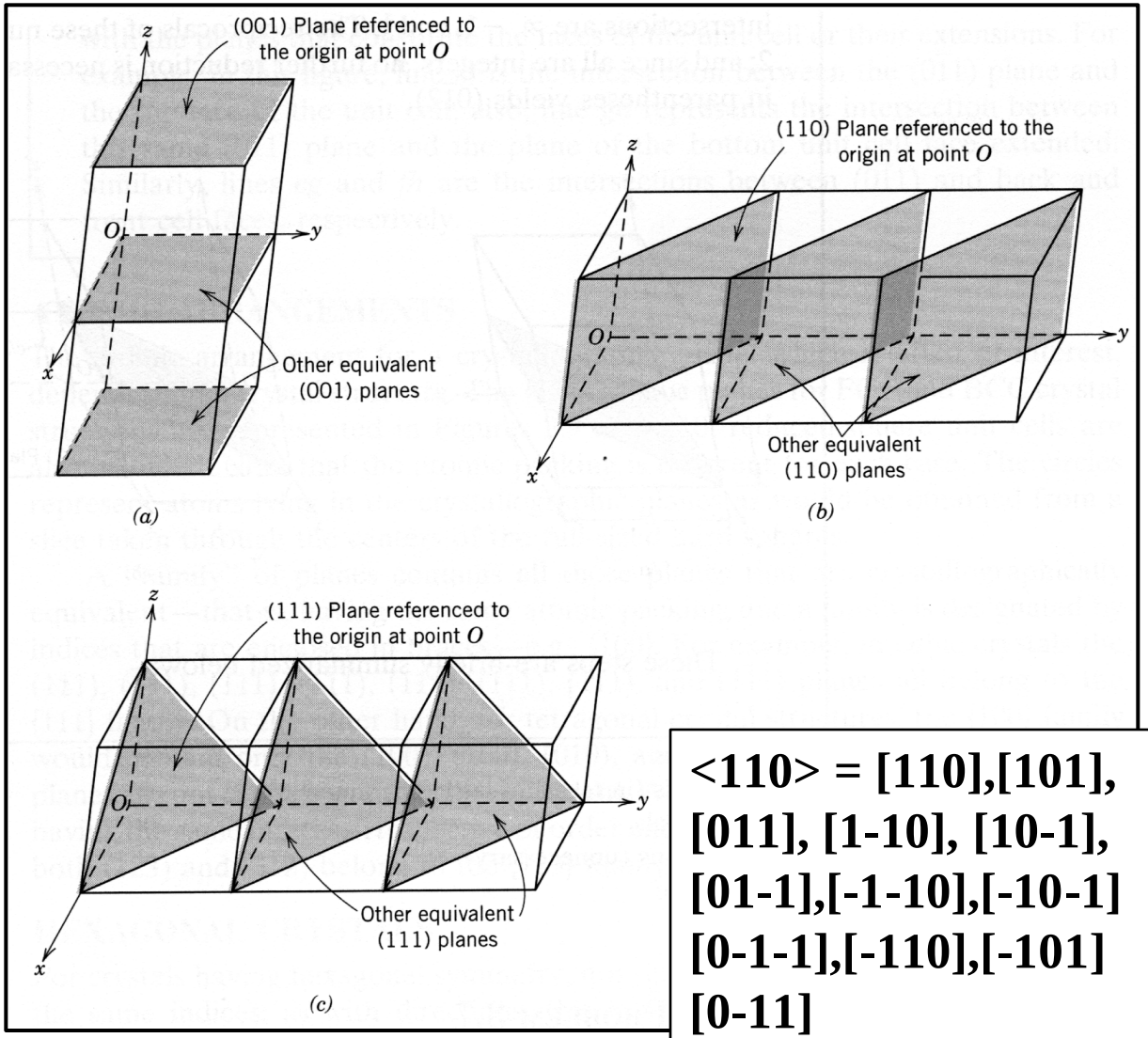
1.2 Planes

( ) ?



1) **Identify the locations where the plane intercepts the x, y, z axes as the fractions of the unit cell edge lengths a, b, c.**
2) **Infinity if the plane is parallel.**
3) **Take the reciprocal of the intercepts.**
4) **Clear any fraction but do not reduce to lowest terms.**
5) **Example: 1/3,1/3,1/3 is (333) not (111)!!!**
6) **Use parentheses to indicate planes (hkl) again with a hat over the negative indices.**
7) **Families are indicated by {hkl}**

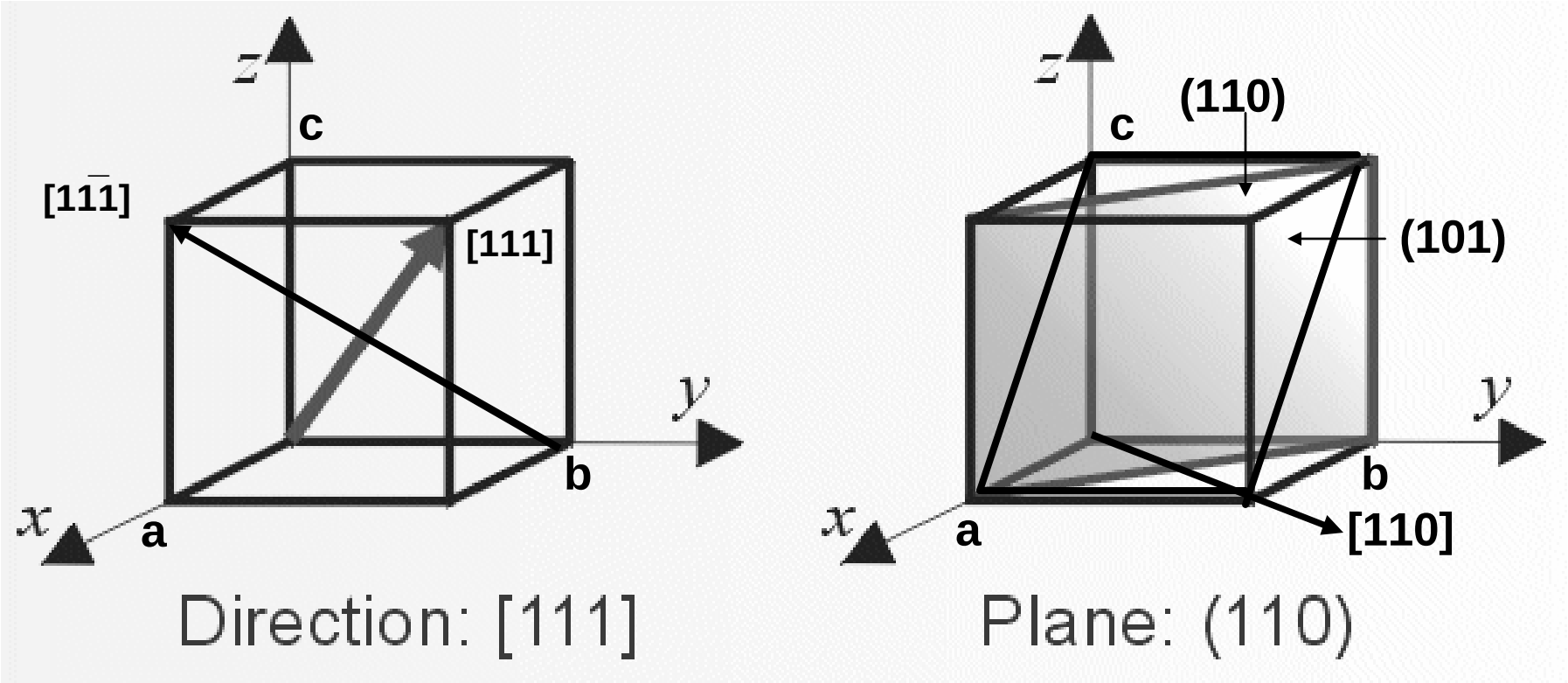
1.2 Planes



<110> = [110],[101], [011], [1-10], [10-1], [01-1],[-1-10],[-10-1] [0-1-1],[-110],[-101] [0-11]

Representation of a series each of (a) (001), (b) (110), and (c) (111) crystallographic planes.

1.2 Indexing of Planes and Directions



[uvw]-one direction, [111]

<uvw> - a family of equivalent directions
<111> - [111], [-111],[1-11] [11-1], etc. total: 8

(hkl) - one plane, (110)

{hkl} - a set of equivalent planes

{110} - ($1\bar{1}0$),(101),(011) (110), etc. 12

• Directions are always perpendicular to their respective planes, i.e. [111]direction is perpendicular to the (111) plane (for cubic systems, not true in all systems) .

• Families of equivalent planes are equal with respect to symmetrical structures, they do not have to be parallel. Equivalent planes must be translated to the correct atomic positions in order to maintain the proper crystal symmetry.

• Families of directions are equivalent in absolute magnitude.

• (222) planes are parallel to the (111) planes but not equal.

• Intercepts for the (222) planes are 1/2,1/2,1/2

• Intercepts for the (333) planes are 1/3,1/3,1/3, remember this is in what we call “reciprocal space”. If you draw out the (333) plane it is parallel to the (111) plane but not equivalent.

1.3 Crystal Structures

- **Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling**

- **The atomic bonding in metals is non-directional Þ no restriction on numbers or positions of nearest-neighbor atoms Þ large number of nearest neighbors and dense atomic packing**

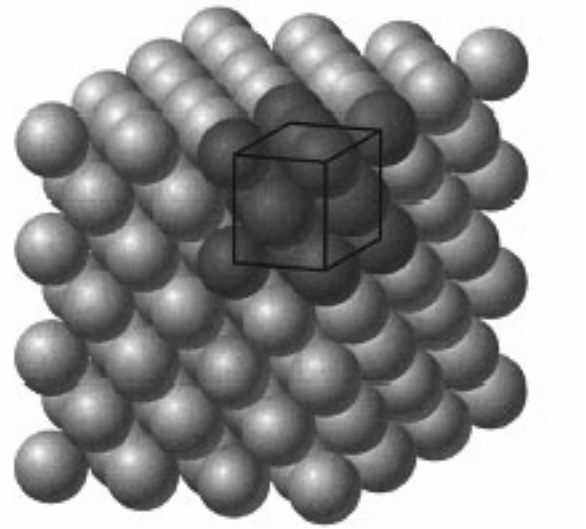
- **Atom (hard sphere) radius, R, defined by ion core radius - typically 0.1 - 0.2 nm**

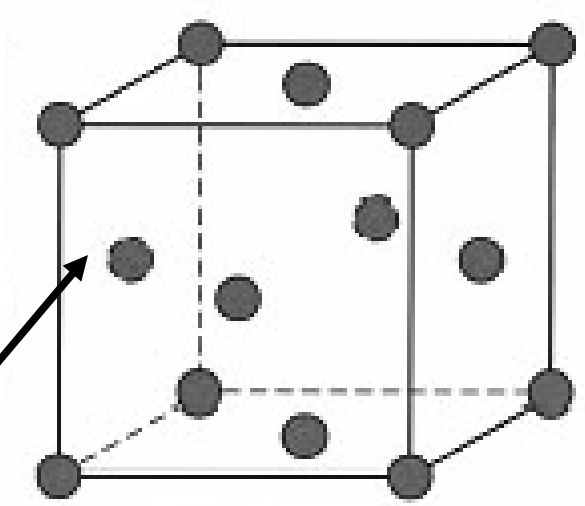
- **The most common types of unit cells are the faced-centered cubic (FCC), the body-centered cubic (BCC) and the hexagonal close-packed (HCP).**

1.3 Crystal Structures

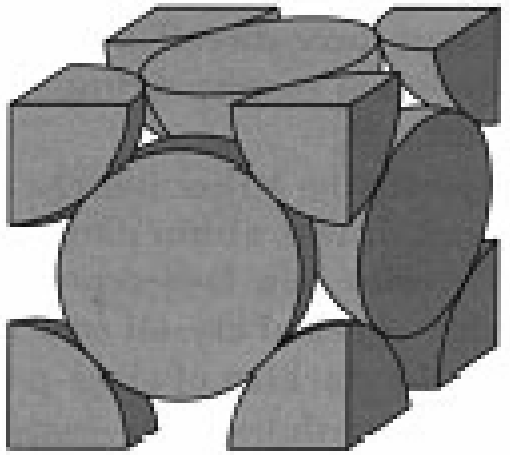
Face-Centered Cubic (FCC) Crystal Structure (I)

- Atoms are located at each of the corners and on the centers of all the faces of cubic unit cell
- Cu, Al, Ag, Au have this crystal structure





Two representations of the FCC unit cell

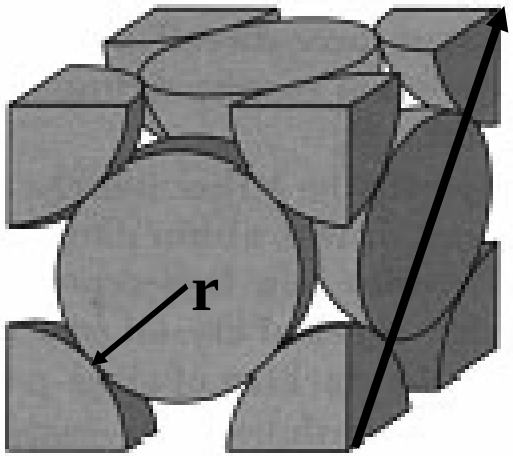


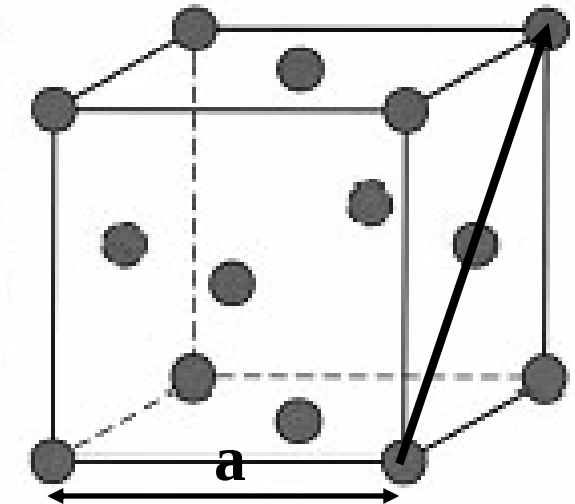
1.3 Crystal Structures

FCC (II)

- The hard spheres or ion cores touch one another across a face diagonal ⇒ the cube edge length, **a= 2rÖ2 (or 4r/ Ö2)**
- **The coordination number, CN** = the number of closest neighbors to which an atom is bonded = number of touching atoms, **CN = 12**
- **Number of atoms per unit cell, n = 4**. In FCC unit cell we have: 6 face atoms shared by two cells: 6 x 1/2 = 3

  8 corner atoms shared by eight cells: 8 x 1/8 = 1
- **Atomic packing factor, APF** = fraction of volume occupied by hard spheres = (Sum of atomic volumes)/(Volume of cell) **= 0.74**

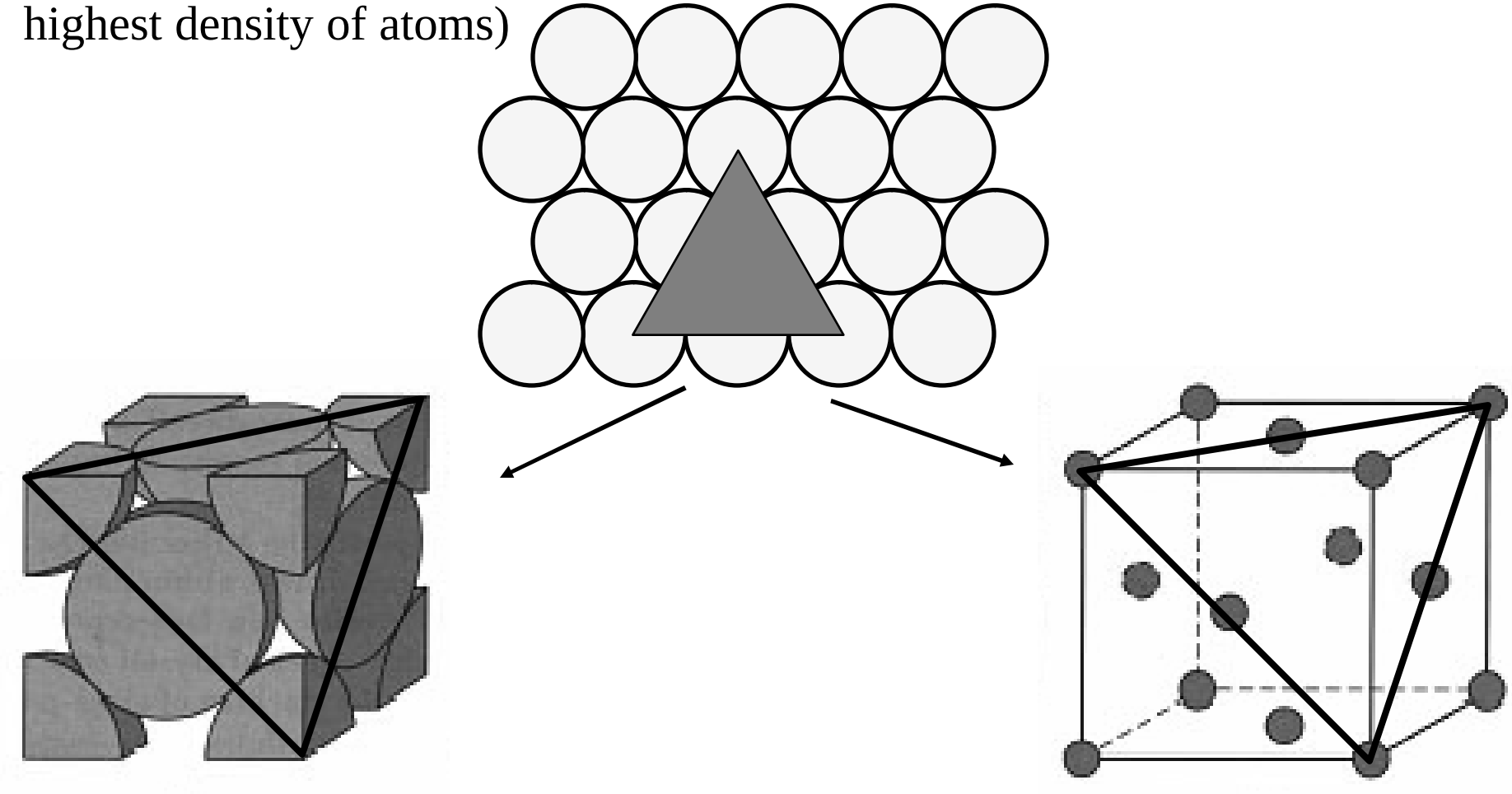




1.3 Crystal Structures

FCC (III)

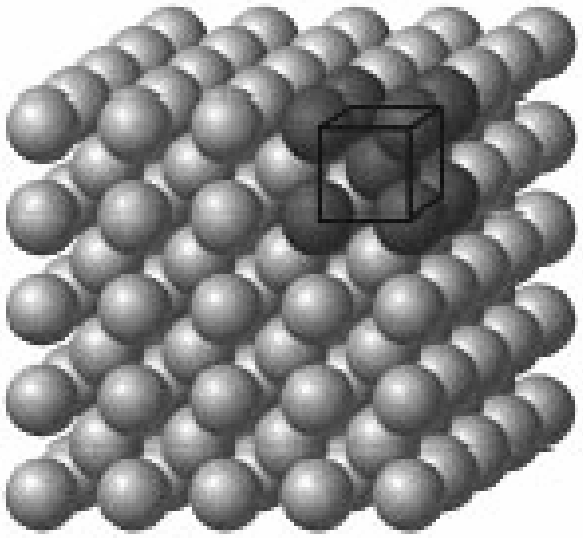
- Corner and face atoms in the unit cell are equivalent
- FCC crystal has APF of 0.74, the maximum packing for a system equal-sized spheres ⇒ FCC is a **close-packed structure**
- FCC can be represented by a stack of **close-packed planes** (planes with highest density of atoms)

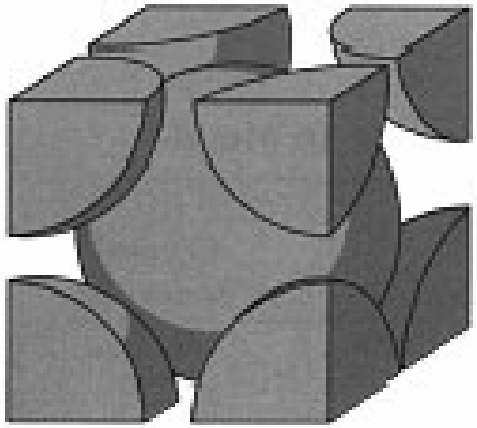


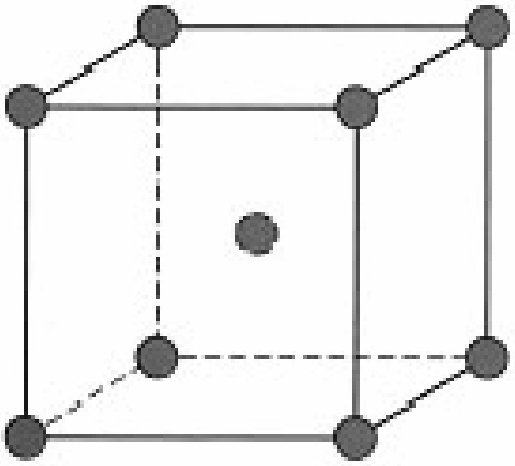
1.3 Crystal Structures

Body-Centered Cubic (BCC) Crystal Structure (I)

Atom at each corner and at center of cubic unit cell: Cr, α-Fe, Mo

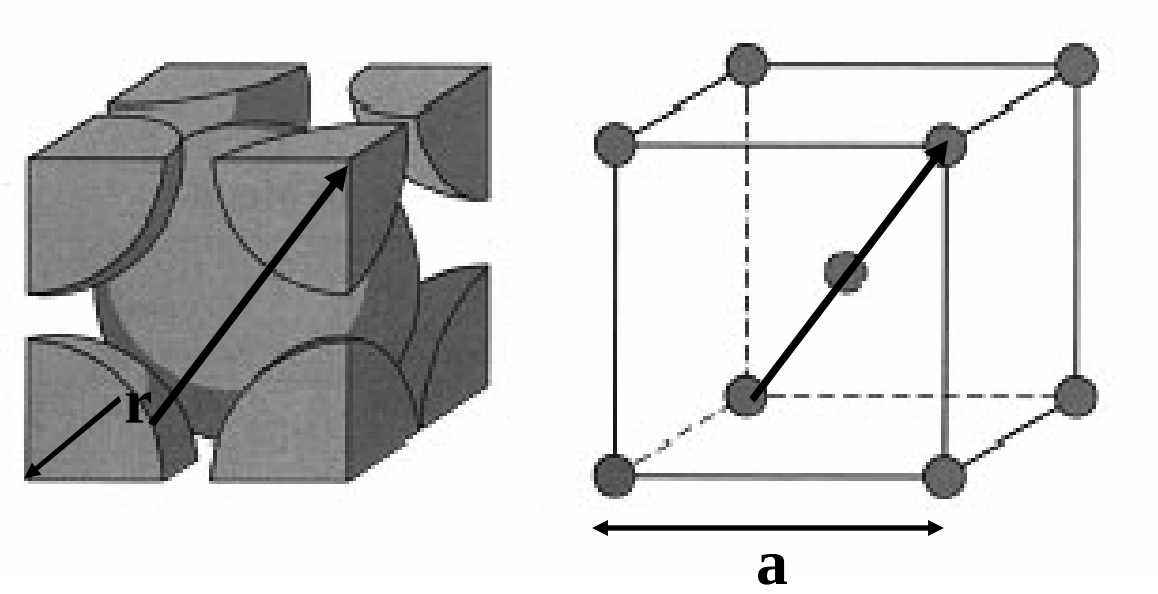






1.3 Crystal Structures

BCC (II)



- The hard spheres touch one another along cube diagonal ⇒ the cube edge length, **a= 4r/Ö3**
- **The coordination number, CN = 8**
- **Number of atoms per unit cell, n = 2**

  Center atom (1) shared by no other cells: 1 x 1 = 1

  8 corner atoms shared by eight cells: 8 x 1/8 = 1
- **Atomic packing factor, APF = 0.68**
- Corner and center atoms are equivalent

2.0 Basic Principles

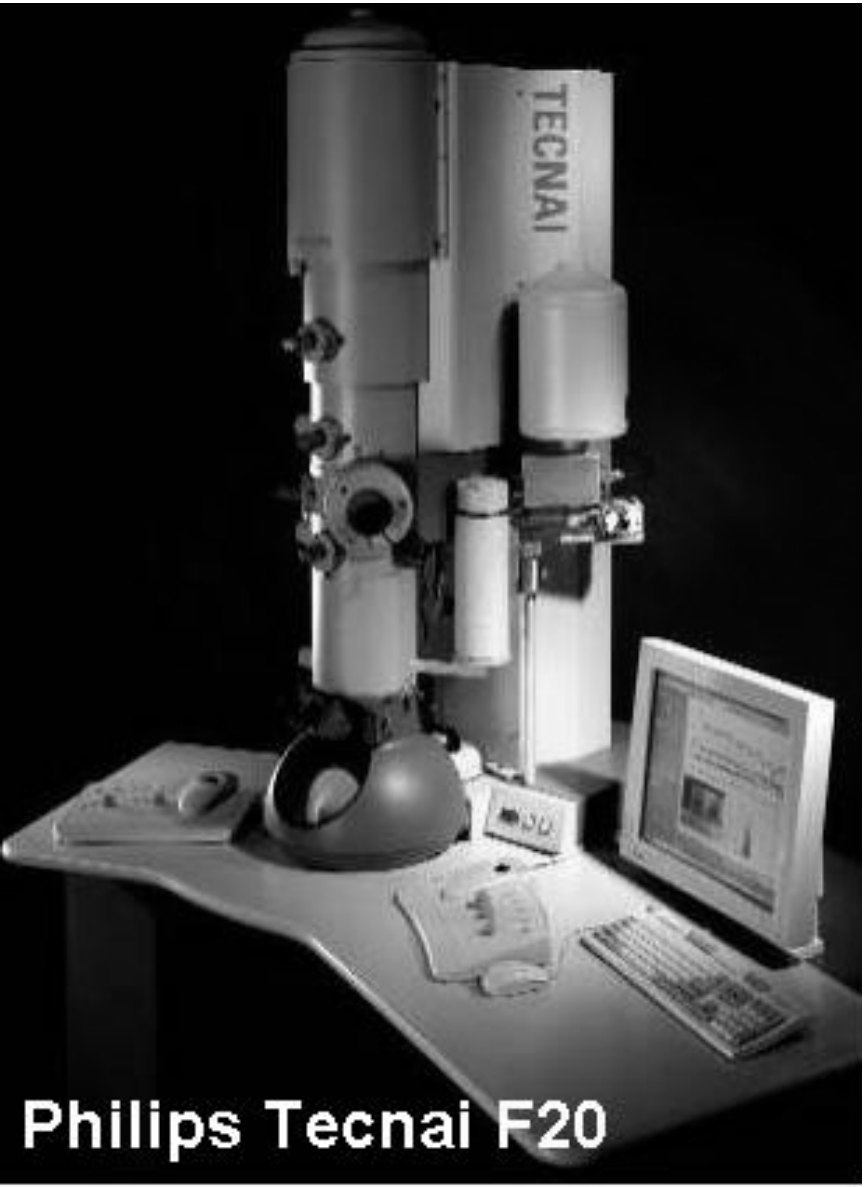
Microscopy (TEM)/Scanning Transmission Electron Microscopy (STEM)

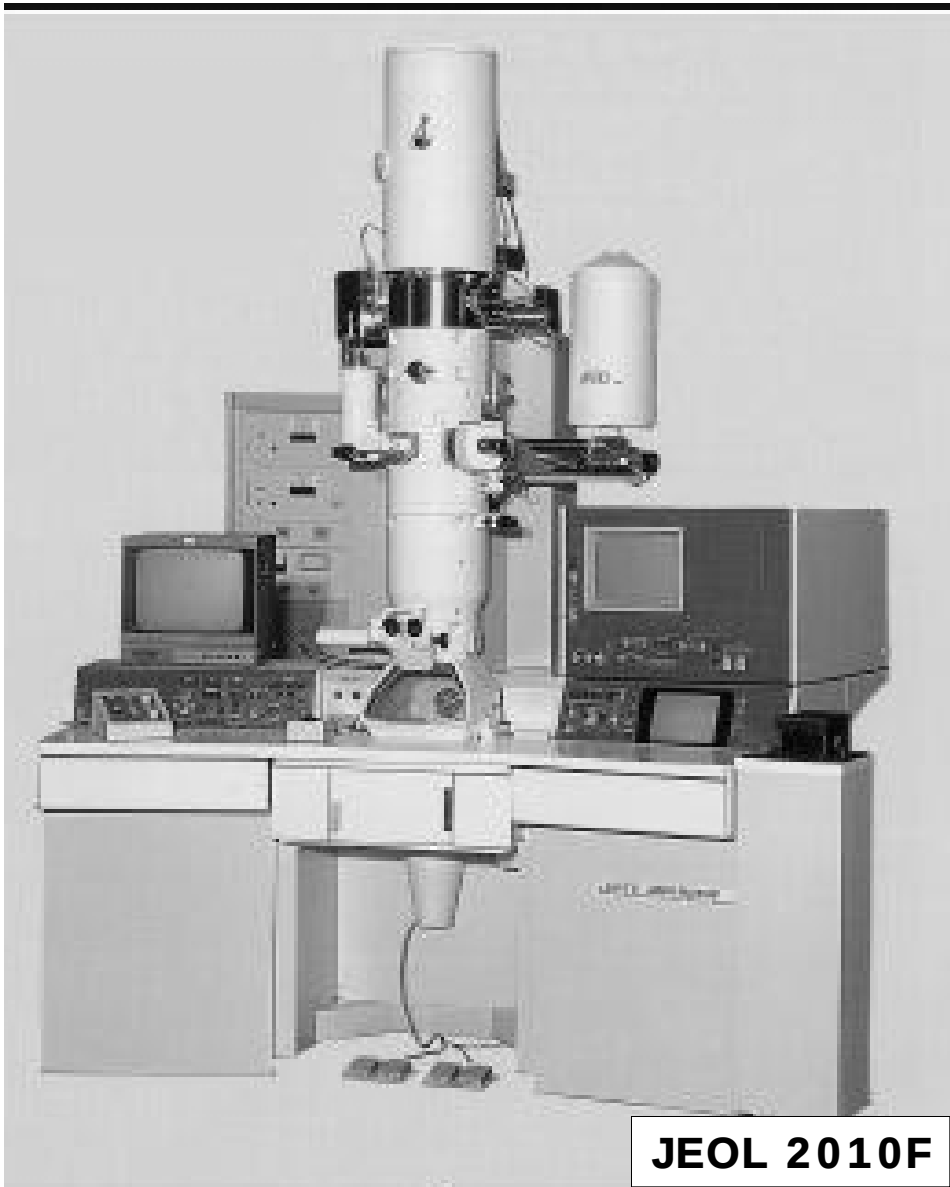
- **What is a TEM?**
- **Example instruments: JEOL and Philips**
- **How it works-gun, lenses, specimen**
- **Why use electrons?**
- **What can a TEM do?**
  (i) Imaging and diffraction
  (ii) Imaging-diffraction and phase contrast diffraction
  (iii) Chemical analysis

What is a TEM?

In a typical TEM a static beam of electrons at 100 - 400kV accelerating voltage illuminate a region of an electron transparent specimen which is immersed in the objective lens of the microscope. The transmitted and diffracted electrons are recombined by the objective lens to form a diffraction pattern in the back focal plane of that lens and a magnified image of the sample in its image plane. A number of intermediate lenses are used to project either the image or the diffraction pattern onto a fluorescent screen for observation. The screen is usually lifted and the image formed on photographic film for recording purposes.

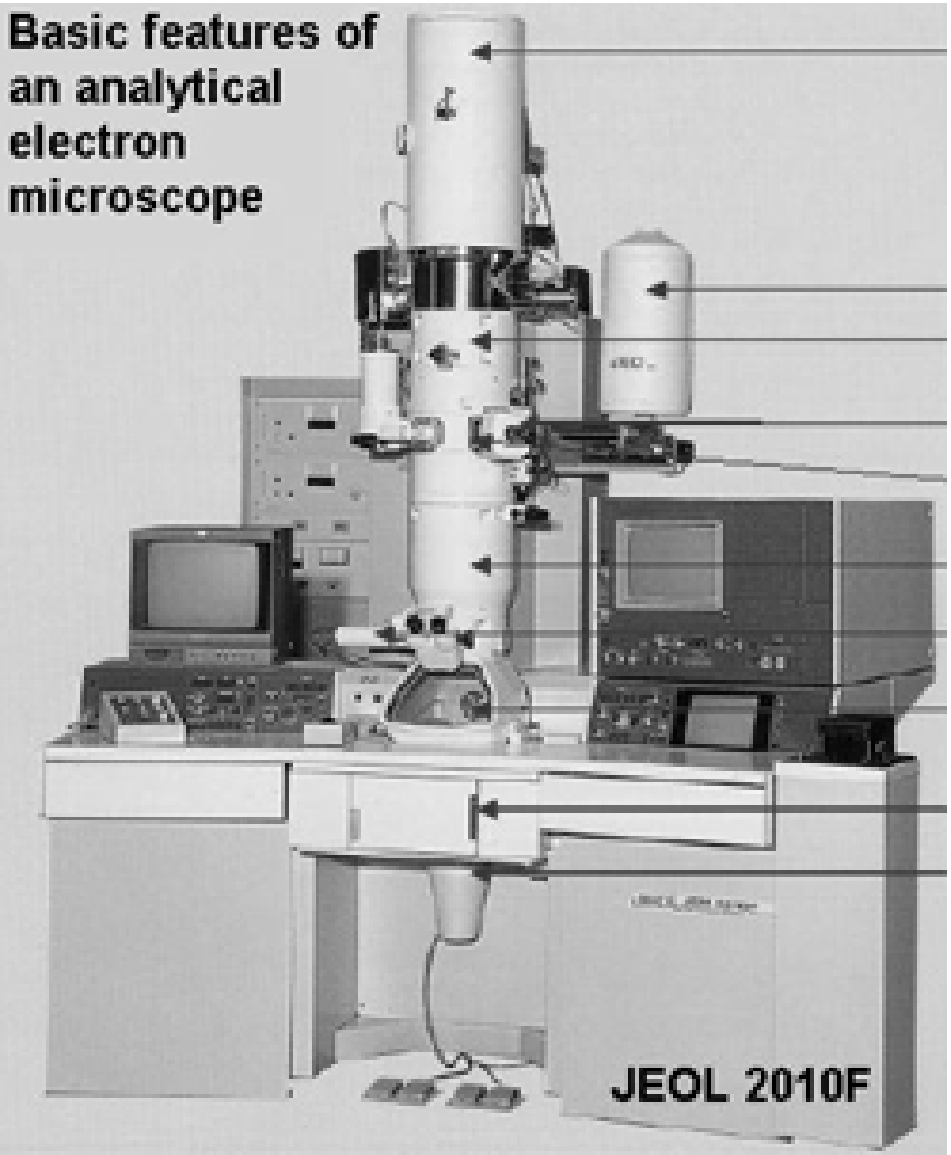
Modern TEMs





2.1 The Microscope Column

Basic features of An Analytical TEM



Electron Gun

EDS Detector
Condenser Lens

Specimen Holder
Objective Lens

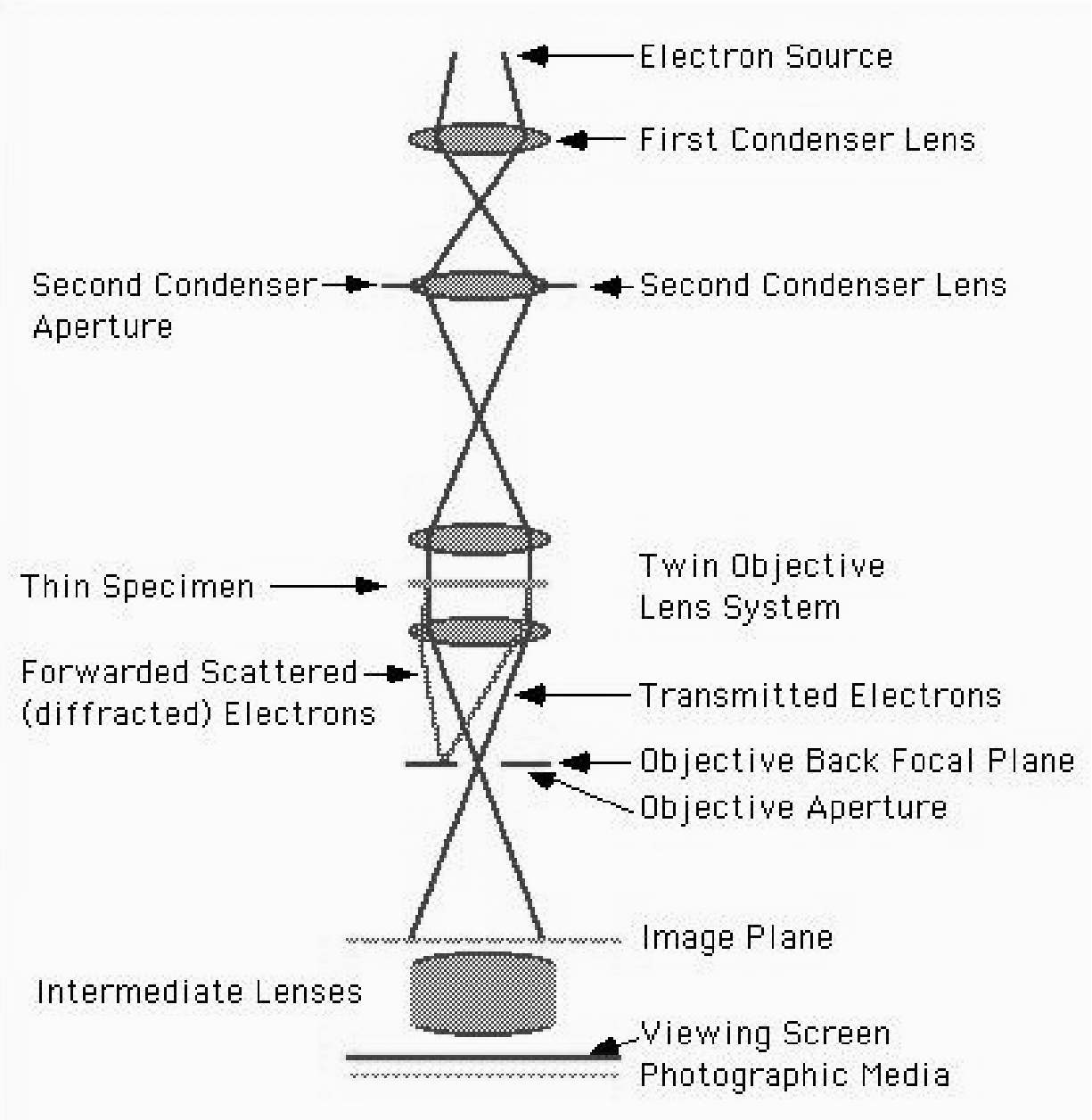
Magnifying Lenses

HAADF Detector
Viewing Chamber

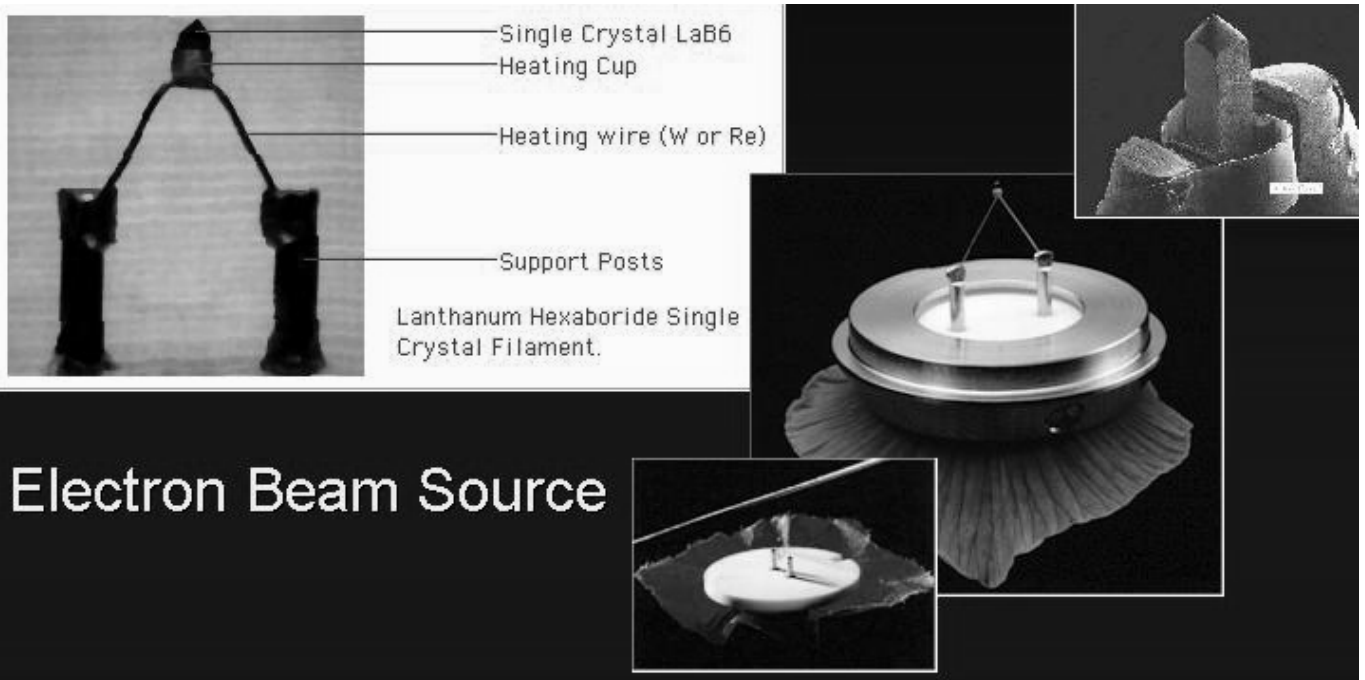
Camera Chamber

STEM Detector or EELS

Electron Optics of a TEM



Electron beam Source

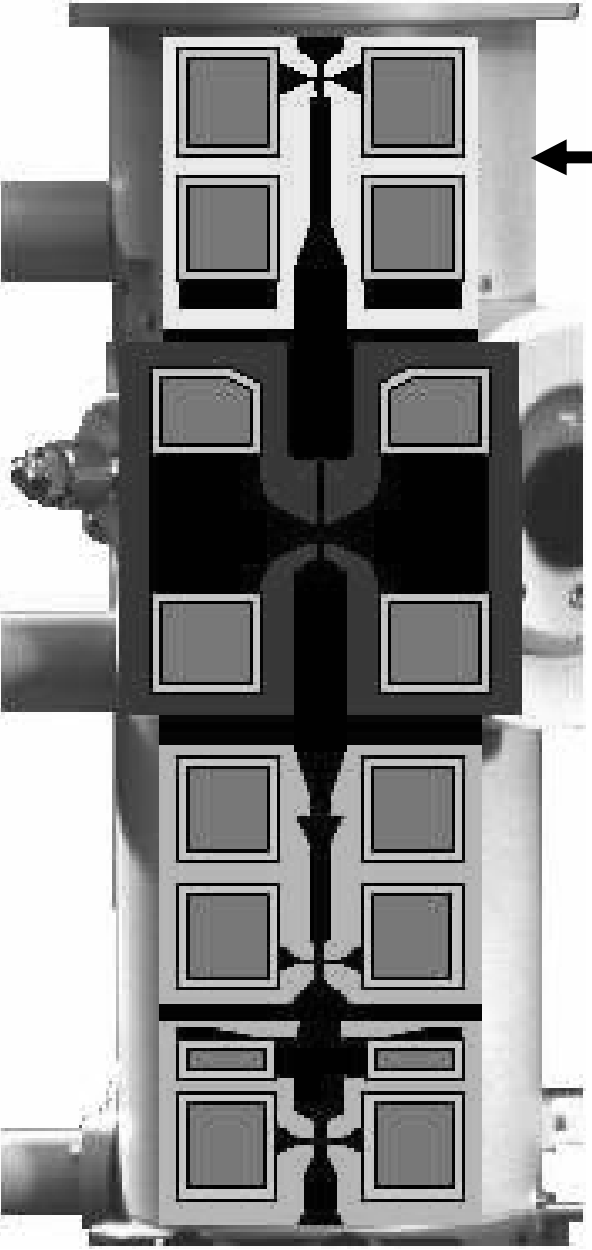


W Filament - Current density ~10A/cm^2, probe size ~5.0nm

LaB_6 - Current density ~10^3A/cm^2, probe size ~1.5nm

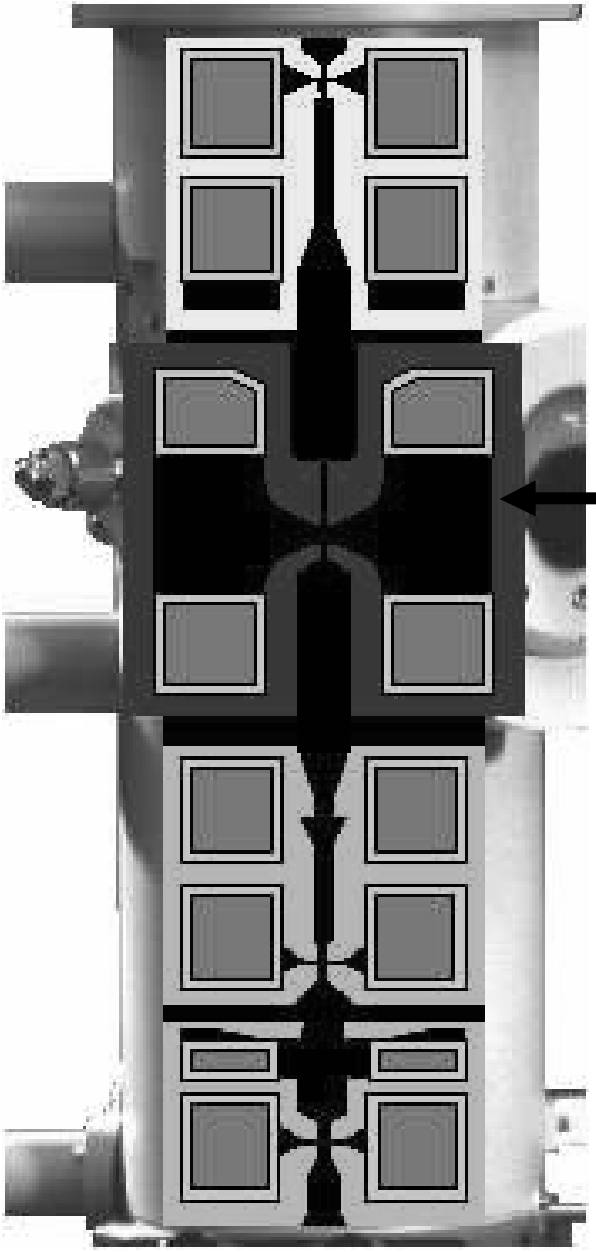
FEG - Current density ~10^5A/cm^2 , probe size ~<1.0nm

The Lenses in a TEM



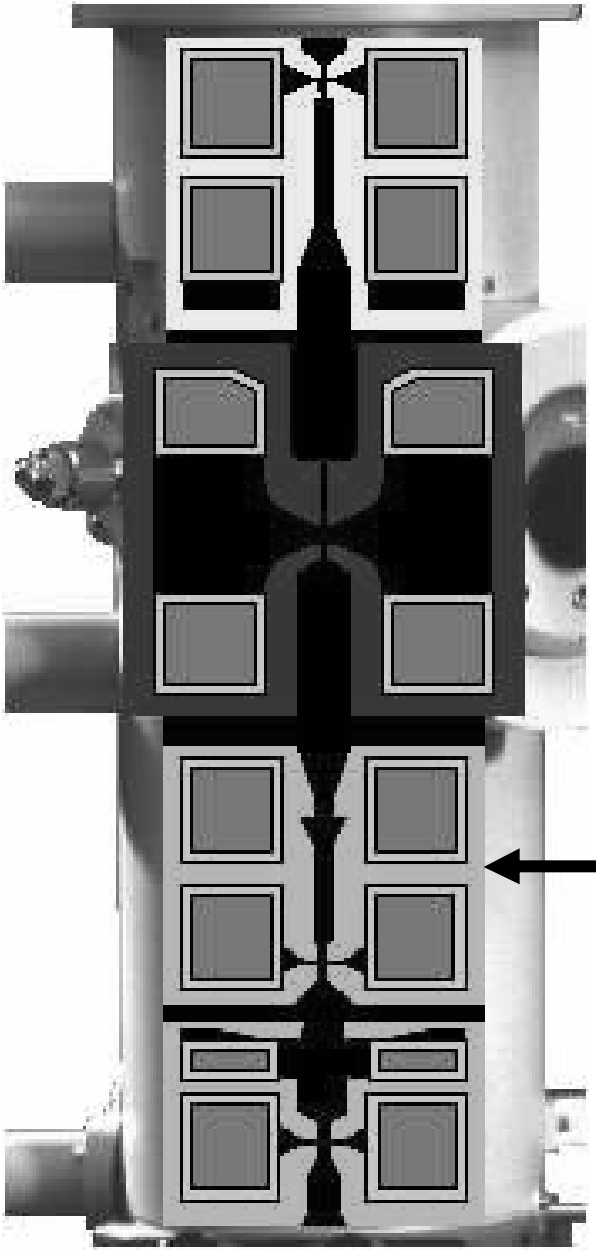
Condenser lenses(two)-control how strongly beam is focused (condensed) onto specimen. At low Mag. Spread beam to illuminate a large area, at high Mag. strongly condense beam.

The Lenses in a TEM



Objective lens-focus image (image formation) and contribute most to the magnification of the image.

The Lenses in a TEM



Four lenses form magnification system-determine the magnification of the microscope. Whenever the magnification is changed, the currents through these lenses change.

Q: Why Electrons?
A: Resolution!

In the expression for the resolution

(Rayleigh's Criterion)

$r = 0.61\lambda/n\sin\alpha$

λ-wavelength, $\lambda = [1.5/(V+10^{-6}V^2)]^{1/2}$ nm

V-accelerating voltage, n-refractive index

α-aperture of objective lens, very small in TEM

$\rightarrow \sin\alpha \rightarrow \alpha$ and so $r = 0.61\lambda/\alpha$ α~0.1 radians

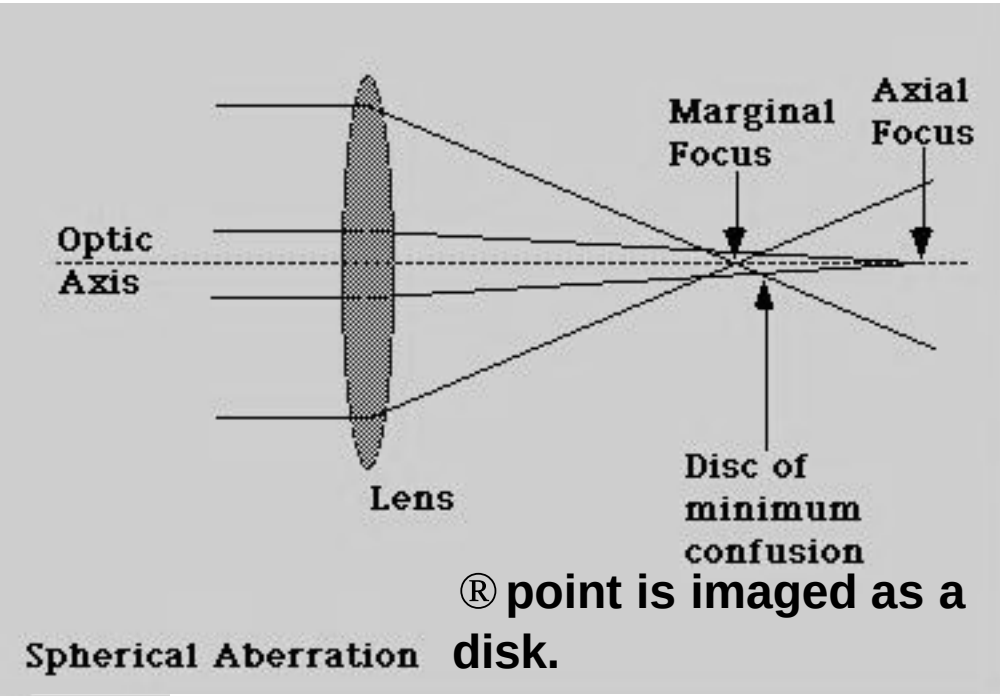
Green Light
λ~400nm
n~1.7 oil immersion
r~150nm (0.15μm)

200kV Electrons
λ~0.0025nm
n~1 (vacuum)
r~0.02nm (0.2Å)

1/10th size of an atom!
UNREALISTIC! WHY?

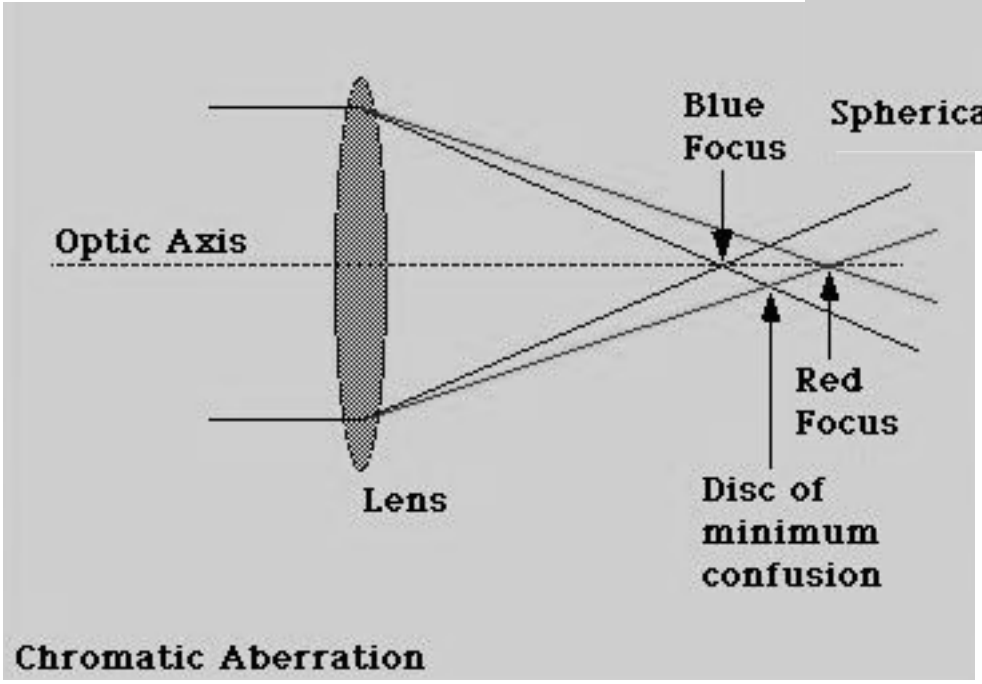
Resolution is Limited by Lens Aberrations

Chromatic aberration is caused by the variation of the electron energy and thus electrons are not monochromatic.



Spherical Aberration

® point is imaged as a disk.



Chromatic Aberration

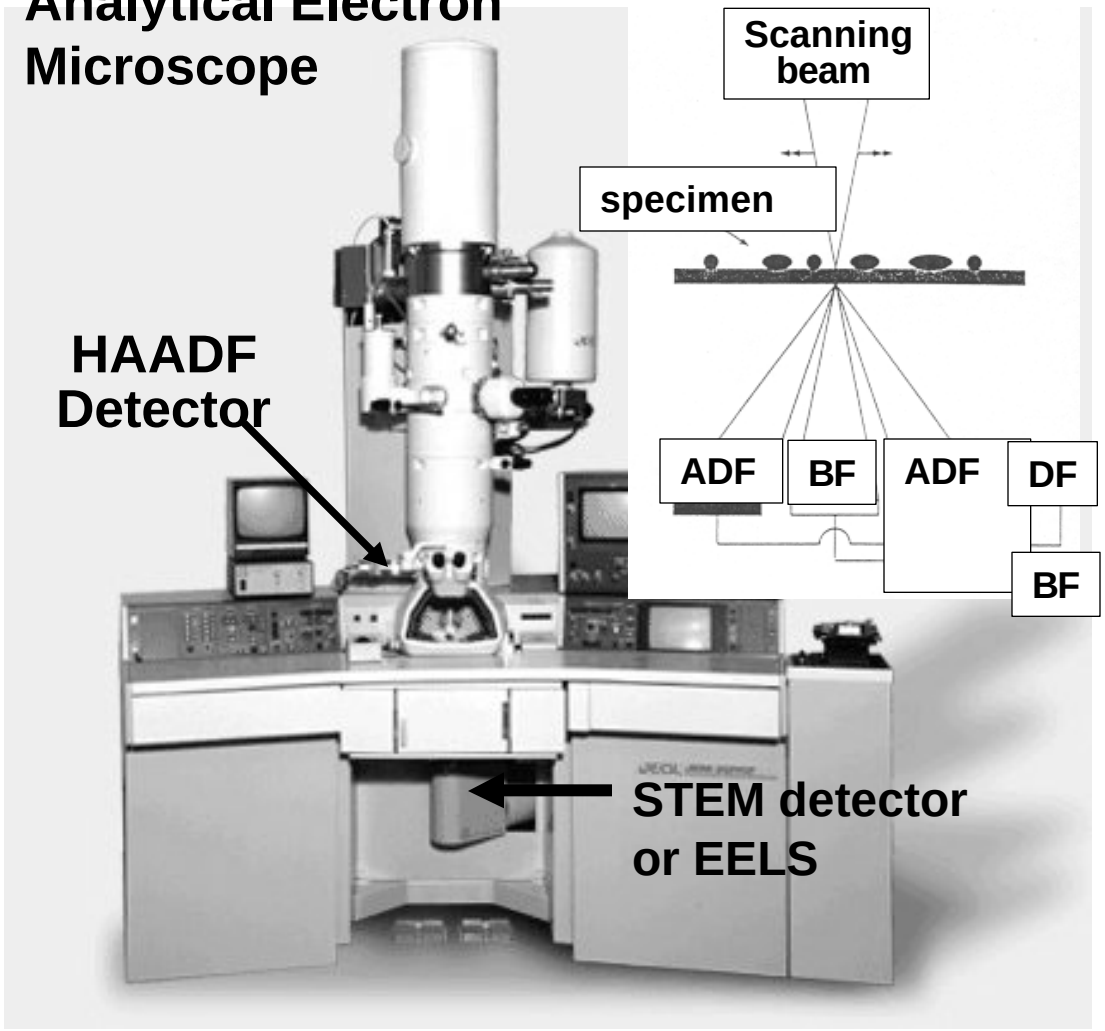
Spherical aberration is caused by the lens field acting inhomogeneously on the off-axis rays.

$$r_{min} \approx 0.91(C_s \lambda^3)^{1/4}$$

Practical resolution of microscope. C_s– coefficient of spherical aberration of lens (~mm)

Scanning Transmission Electron Microscopy (STEM)

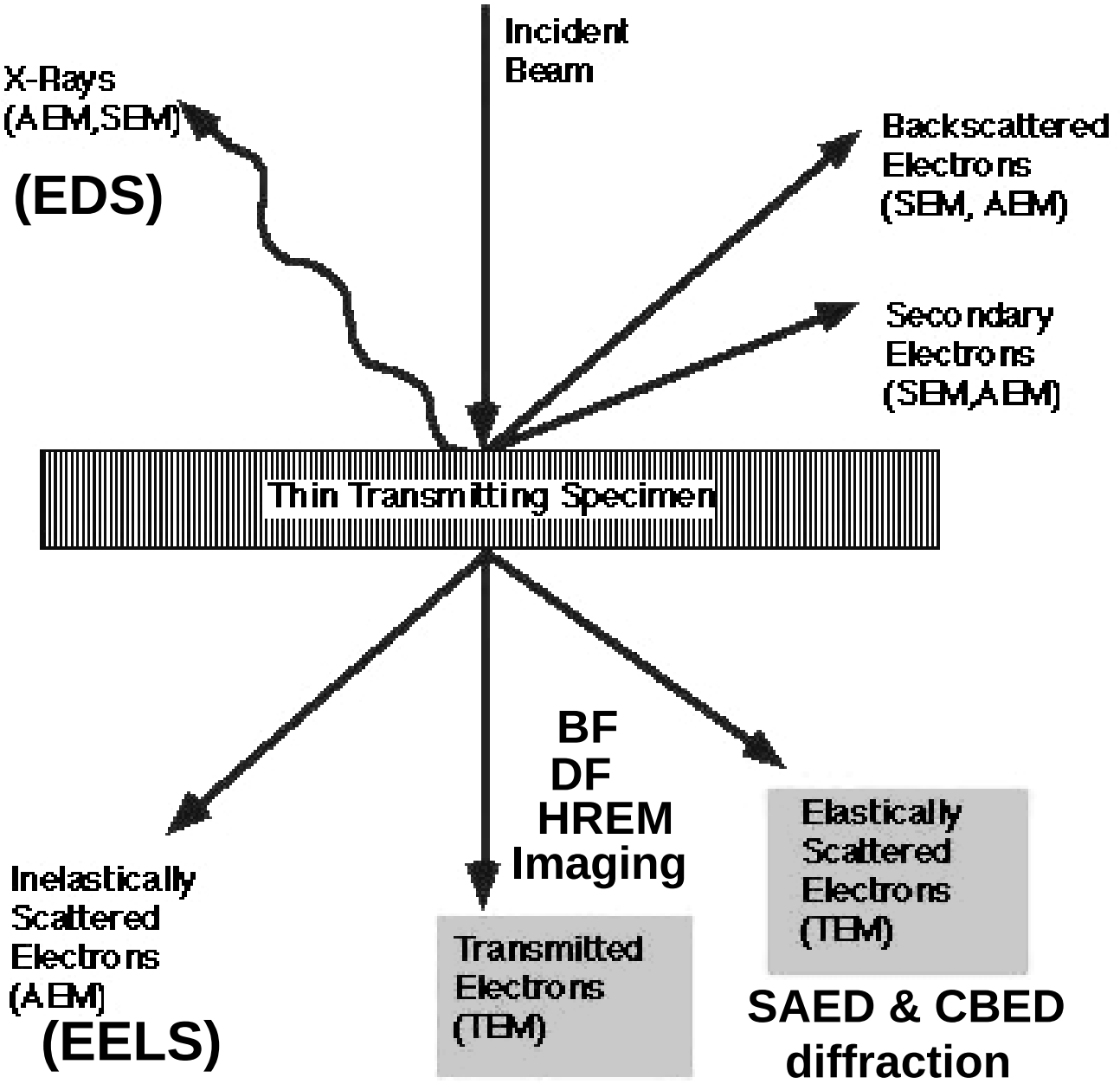
JEOL 2000FX Analytical Electron Microscope



In STEM, the electron beam is rastered (scan coil) across the surface of a sample in a similar manner to SEM, however, the sample is a thin TEM section and the diffraction contrast image is collected on a solid-state (ADF) detector.

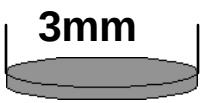
HAADF-high angle annular dark-field

2.2 Beam and Specimen Interaction



2.3 Conventional Specimen Preparation

Ion-milling a ceramic

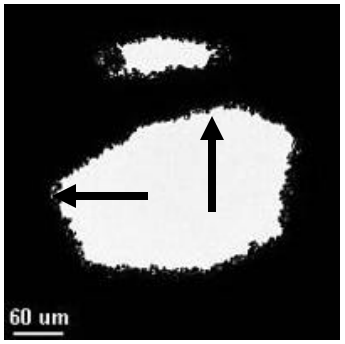


Ultrasonic cut grind

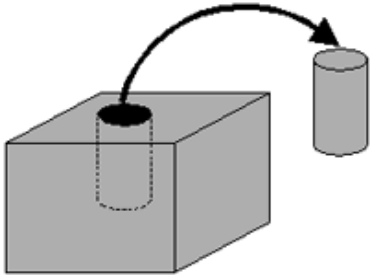
Dimple center part of disk to ~5-10㎜

Ar (4-6keV, 1mm A)

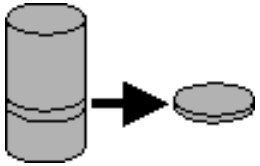
ion-mill until a hole appears in disk



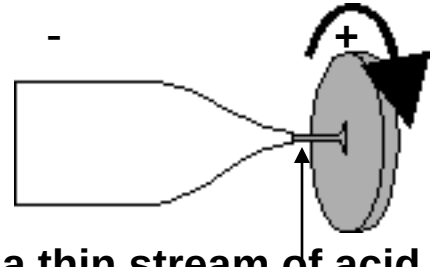
Jet-polishing metal



Drill a 3mm cylinder

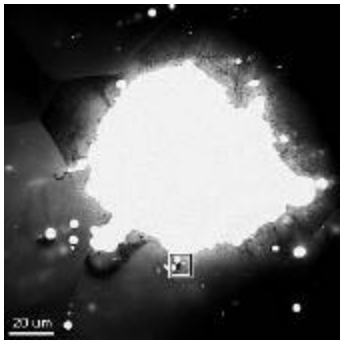


Cut into disks and grind



a thin stream of acid

A disk is mounted in a jet-polishing machine and is electro-polished until a small hole is made.



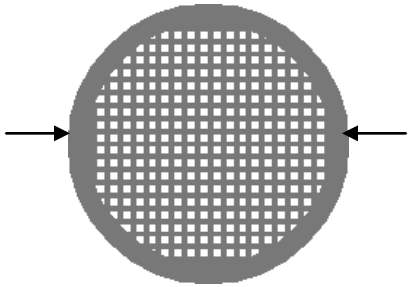
Ultramicrotomy-using a (diamond) knife blade

Mainly for sectioning biological materials.

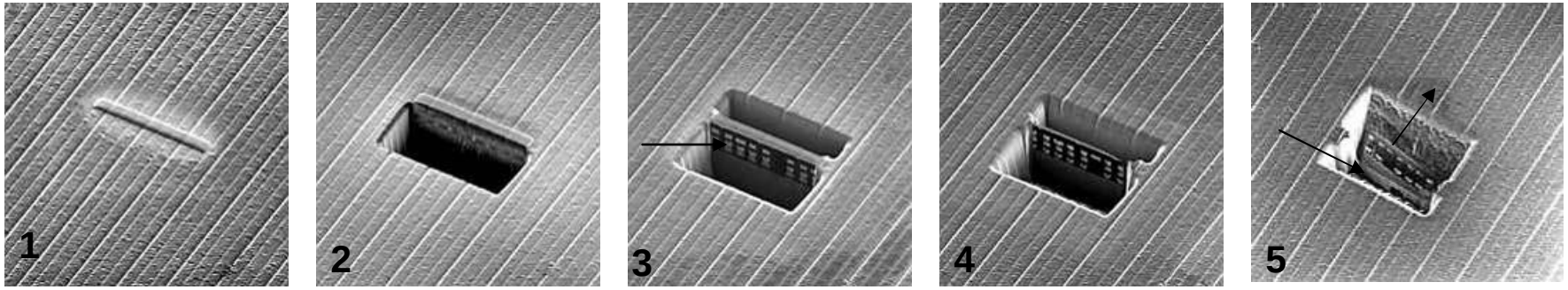
To avoid ion-milling damage ultramicrotome can also be used to prepare ceramic TEM specimens.

Specimen Preparation on Grids

Dispersing crystals or powders on a carbon film on a grid



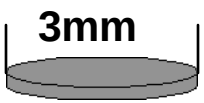
Making a semiconductor specimen with a Focused Ion Beam (FIB)



1. a failure is located and a strip of Pt is placed as a protective cover.
2. On one side of the strip a trench is milled out with the FIM.
3. The same is done on the other side of the strip (visible structure).
4. The strip is milled on both sides and then the sides connecting the strip to the wafer are cut through.
5. The strip is tilted, cut at the bottom and deposited on a TEM grid.

Conventional Specimen Preparation

Ion-milling a ceramic

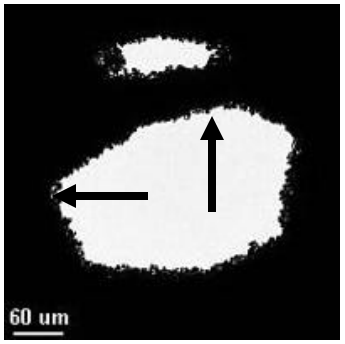


Ultrasonic cut grind

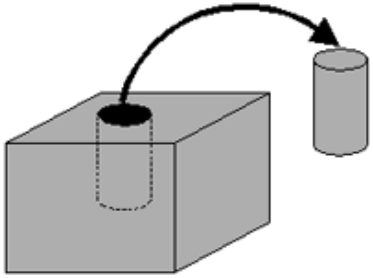
Dimple center part of disk to ~5-10㎜

Ar (4-6keV, 1mm A)

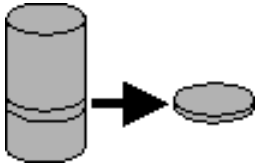
ion-mill until a hole appears in disk



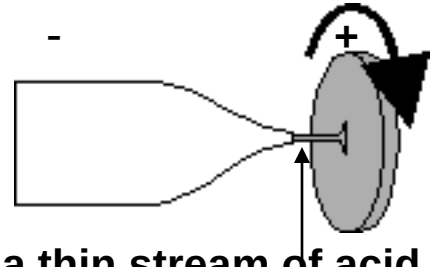
Jet-polishing metal



Drill a 3mm cylinder



Cut into disks and grind



a thin stream of acid

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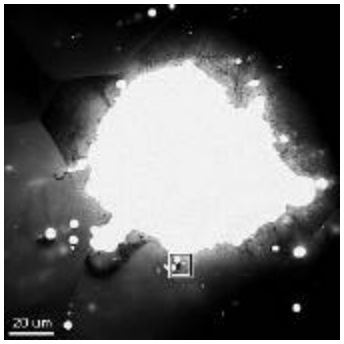


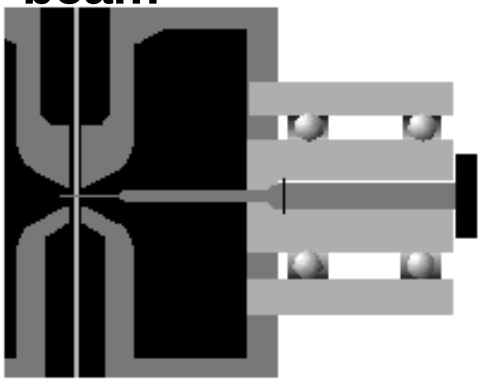
Ultramicrotomy-using a (diamond) knife blade

Mainly for sectioning biological materials.

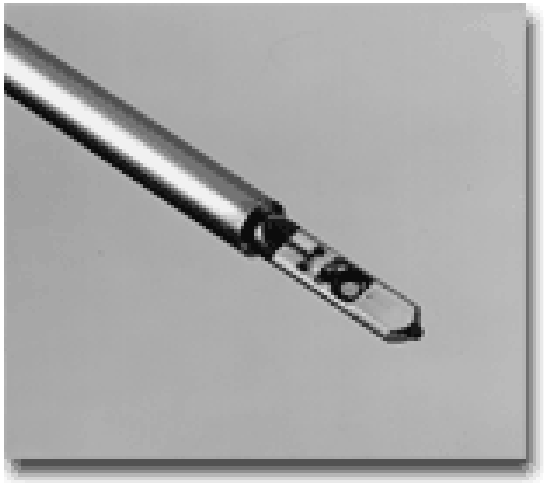
To avoid ion-milling damage ultramicrotome can also be used to prepare ceramic TEM specimens.

2.4 Specimen Holders

Rotation, tilting, heating, cooling and straining

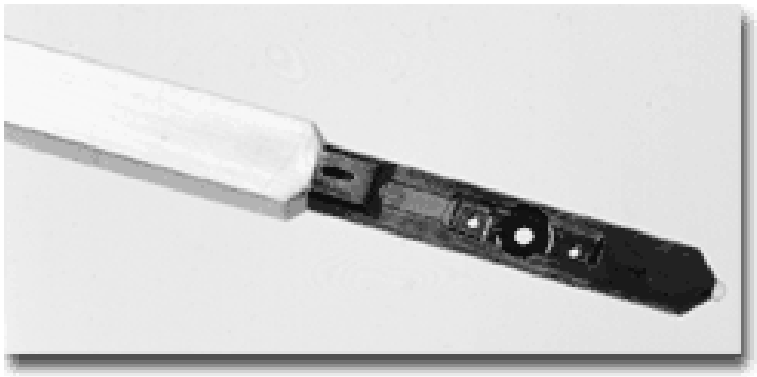


a split pole piece objective lens



Double tilt heating

Twin specimen holder



Heating and straining

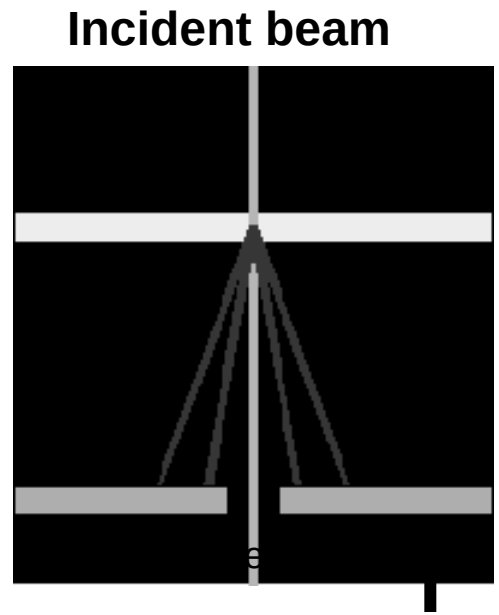
3.0 Imaging

Two principal kinds:

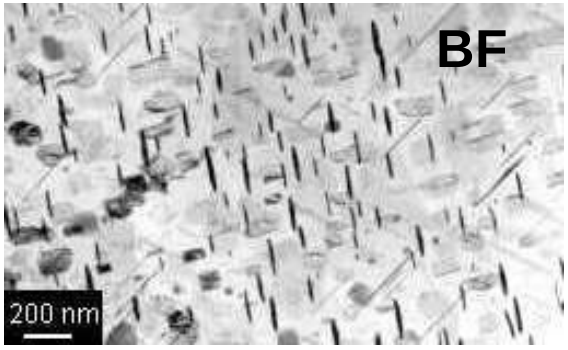
• Diffraction contrast imaging - BF and DF imaging
Use either an non-diffracted or diffracted beam and remove all other beams from the image by use of an objective aperture

• Phase contrast or high resolution imaging *HREM*
Use all of the diffracted and non diffracted beams (by using a large objective aperture or none at all) and add them back together, phase and intensity to form a phase contrast image.

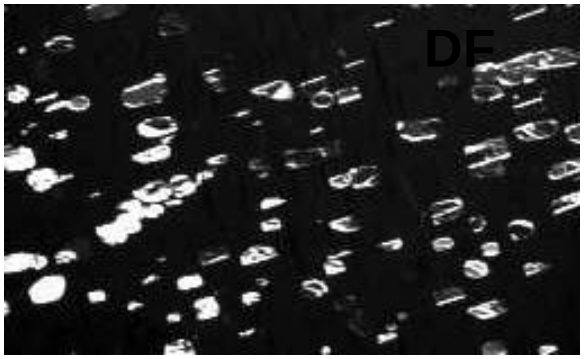
Bright Field (BF) and Dark Field (DF) Imaging



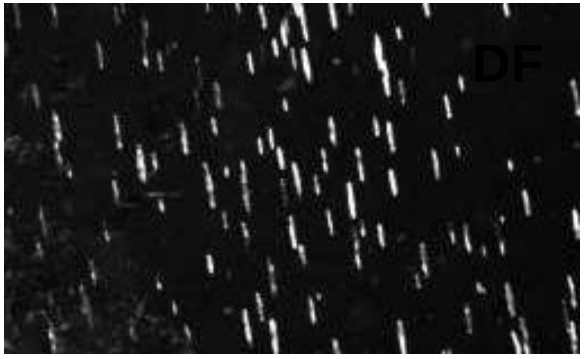
In BF imaging - only the transmitted beam is allowed to pass objective aperture to form images, mass-thickness contrast



DF imaging: Only diffracted beams are allowed to pass the aperture to form images.

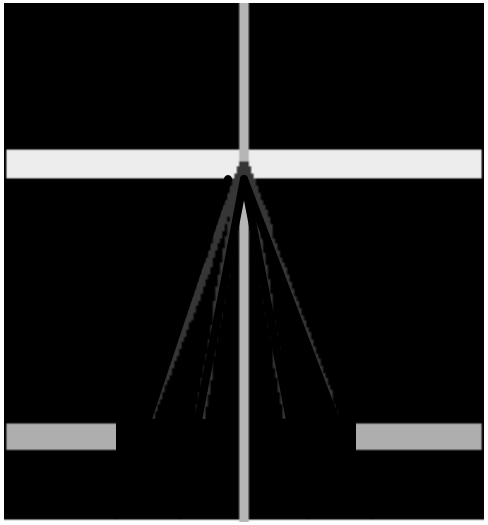


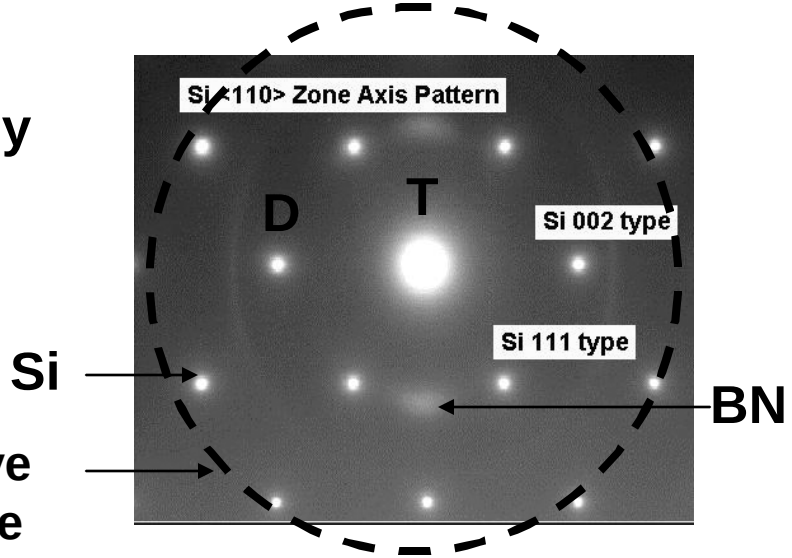
Particles in Al-Cu Alloy. Thin platelets ll e Vertical, dark Particles ^e.



Phase Contrast Imaging

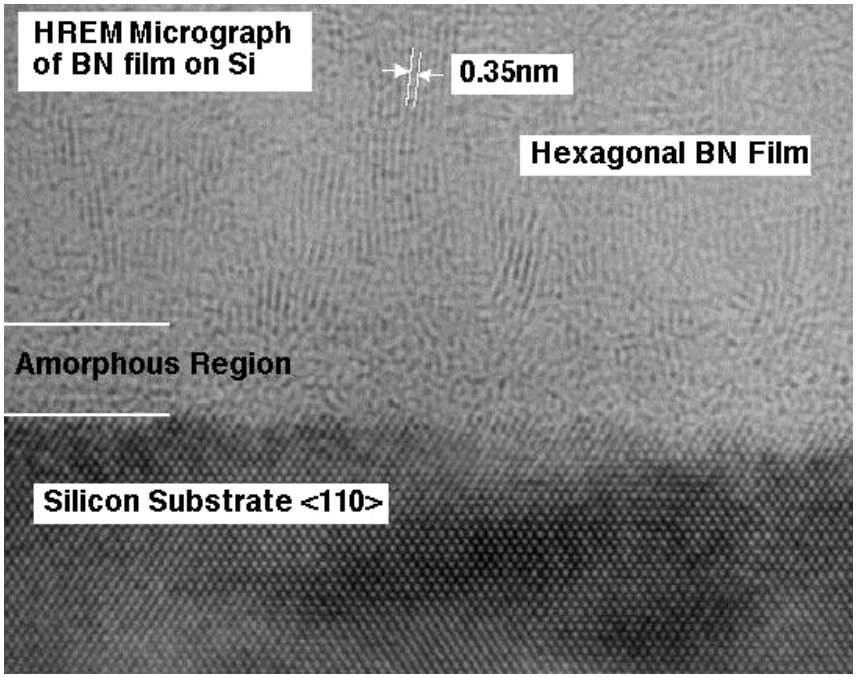
High Resolution Electron Microscopy (HREM)



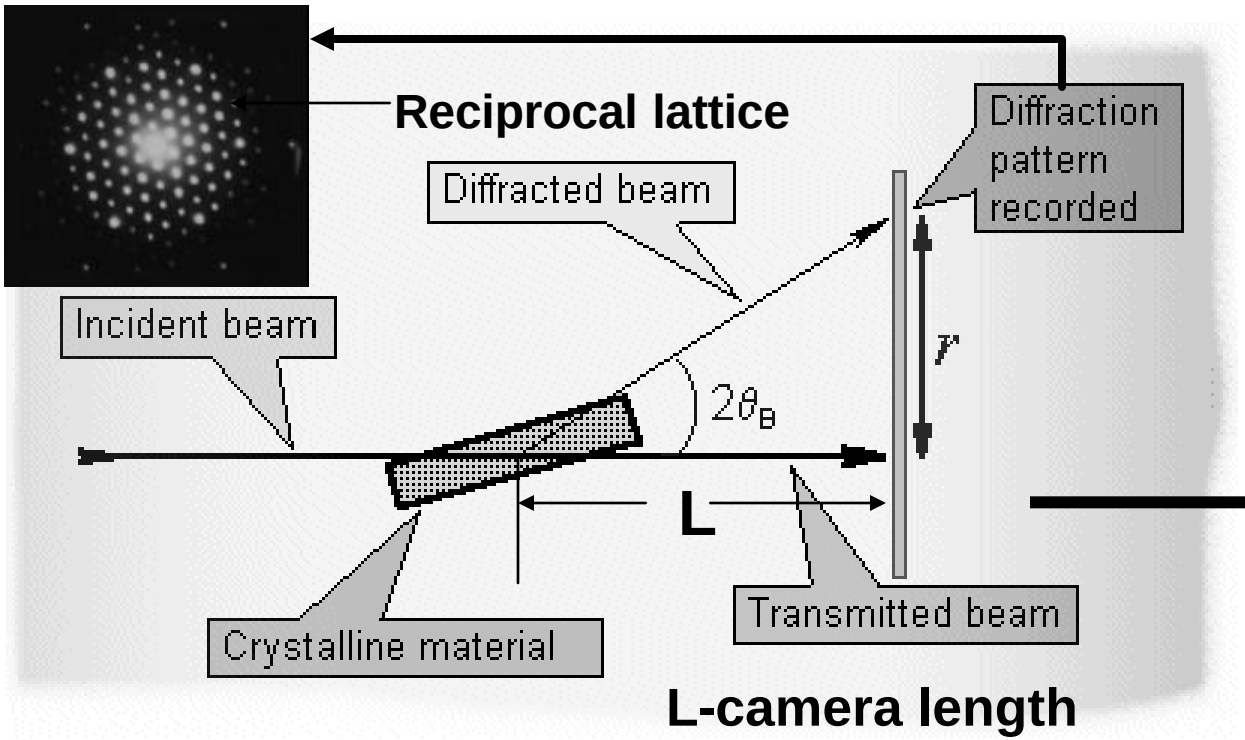


Electron diffraction pattern recorded From both BN film on Si substrate.

Use a large objective aperture. Phases and intensities of diffracted and transmitted beams are combined to form a phase contrast image.



Basic Features of Electron Diffraction



L-camera length

$\lambda = 2d\sin\theta$

λ =0.037Å (@100kV)

θ=0.26° if d=4Å

$\lambda = 2d\theta$

r/L=sin2θ

as $\theta \to 0$

r/L = 2θ

r/L = λ /d

or

r = λL/d

λ L–camera length constant of microscope

1/d-reciprocal of interplanar distance(Å- 1)

A reciprocal lattice is another way of view a crystal lattice and is used to understand diffraction patterns. A dimension of 1/d is used in reciprocal lattices.

Applications of TEM

TEM

Conventional TEM

Microstructure, morphology (grain size, orientation), phase distribution and defect analysis (point defects, dislocations and grain boundaries)

In situ TEM

Irradiation and deformation experiments
Environmental cells (corrosion)
Phase transformations
(hot- and cold-stage, electric field)

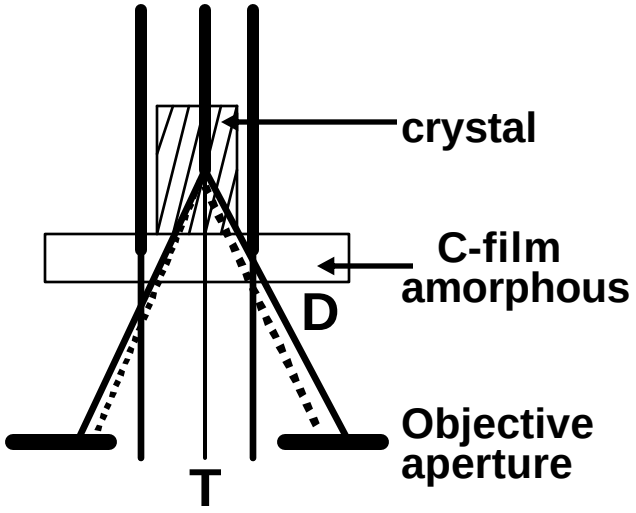
Analytical TEM (Z-contrast imaging)

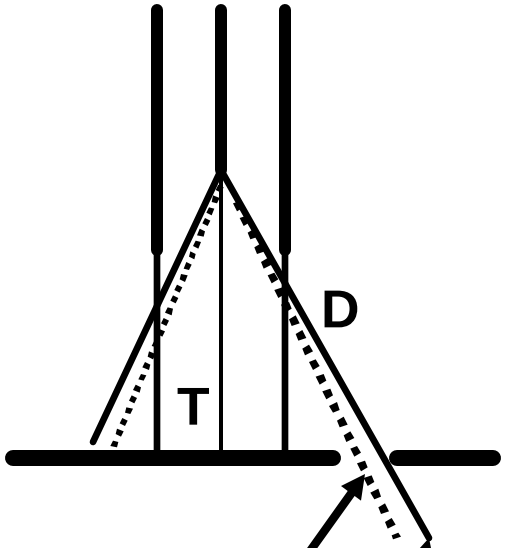
Chemical composition-EDS, EELS, ELNES, EXELFS, Z-contrast imaging

HRTEM

Lattice imaging, Structure of complex materials and atomic structure of defects (interfaces)

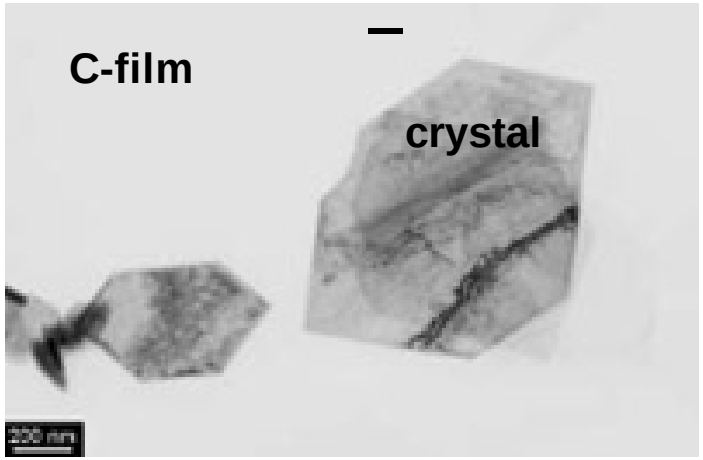
Diffraction Contrast –BF & DF Imaging

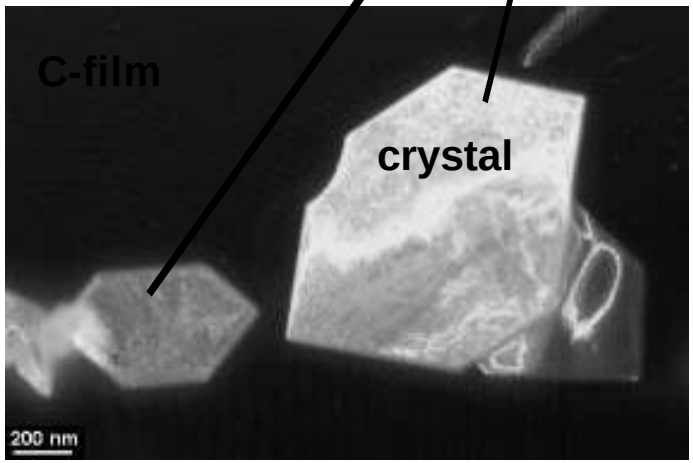




BF image

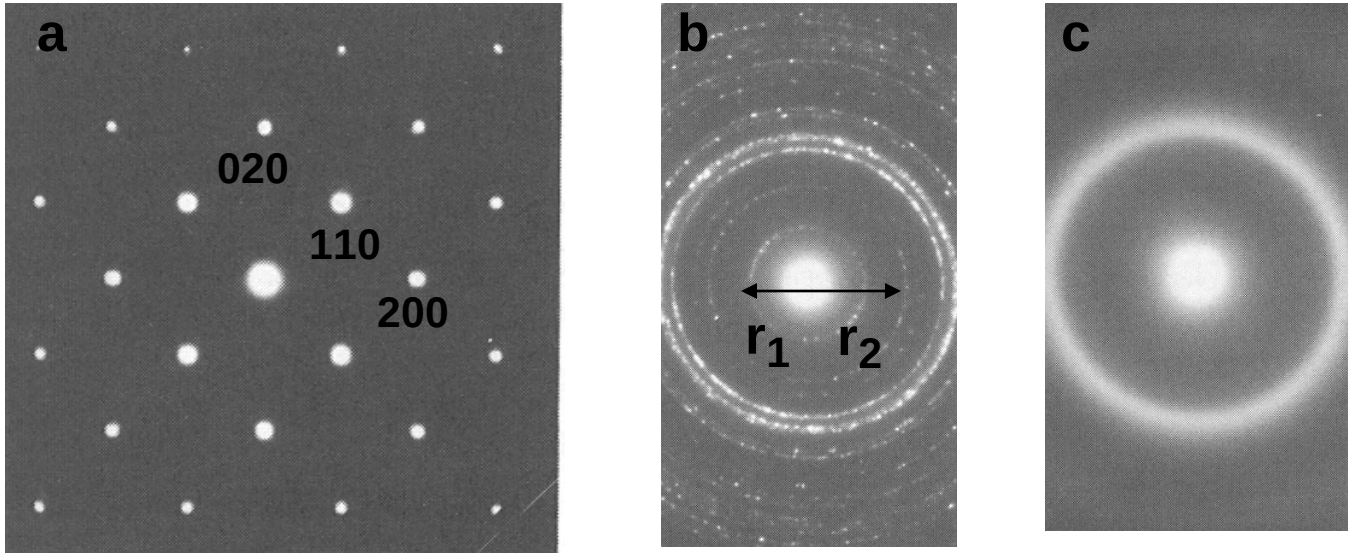
DF image





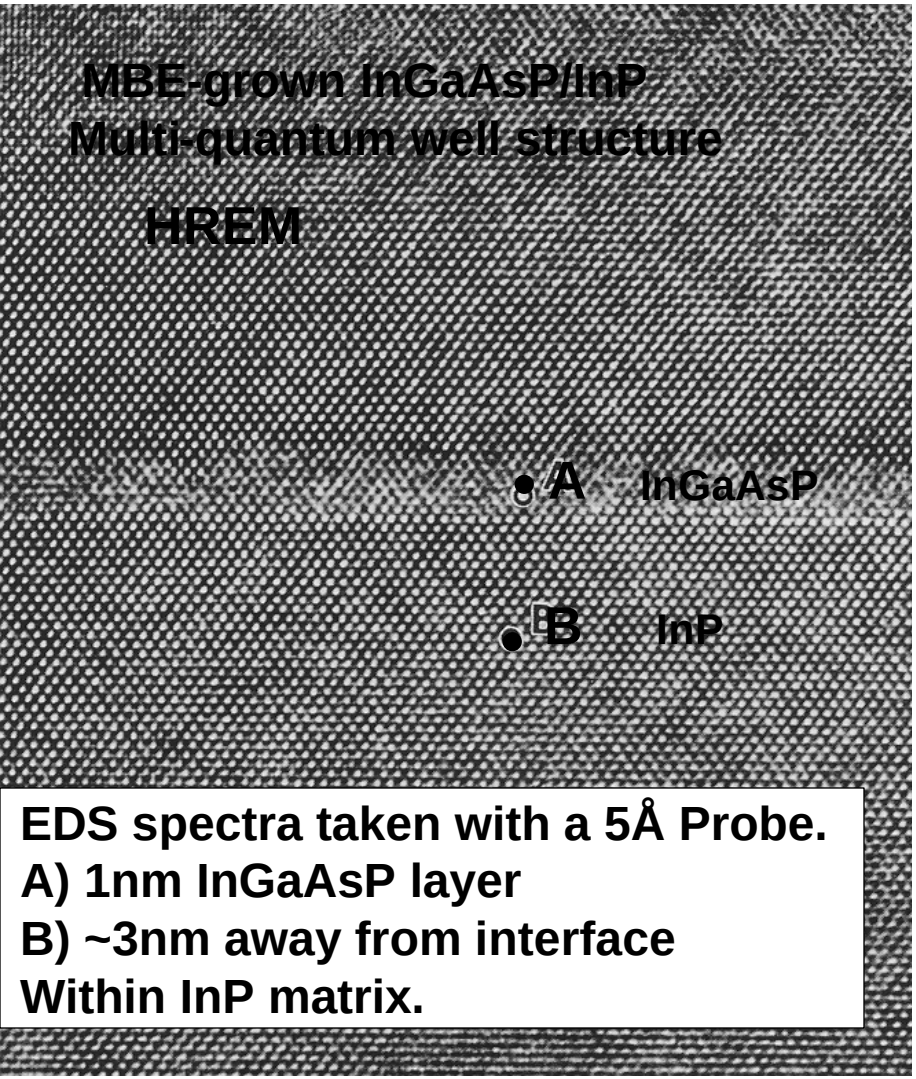
Diffraction + mass-thickness Contrast

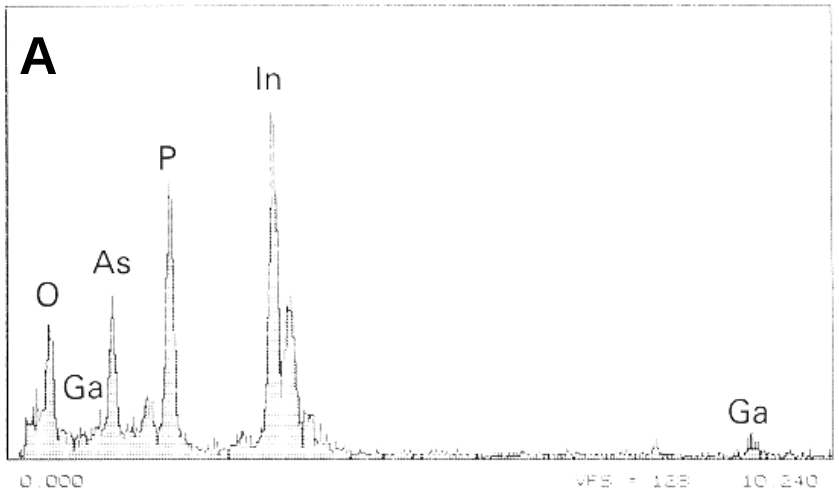
SAED Patterns of Single Crystal, Polycrystalline and Amorphous Samples



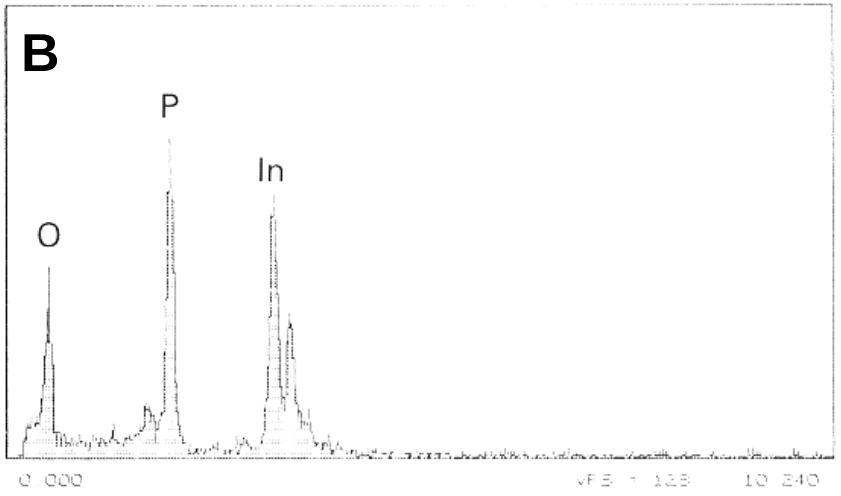
a. Single crystal Fe (BCC) thin film-[001]
b. Polycrystalline thin film of Pd_2Si
c. Amorphous thin film of Pd_2Si. The diffuse halo is indicative of scattering from an amorphous material.

Sub-Nanometric EDS Analysis
(JEOL-2010F Field-emission TEM)



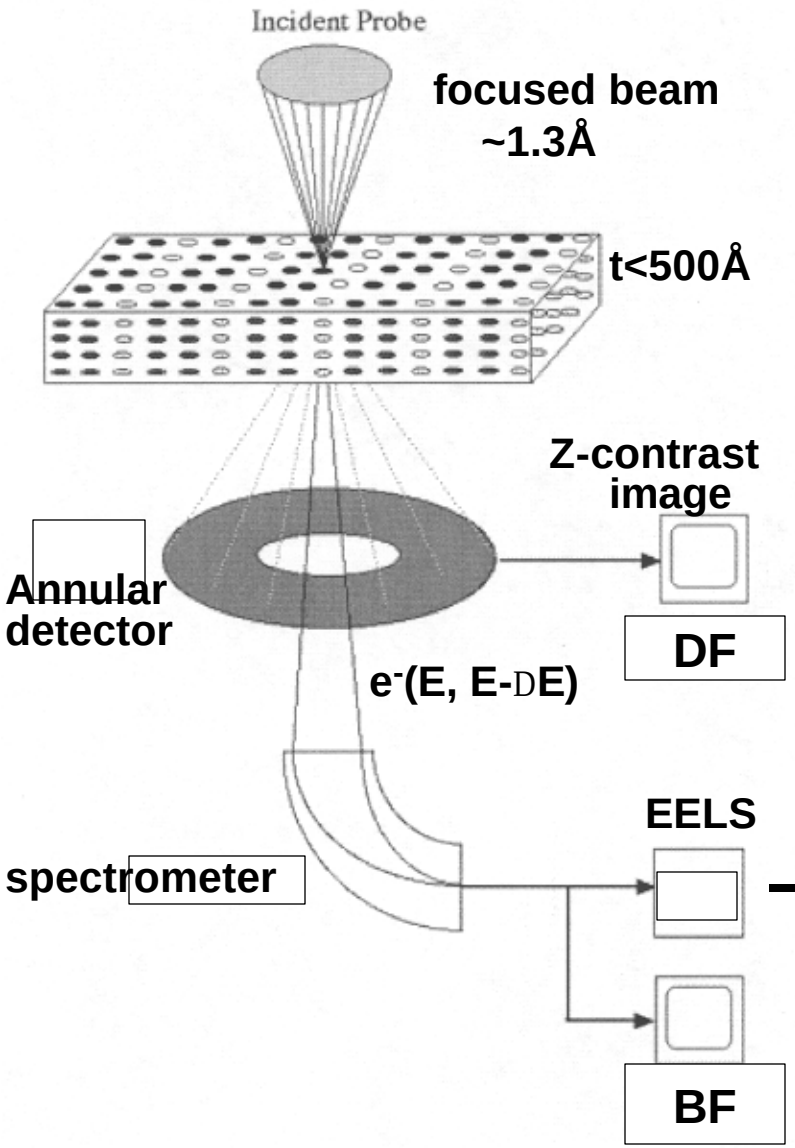


(a)

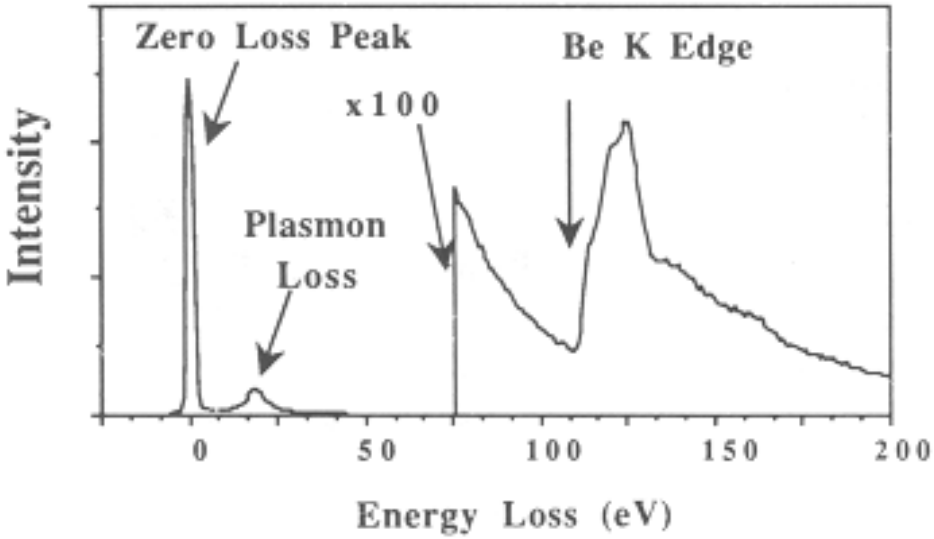


EDS spectra taken with a 5Å Probe.
A) 1nm InGaAsP layer
B) ~3nm away from interface
Within InP matrix.

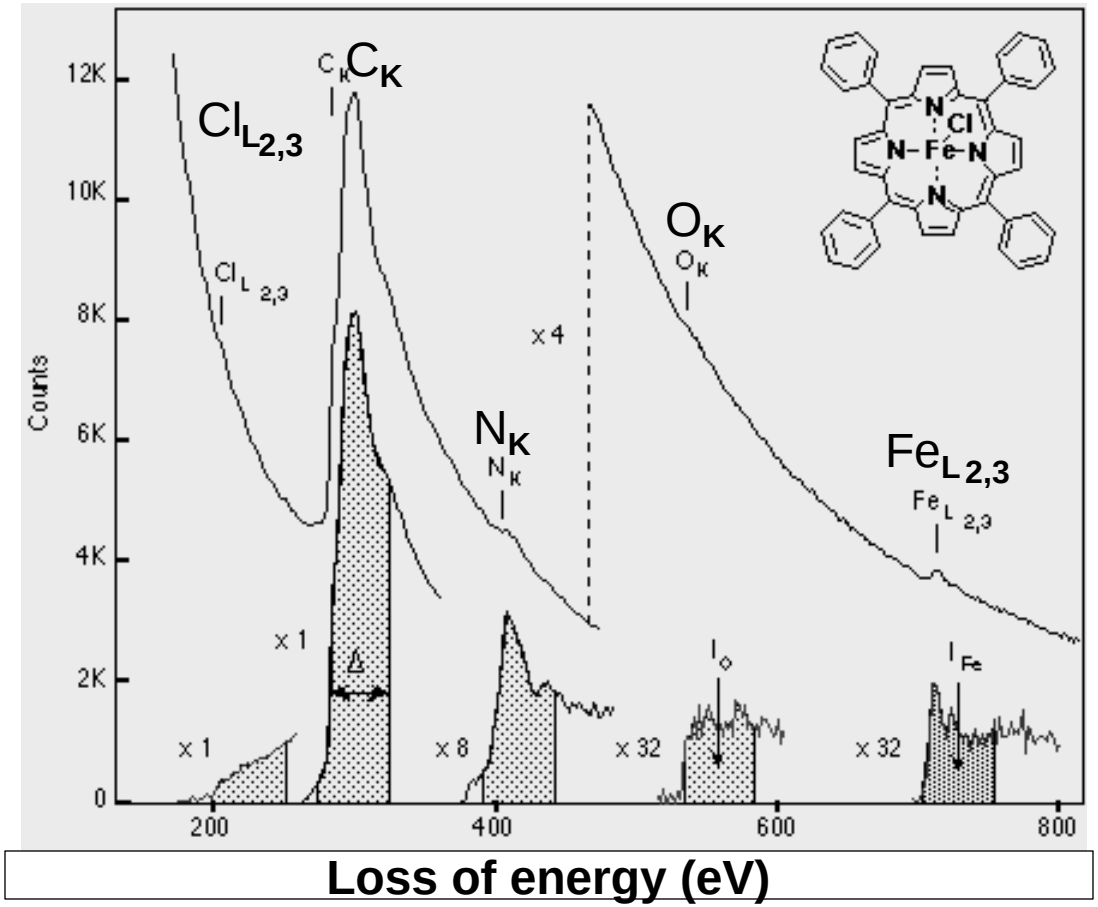
Electron Energy Loss Spectroscopy (EELS)



EELS is a microanalytical technique that uses the characteristic spectrum of energy losses of transmitted electrons to obtain information about elemental composition, chemical bonding, and electronic structure (oxidation state). Moreover, by selecting electrons with a specific loss energy by a slit so as to image them, element distribution in the specimen can be visualized (Elemental mapping). The spatial resolution is limited by the diameter of the incident illumination focused on the sample.



Elemental Analysis by EELS

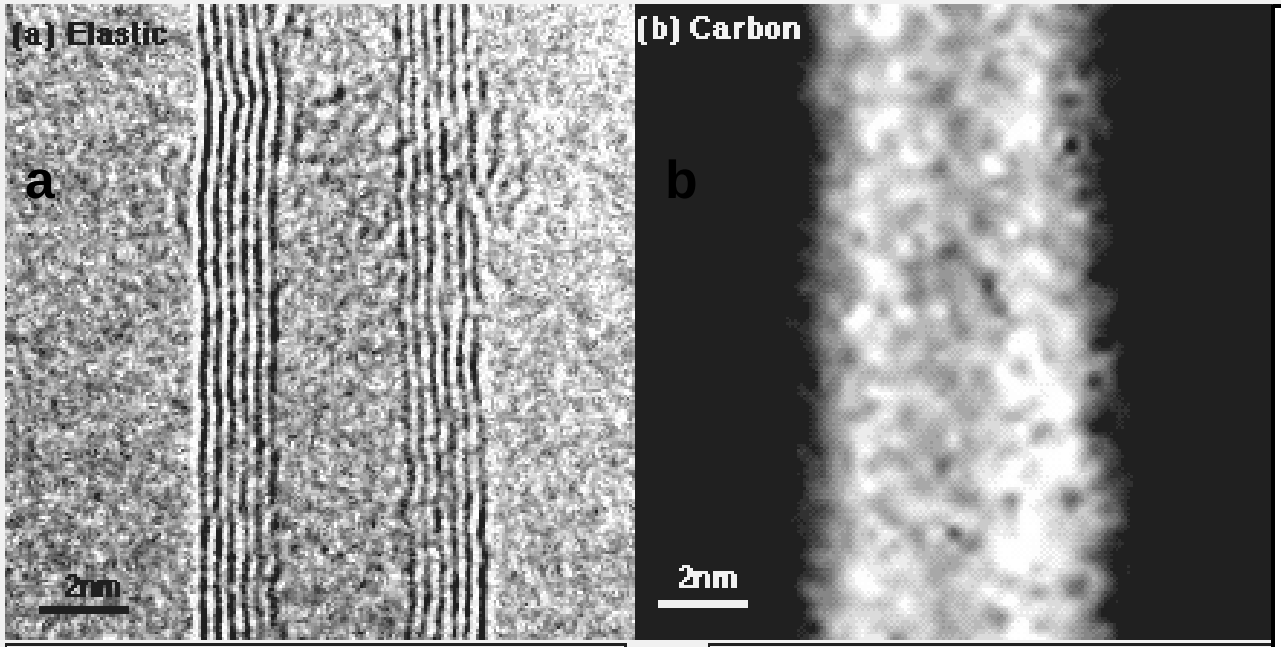


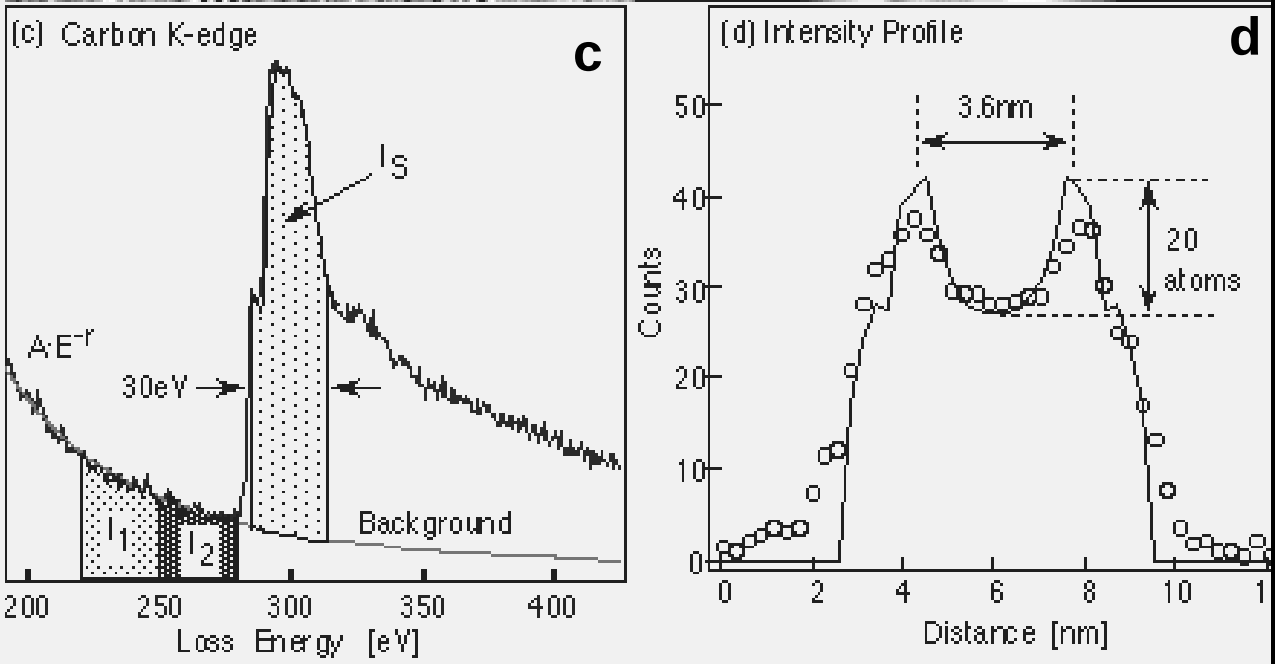
Loss of energy (eV)

EELS spectrum from the region of 1 um diameter of iron tetraphenylporphyrin monochloride crystal.

Integral peak intensity is proportional to the number of each atom in the measured region. From the intensity and the cross-section of *inelastic* scattering, the elemental ratio is determined as C:N:Cl:Fe=42.9:3.9:1.1:0.9. This value is corresponding well to the expected molecular composition (43:4:1:1). This result is obtained from the sample weight of $1X10^{-13}$ g.

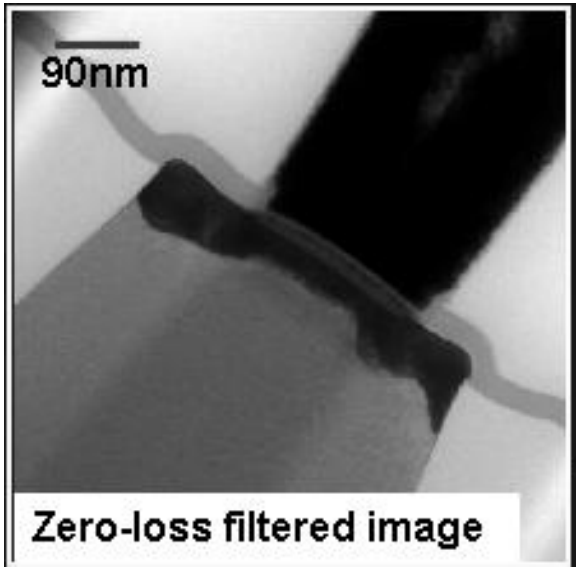
Quantification of Elemental Mapping



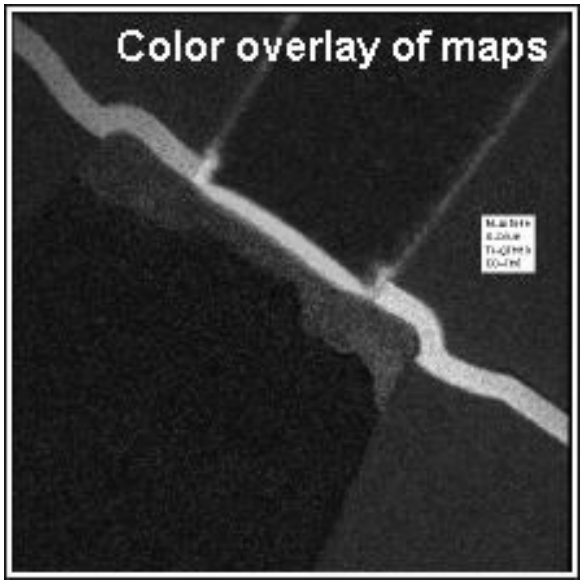


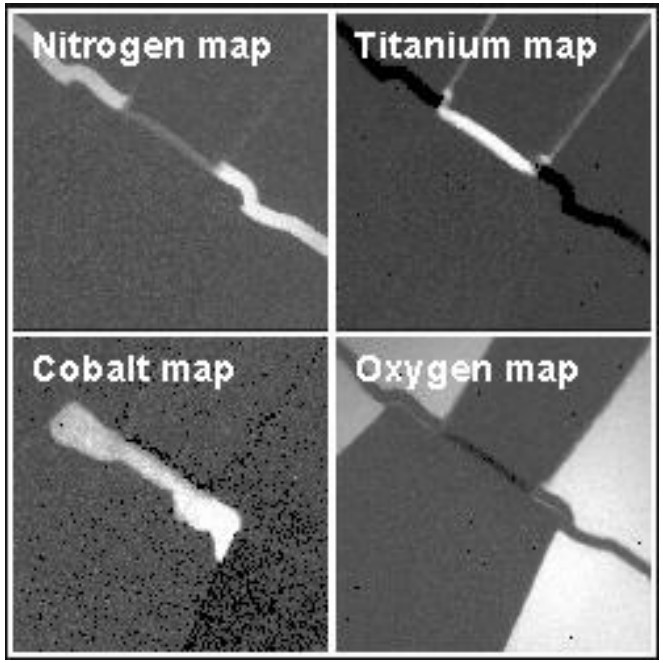
a.HREM image of carbon nanotube.
b.Carbon map at the same region.
c.EELS spectrum.
d.Intensity profile of carbon map perpendicular to the tube axis. The intensity profile corresponds well to the calculated number distribution of carbon atoms (solid line) based on the size and the shape of the nanotube.
The intensity dip at center part is corresponding to 20 carbon atoms.

Energy Filtered Imaging (EELS)



Different elements can be imaged at the nm scale.

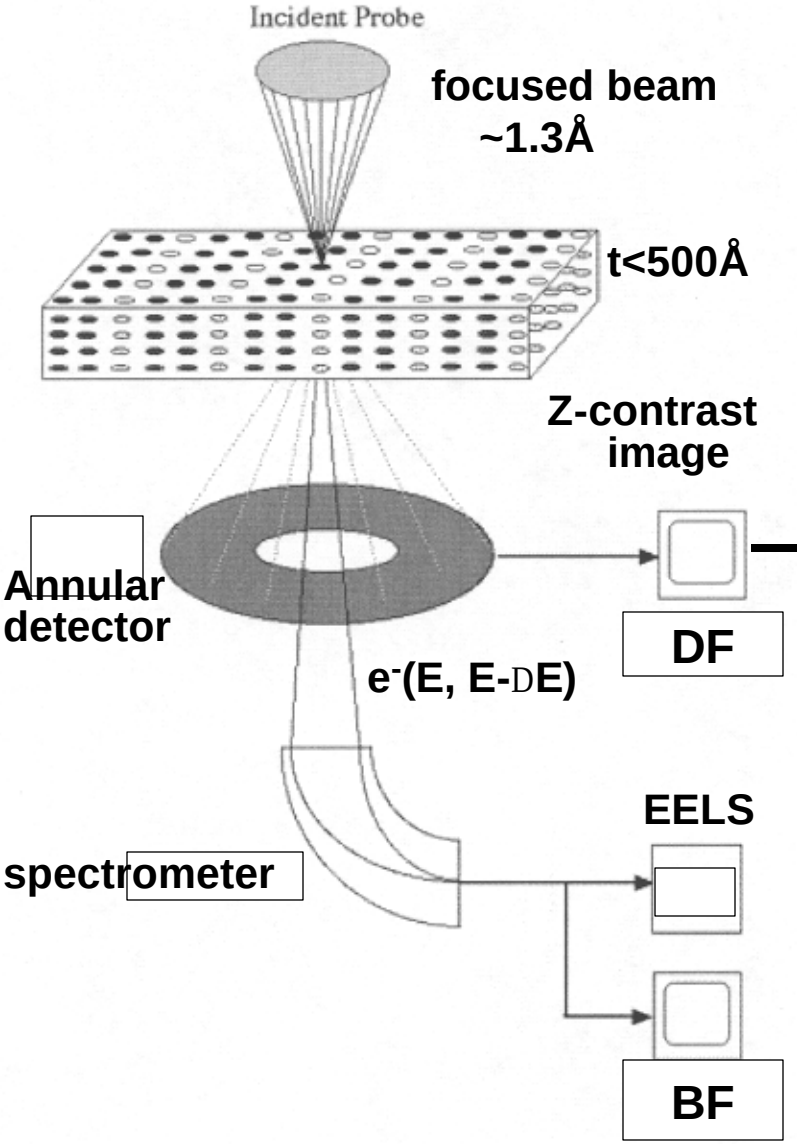




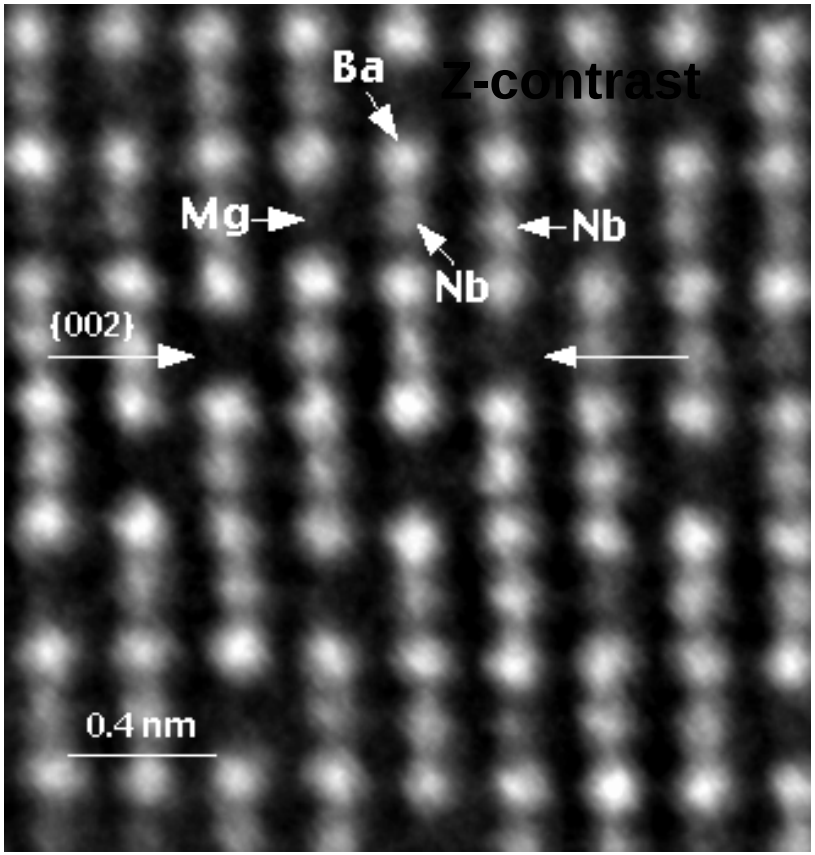
Cross section of microelectronic transistor.

High Resolution Z-contrast Imaging

Atomic Ordering in $Ba(Mg_{1/3}Nb_{2/3})O_3$



$I \; a \; Z^2$



(STEM)

4.0 Limitations of TEM

- **Sampling**
- ***Interpretation of image***
- **Beam damage**
- **Specimen preparation**

5.0 Summary I

The uniqueness of TEM is the ability to obtain crystallographic, atomic, structural and microanalytical data such as:

- **Chemical composition**
- **Bonding (distance and angle)**
- **Electronic structure**
- **Coordination number data from the sample.**
- **TEM is the most efficient and versatile technique for the characterization of materials.**

5.0 Summary II

- **UHV instrument**
- **Operation from 80 kV to 1000kV**
- **New techniques have made breakthroughs in sample prep (FIB)**
- **Image interpretation**
- **Cost is prohibitive: 2-3.5 million$$**
- **Facilities and bldg. quality**
- **Training**