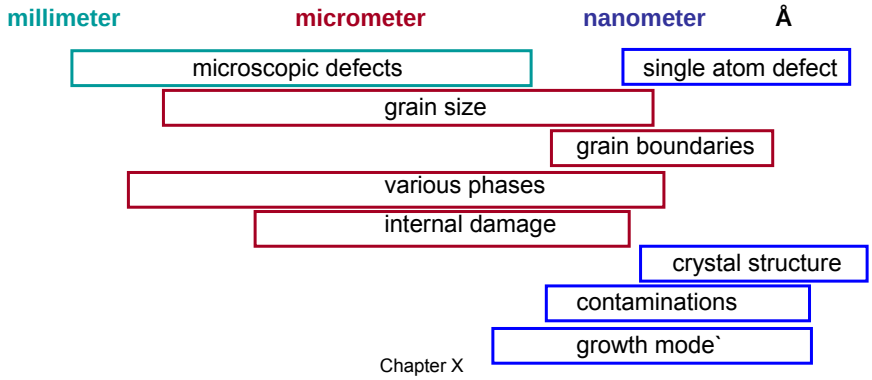
Chapter X: Characterization Techniques

Crystal structure analysis; microstructure and defects in crystal structure

Various instruments are necessary to examine materials at



Bibliography

X-ray diffraction

- Smith & Hashemi, Chapter 3.11
- Elements of X-ray diffraction, 3rd edition, by Cullity B.D. and Stock S.R., Addison-Wesley, 1978.

SEM and TEM

- Smith & Hashemi, Chapter 4.5.2-4
- Callister, Chapter 4.9-4.10

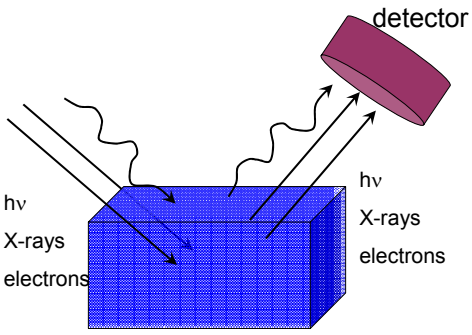
STM and AFM

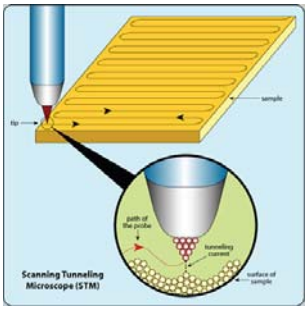
- Smith & Hashemi, Chapter 4.5.5
- Modern Techniques of Surface Science, Woodruff and Delchar, 1994

LEEM

- http://www.research.ibm.com/leem/

Probes of materials structure and properties





- information about **bulk** (*average*)
- X-ray diffraction (X-rays in and out)
- Optical microscopy (light in and out)

- *local* information about **surface**
- Scanning tunneling microscopy (STM)
- Atomic Force microscopy (AFM)
- Low energy electron microscopy (LEEM)

X.1 X-ray diffraction

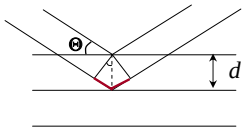
Main method for determining crystal structure

Consider an X-ray of wavelength λ hits a set of planes separated by *d* under an angle Θ

- some of the X-rays go straight through

- some are reflected (scattered), but only if specific conditions met

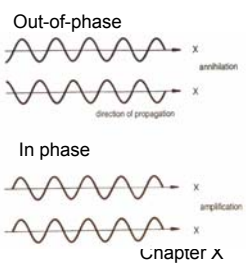
Consider a material to be a stack of planes at a constant separation - *d*

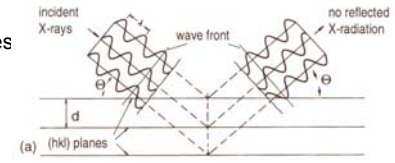


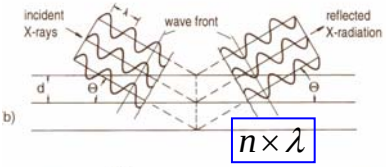
$n \times \lambda$

whole number

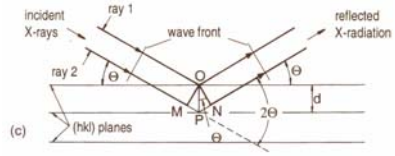
$2d \sin\Theta$







$n \times \lambda$



Bragg's law

The diffraction (the coherent elastic scattering of waves by the crystal lattice) condition

$$n \times \lambda = 2d \sin\Theta$$

Bragg's law (X-rays, neutrons, electrons)

where λ – wavelength of X-ray beam, d – spacing of reflecting planes, Θ– angle of incidence and reflection, n – order of diffraction (for most of the cases we discuss n=1)

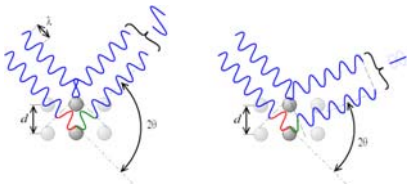
The lattice plane spacing *d* depends on the crystal structure and indices {hkl} of the planes

$$d_{cubic\_str} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad d_{hexagonal\_str} = \frac{a}{\sqrt{\frac{4}{3}\left(h^2 + k^2 + hk\right) + \frac{l^2 a^2}{c^2}}}$$

d – set by the crystal

λ – set by apparatus (constant for a given setup)

can change Θ (theta) or often 2Θ!!!



Constructive and destructive interference

X-ray waves scatter ***in phase*** (constructive interference): λ, 2λ, 3λ, …, nλ (n – whole number)

Out of phase (destructive interference): 1/2λ, 3/2λ, 5/2λ, …

What about the other planes?

- if in phase condition holds for plane 1 and 2, it also holds for the plane 3, 4, etc.
- if plane 1 and 2 are out of phase, the 3rd will be in phase will the 1st, … but the 4th will cancel it out

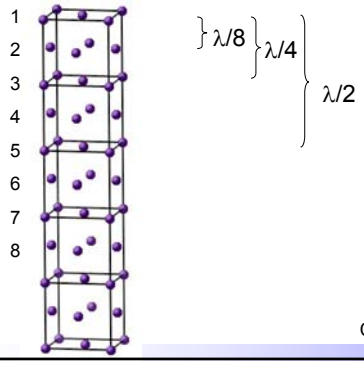
1 _____

2 _____

3 _____

4 _____

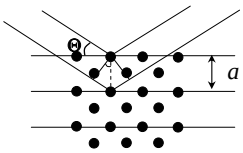
Other planes are also important:



Unless ***constructive interference*** condition met (n – whole number), there is very little intensity at a given angle

Additional rules

- Consider diffraction from the (100) face of the *fcc* crystal

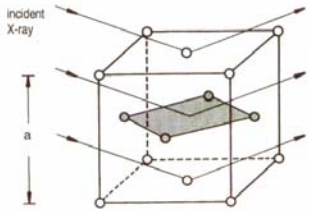


If $2d \sin\Theta = \lambda$ (i.e., n=1)

but there is always another plane at (n=1/2)

$\Rightarrow$ no intensity…

Rules for determining the diffracting {hkl} planes in cubic crystals



Schematic illustration of (100) - (200) annihilation in a fcc lattice.

Lattice	Reflection present	Reflection absent
bcc	(h+k+l)=even	(h+k+l)=odd
fcc	(h,k,l) all odd or even	(h,k,l) not all odd or even

Details of crystal unit cell are important

Different rules for different unit cells

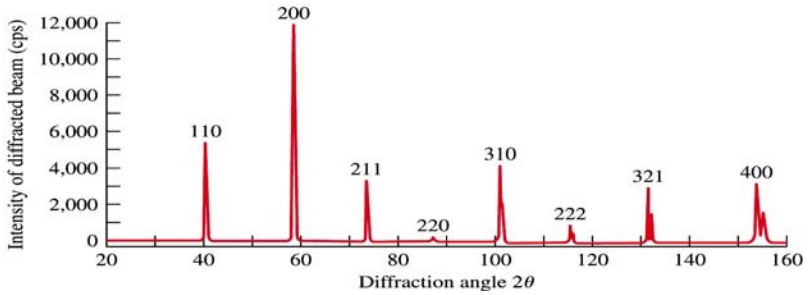
Possible peaks for cubic structures

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

d_{hkl}	*Family of planes*	*sc*	*fcc*	*bcc*
a	{100}			

Powder diffraction

- Use polycrystalline sample
  - All possible planes are at angle Θ to beam
  - Only ones satisfying Braggs condition provide diffraction
  - Need to change angle Θ to detect all “Bragg peaks”

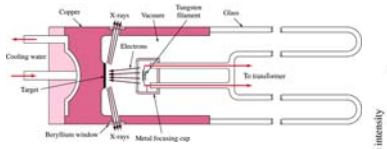


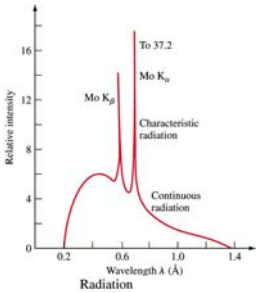
Record of the diffraction angles for a W (tungsten) sample obtained by the use of a diffractometer with Cu radiation

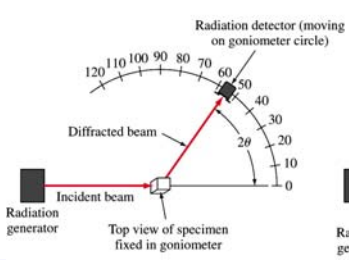
Experimental details (powder diffraction)

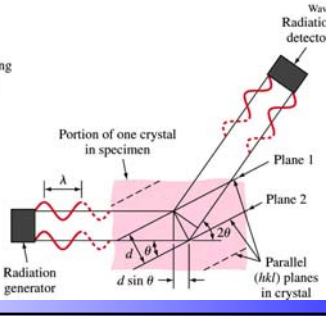
Use polycrystalline sample

- Source
- Collimator (slits)
- Sample holder (need rotation)
- Detector (moves in arc around sample; intensity *vs* 2Θ is recorded)









Q.: A metal is known to have a cubic structure. An X-ray diffraction pattern (using wavelength λ of the incoming radiation of 0.1542 nm) has its three lowest peaks at θ angles: 20.27°, 29.33°, 36.87

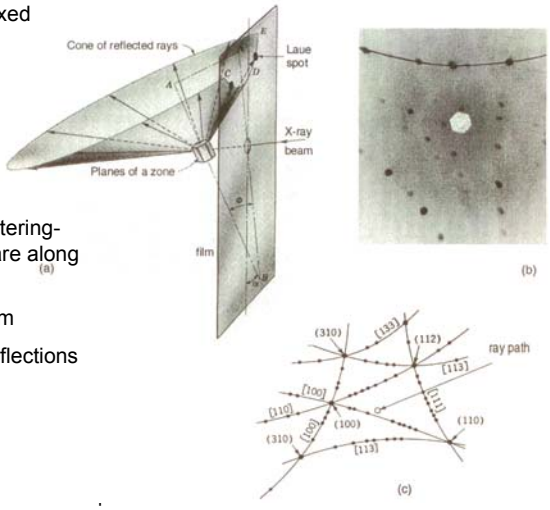
a) Determine the lattice constant of the element

b) Determine the crystal structure of the element.

c) Identify the element (use Appendix tables at the last slide)

Laue method

- If single crystal is illuminated with monochromatic X-rays → no intensity !!!
- White (not monochromatic X-rays) used
- Sample, detector (or film) are fixed



(a) Schematics for Laue-back-scattering-image: reflections from one zone are along a hyperbola on the film

(b) sample Al: reflections on the film

(c) sample Fe, zones and major reflections are indexed

X.2 Positron Annihilation

- An accurate method to determine the **vacancy** concentration
- Positron (e+) has the same mass but the opposite charge of an electron (e-)
- Interaction of a vacancy with a positron increases the life time of a positron in a material
- Can be measured by the emitted γ-ray intensity

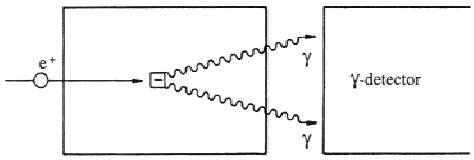


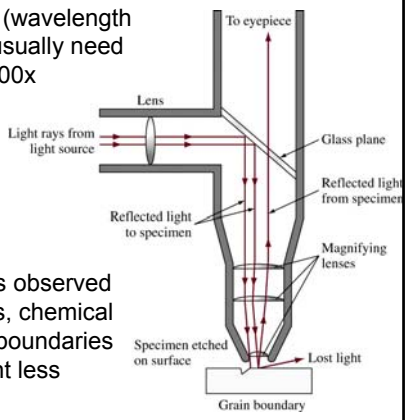
Fig. 3.6. Illustration of the principle of detecting vacancies with positrons. A vacancy has the same effect as a missing ion core and corresponds to a free negative charge, which reacts with a positron.

http://www.physics.uwo.ca/~psimpson/

X.3 Optical Microscopy

The ordinary light microscope

- **Advantages**: easy, cheap, direct
- **Disadvantages**: resolution only to ~0.3μm (wavelength of light, can't see inside opaque samples, usually need sample preparation), max magnification 2000x



Typical sample preparation:

- cut, grind, and polish sample
- use chemicals to etch

- Shows grain boundaries! (Grain boundaries observed easily as they etch more rapidly than grains, chemical etching produces tiny grooves along grain boundaries which appear as dark lines (they reflect light less intensely)
- Can give different grains different texture (since different surface planes exposed)

Grain boundaries

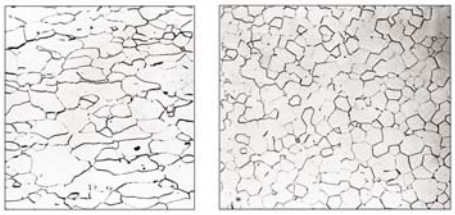


Table 4.2 ASTM grain sizes

Grain-size no.	Nominal number of grains: Per sq mm at 1×	Per sq in. at 100×
1	15.5	1.0
2	31.0	2.0
3	62.0	4.0
4	124	8.0
5	248	16.0
6	496	32.0
7	992	64.0
8	1980	128
9	3970	256
10	7940	512

Source: "Metals Handbook," vol. 7, 8th ed., American Society for Metals, 1972, p. 4.

Surfaces of polished and etched samples as revealed in the optical microscopy
(a) Low-carbon steel (100 x); (b) Magnesium oxide (225 x)

Measuring grain size (American Society for Testing and Materials (ASTM) method

Grain size number is identified by: $N = 2^{n-1}$

where N is the number of grains/square inch, n – ASTM grain size number, integer (Table 4.2)

Ex.: what is the grain-size number of the metal if there are 64 grains/in2 (as observed in microscope at a magnification of 100x)

64 grains/in^2 = 2^{n-1}; log 64 = (n-1)(log 2); 1.806 =(n-1)(0.301) $\Rightarrow$ n = 7

X.4 Scanning Electron Microscopy (SEM)

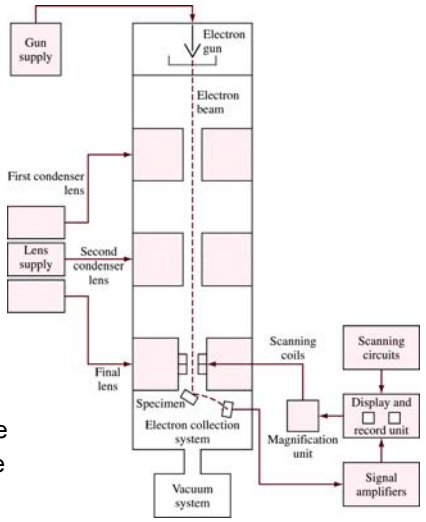
Scanning electron microscopy (SEM)

- Use electron beam instead of light

- records how many secondary electrons come out of sample at each spot

- 30keV electron energy
- field of view 0.1 - 100 μm
- 5 nm resolution in plane
- Magnification 15x – 100,000x
- Typical operating pressure <1atms
- build up image line by line

- **Advantages**: surface, common technique
- **Disadvantages**: need conductive sample to prevent charging



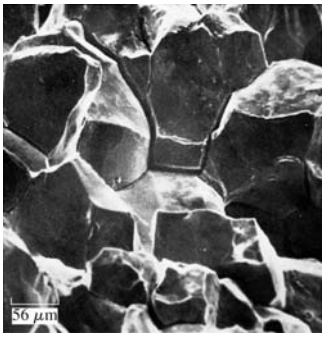
Schematic diagram of the basic design of a SEM

Applications

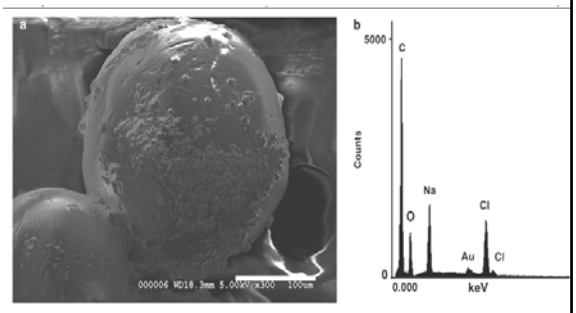
- Microscopic feature measurements
- Fracture characterization
- Failure analysis

Quantitative and qualitative information – additional x-ray spectrometer (Energy Dispersive X-ray analysis, EDX)

• lateral resolution



SEM of intergranular corrosion fracture near a weld



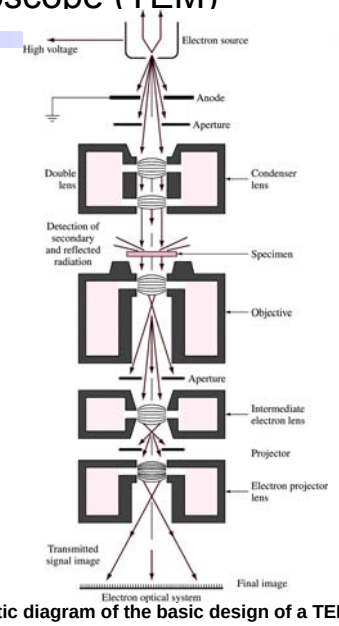
X.5 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM)

- e-beam goes fight through sample
- some areas diffract or scatter the beam
- record how much reaches a screen
- need thin samples (~ 100nm = 0.1 mm)

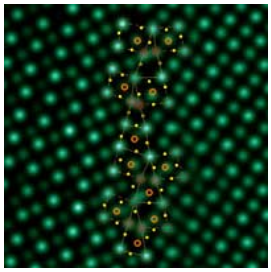
- 100-300keV electron energy
- resolution in plane 1nm (TEM)
  0.6Å (HRTEM, current record)
- Need ultra-high vacuum

- **Advantages**: high-resolution
- **Disadvantages**: difficult sample preparation



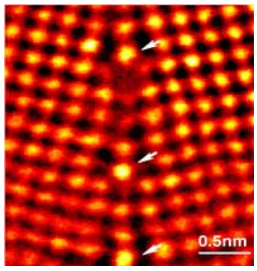
Schematic diagram of the basic design of a TEM

Applications of HRTEM



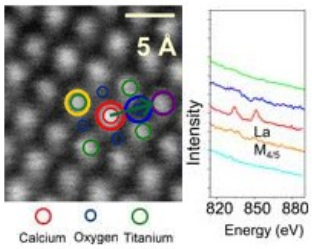
Direct Determination of Grain Boundary Atomic Structure In $SrTiO_3$

McGibbon MM et al., *Science* **266,** 102 (1994)



Impurity-Induced Structural Transformation of a Grain Boundary

Y. Yan et al, *Phys. Rev. Lett.* 81, 3675 (1998)



Single Atom Spectroscopy

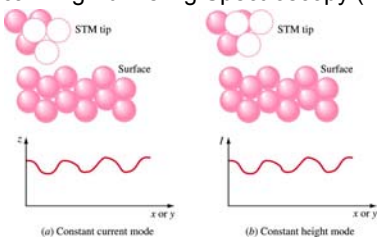
M. Varela et al., *Physical Review Letters* **92**, 095502 (2004)

http://stem.ornl.gov/highlights.html

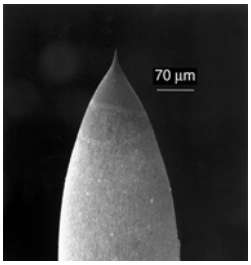
X.6 Scanning Tunneling Microscopy (STM)

STM used for direct determination of images of surface, with **atomic** resolution.
Method is based on **electron tunneling** between tip and surface

- Was developed by G.Binnig and H. Rohrer (IBM) in early 1980
- Nobel prize in Physics (1986)
- Scanning Tunneling Spectroscopy (W. Ho, Cornell)



Get structural information by scanning tip across surface in constant **height** or constant **current** modes



STM tip made from Pt-Ir alloy chemical etching)

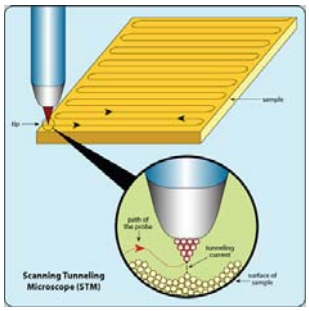
Tersoff and Hamann developed a simple theory of STM: the tunneling current I

$I \sim V \times \rho_{tip} \times \rho_{sample}$,

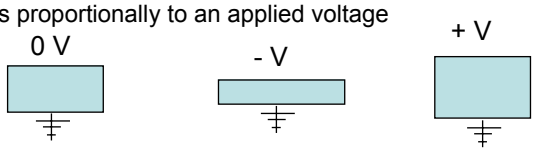
where V - voltage applied,

ρ_{tip} and ρ_{sample} are the density states of the tip and sample

Piezoelectric Scanners



- Scanners are made from a piezoelectric material that expands and contracts proportionally to an applied voltage



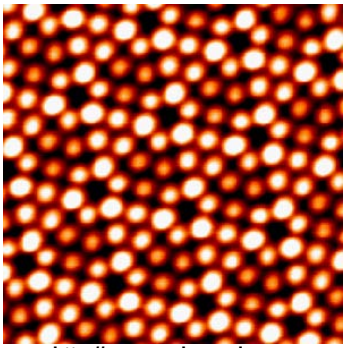
No applied voltage | Extended | Contracted

STM image Si(111) (7x7)

- **Advantages**: atomic resolution on the surface, spectroscopic studies for a single atom are possible
- **Disadvantages**: conductive samples, often need UHV, good vibration isolation is critical

See topmost atom layer

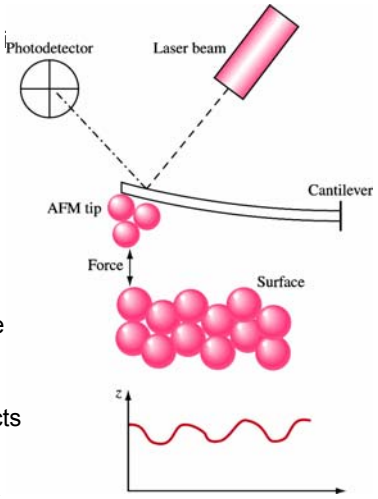
(or electron density in the topmost layer)



http://www.omicron.de

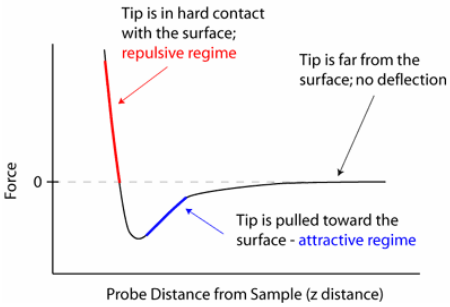
X.7 Atomic Force Microscope (AFM)

- A very high-resolution type of scanning probe microscope
- was invented by Binnig, Quate and Gerber



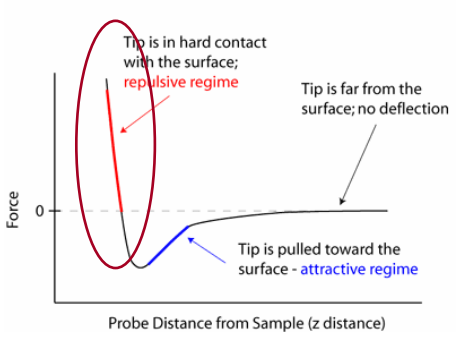
- **Advantages**: > 1000 times better than the optical diffr. limit, non-conductive samples
- **Disadvantages**: image size (max 150x150μm), tip effects, and image artifacts

AFM Operation modes

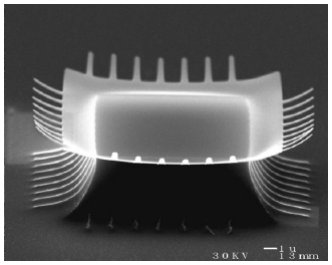


- Contact mode
  - repulsive forces ~10^{-9} N
- Non contact
  - attractive (van der Waals) forces regime
- Tapping (Intermittant contact) mode
  - cantilever is oscillated at its resonant frequency
  - repulsive force region, but touches the surface only for short periods of time

Contact Mode AFM

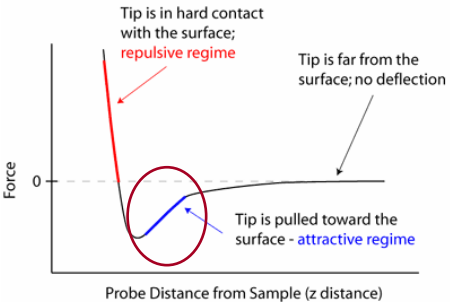


- Tip is in contact with the surface ⇒ the deflection of the cantilever or the movement in the z piezo required to keep the deflection
- Force constants for commercial cantilevers ~0.1N/m ⇒ a displacement of 1nm corresponds to a force 0.1nM

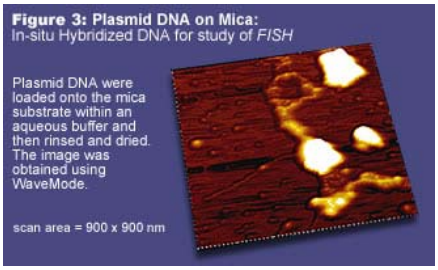


- high resolution, but wears out the tip
- high scan speed
- surface damage, if the surface is soft
- good for nanomechanical testing

Non-contact Mode AFM



- The cantilever is oscillated slightly above its resonant frequency.
- Oscillations <10nm
- The tip does not touch the sample
- A constant oscillation amplitude is maintained



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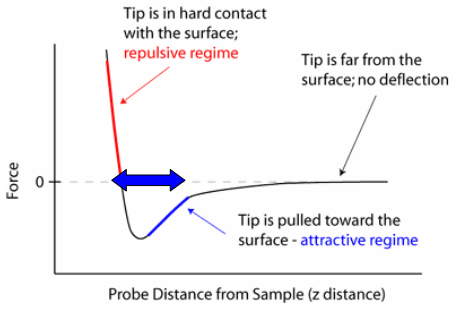
- resolution is slightly worse
- useful for sensitive (biological soft) samples

Intermittant (Tapping) Mode AFM

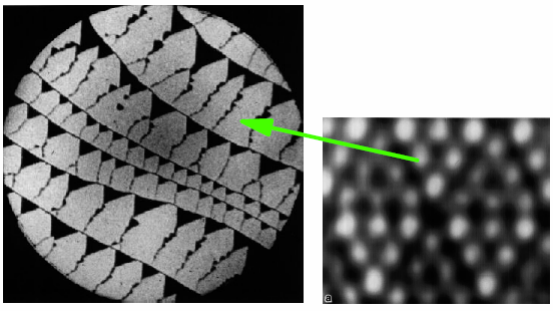


- A cantilever with attached tip is oscillated at its resonant frequency and scanned across the sample surface.
- A constant oscillation amplitude (and thus a constant tip-sample interaction) are maintained during scanning. Typical amplitudes ~ 20-100 nm.
- Forces can be <200 pN
- The amplitude of the oscillations changes when the tip scans over bumps or depressions on a surface

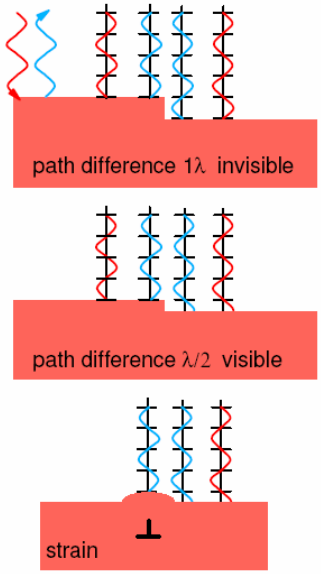
X.8 Low Energy Electron Microscope (LEEM)

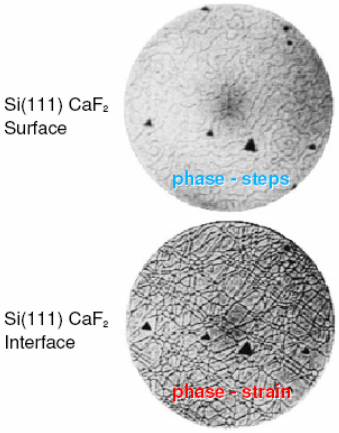
LEEM history

- 1962 Invention by Ernst Bauer
- 1985 Operational LEEM instrument (Telieps and Bauer)
- 1991 IBM LEEM-I (Tromp and Reuter)
- 1998 IBM LEEM-II
- 2006 SPECS FE-LEEM P90



Phase contrast





Problems:

X.1 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2 θ angles: 40.663°, 47.314°, 69.144°, and 83.448°. (Wavelength λ of the incoming radiation was 0.15405 nm.)

a) Determine the crystal structure of the element.

b) Determine the lattice constant of the element.

c) Identify the element.

X.2 The distance between atoms in a crystal are ~ 1-2 Å, so waves with approximately this wavelength are required to explore the crystal structure. Using de Broglie law ($\lambda = h/p$), calculate the energies of (a) neutrons ($m=1.675\times10^{-24}$kg), (b) electrons ($m=0.911\times10^{-28}$kg) and (c) X-rays required for the structural studies.

X.3 Name and briefly describe three different AFM operation modes. In which mode separation between the probe and the surface is the highest?

X.4 What incident particles (X-rays, electrons, or photons (light)) do we use in

(a) X-ray diffraction, (b) optical microscopy, (c) TEM, (d) LEEM.

What particles do we detect in each of these techniques?

X.5 Why are grain boundaries easily observed in optical microscope?

Appendix:

Table 3.2 Selected metals that have the BCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

Metal	Lattice constant a (nm)	Atomic radius R^* (nm)
Chromium	0.289	0.125
Iron	0.287	0.124
Molybdenum	0.315	0.136
Potassium	0.533	0.231
Sodium	0.429	0.186
Tantalum	0.330	0.143
Tungsten	0.316	0.137
Vanadium	0.304	0.132

*Calculated from lattice constants by using Eq. (3.1), $R = \sqrt{3}a/4$.

Table 3.3 Selected metals that have the FCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

Metal	Lattice constant a (nm)	Atomic radius R^* (nm)
Aluminum	0.405	0.143
Copper	0.3615	0.128
Gold	0.408	0.144
Lead	0.495	0.175
Nickel	0.352	0.125
Platinum	0.393	0.139
Silver	0.409	0.144

*Calculated from lattice constants by using Eq. (3.3), $R = \sqrt{2}a/4$.