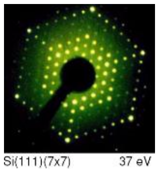
Lecture 3

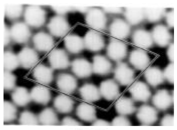
Surface Structure, continued:
Low Energy Electron Diffraction and Microscopy

How to determine surface structure:

- Theoretical background
- Low Energy Electron Diffraction (LEED)
- Reflection High-Energy Electron Diffraction (RHEED)
- Low Energy Electron Microscopy (LEEM)

Additional: Scanning Electron Microscopy





References:

1) Zangwill, Chapter 3
2) Woodruff & Delchar, Chapter 2 and pp. 449-460
3) Attard and Barnes, pp,25-28, 47-62
4) Kolasinski, pp.84-91
5) LEEM: http://www.research.ibm.com/leem/#item2

Electron Backscattering: concepts of diffraction

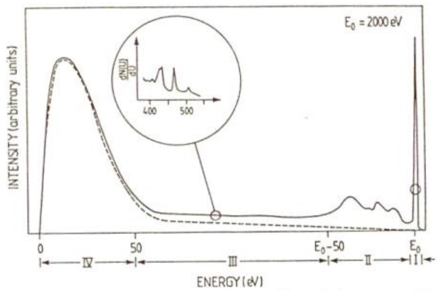
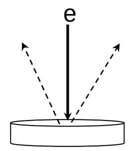


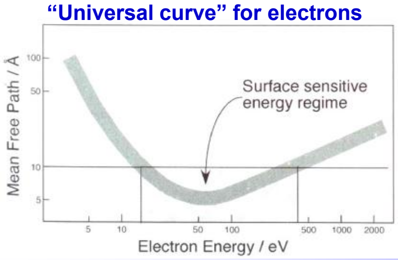
Fig. V.2. Qualitative large-scale overview of the energy distribution of electrons emitted from a surface which is irradiated by an electron beam of primary energy E_0.

Electron diffraction and microscopy:

Elastic backscattered e^-, ~ few % at 100eV



"Universal curve" for electrons

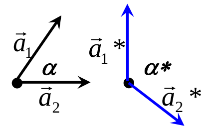


Short inelastic mean free path for electrons means that elastic scattering of electrons is **very surface sensitive**

3.1 Real Space and Reciprocal Space Lattices

- Given a unit cell with basis vectors $(\vec{a}_1, \vec{a}_2)$
- There is a complementary reciprocal lattice $(\vec{a}_1^*, \vec{a}_2^*)$

$\vec{a}_i \cdot \vec{a}_j^* = \delta_{ij} \quad (i, j = 1, 2) \Rightarrow \vec{a}_1^* \perp \vec{a}_2$ and $\vec{a}_2^* \perp \vec{a}_1$



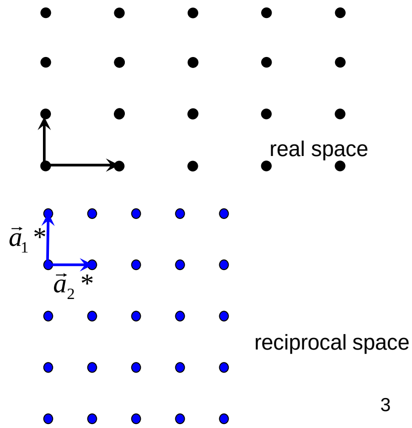
Area of unit cell A

$A = |\vec{a}_1||\vec{a}_2|\sin\alpha$

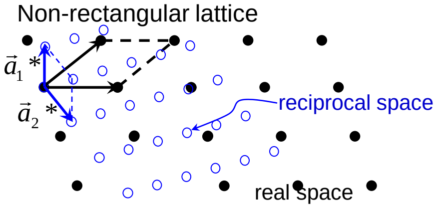
$A^* = |\vec{a}_1^*||\vec{a}_2^*|\sin\alpha^*$

$A^* = \frac{1}{A}$

Rectangular Lattice



Non-rectangular lattice

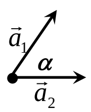


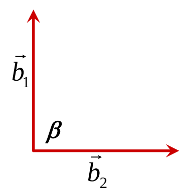
Substrate and Overlayer Structures

Suppose overlayer (or reconstructed surface layer) lattice different from substrate

$\vec{T}_A = n\vec{a}_1 + m\vec{a}_2$

$\vec{T}_B = n\vec{b}_1 + m\vec{b}_2$





Overlayer real space lattice:

$\vec{b}_1 = G_{11}\vec{a}_1 + G_{12}\vec{a}_2$

$\vec{b}_2 = G_{21}\vec{a}_1 + G_{22}\vec{a}_2$

Overlayer reciprocal lattice:

$\vec{b}_1^* = G_{11}^*\vec{a}_1^* + G_{12}^*\vec{a}_2^*$

$\vec{b}_2^* = G_{21}^*\vec{a}_1^* + G_{22}^*\vec{a}_2^*$

where $G^* = \tilde{G}^{-1}$ (inverse transposed matrix)

$$G_{ii} = \frac{G_{jj}^*}{\det G^*} \quad G_{ij} = -\frac{G_{ji}^*}{\det G^*}$$

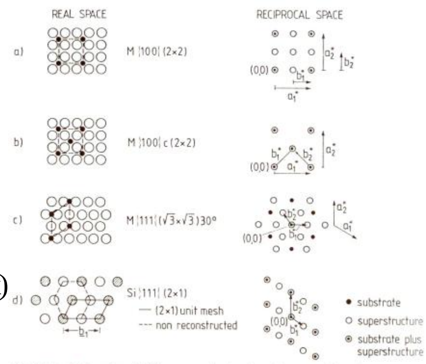
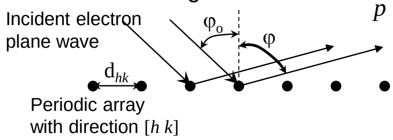


Fig. 3.11a–d. Examples of different superlattices in real space and in reciprocal space: (**a** to **c**) Adsorbed atoms on several low index surfaces of a closed packed metal (M). (**d**) (2x1) unit mesh (*solid line*) of a Si(111) surface prepared by cleavage in UHV

3.2 Reciprocal Lattice and Diffraction

Recall the de Broglie relation: $\lambda = \frac{h}{p} = \frac{2\pi}{k}$



Constructive interference when <u>path length difference = n λ</u>

$d_{hk}(\sin\varphi - \sin\varphi_o) = n\lambda, \quad n = \text{integer}$

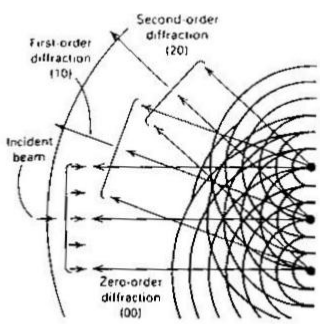
For electrons: $\lambda(\text{Å}) = \sqrt{\frac{150}{\text{E(eV)}}}, \ \sim 1\text{-}2\text{Å}$

For He atom: $\lambda(\text{Å}) = \sqrt{\frac{0.02}{\text{E(eV)}}}$

For normal incidence: $d_{hk}\sin\varphi = n\frac{12.2}{\sqrt{E(eV)}}$

$\varphi_o = 0, \varphi = 90^o, n = 1: \quad E = \frac{150}{d_{hk}^2}$

- as E ↑, beam moves towards normal
- solution for a direction, not intensity



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3.3 LEED Instrumentation

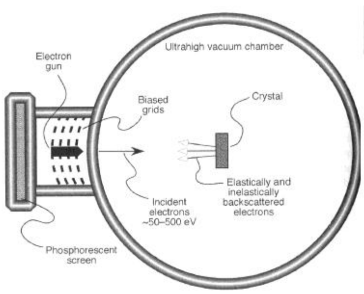


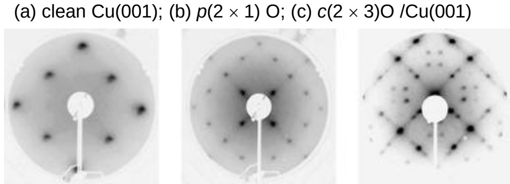
Figure 2.12 Schematic drawing of a LEED chamber.

Screen-type apparatus; also measure beam widths and intensity with **Faraday cup**

from www.omicron.de

LEED patterns for O /Cu(001):

(a) clean Cu(001); (b) *p*(2 × 1) O; (c) *c*(2 × 3)O /Cu(001)



(a) **(b)** **(c)**

<u>**Geometrical Theory of Diffraction**</u>:

- Analysis of LEED beam direction (position of spots) to give symmetry and geometry of unit cell
- Strong interaction between low energy electrons and matter ⇒ dynamic theory for intensities
- Simplification: elastic interactions as scattering of waves at a 2D lattice

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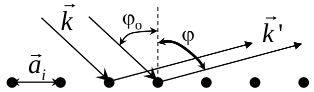
Interference Conditions

In 1D case, interference condition is: $a_i(\sin\varphi - \sin\varphi_o) = n\lambda$



Periodic array with direction [*1 0*]

$$a_i\left[\frac{2\pi}{\lambda}(\sin\varphi - \sin\varphi_o)\right] = 2\pi n \ \text{(for 1D case)}$$

$$\frac{2\pi}{\lambda} = |\vec{k}|$$

$$\vec{a}_i \cdot \vec{k} = a_i \frac{2\pi}{\lambda}\sin\varphi_o, \quad \vec{a}_i \cdot \vec{k}' = a_i \frac{2\pi}{\lambda}\sin\varphi$$

In 2D case: $\vec{a}_1(\vec{k}' - \vec{k}) = 2\pi h; \quad h, k$ are integers

$$\vec{a}_2(\vec{k}' - \vec{k}) = 2\pi k$$

What does this have to do with the reciprocal lattice?

The equations are satisfied if: $\Delta\vec{k}_{II} = (\vec{k}' - \vec{k})_{II} = 2\pi(h\vec{a}_1* + k\vec{a}_2*)$

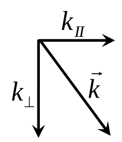
Prove by substitution: $\vec{a}_1(\vec{k}' - \vec{k})_{II} = \vec{a}_1(2\pi h)\vec{a}_1* + \vec{a}_1(2\pi k)\vec{a}_2* = 2\pi h$

Direction of interference maxima determined by vectors of reciprocal lattice:

$$\vec{g}_{hk} = 2\pi(h\vec{a}_1* + k\vec{a}_2*) = \vec{T}_a*$$

Energy and momentum conservation

Recall: **<u>energy is conserved</u>** in an elastic collision:



$$E = \frac{\hbar^2 k^2}{2m}$$

$$k^2 = k'^2 \quad \text{or} \quad k_{II}^2 + k_\perp^2 = k'^2_{II} + k'^2_\perp$$

<u>Parallel</u> momentum is conserved in diffraction:

$$\vec{k}'_{II} = \vec{k}_{II} + \vec{g}_{hk};$$

where $\vec{g}_{hk} = 2\pi(h\vec{a}_1* + k\vec{a}_2*)$ ← substrate

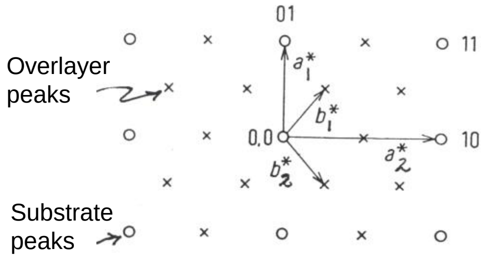
$\vec{g}_{hk} = 2\pi(h\vec{b}_1* + k\vec{b}_2*)$ ← overlayer

⇒ **<u>the LEED pattern is an image of the surface reciprocal net</u>**

Aside: Ewald sphere – a graphical solution to interference eq.

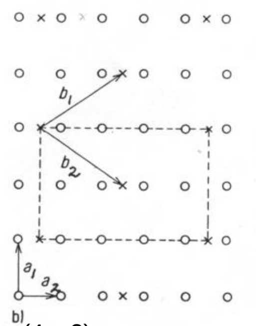
3.4 Analysis of a simple diffraction pattern

Sketch of diffraction pattern (reciprocal lattice):



- Relations between overlayer and substrate reciprocal lattices
- Construct real-space substrate lattice
- Next: construct overlayer lattice based on knowledge of a_1 and a_2

<u>Real space structure:</u>



$c(4 \times 2)$

3.5 Applications and Complications of LEED

<u>Applications of LEED</u>:

1. Surface order and cleanliness – most common
2. Surface atomic structure – need theory
3. Step density – get step height/density from angular beam profile (SPALLED)
4. Phase transition in overlayers - structure may undergo transition with change in coverage or T
5. Dynamics of ordering, disordering, growth, phase transitions - time evolution

<u>Complications and other aspects of LEED:</u>

1. Electron beam damage – sensitive molecular adsorbates
2. Domain structure

– if two domains with different structure coexist ⇒ easy to distinguish

– sometimes difficulties exist (e.g., 3 domains of p(2x1) on fcc(111) = (2x2)

3. Transfer width (for real experimental system $\Delta\varphi$ ~0.01, ΔE~0.5eV)

- the dimensions of ordered regions on the surface are limited to the “transfer width” (Woodruff, p.36-37)

3.6 Theory of LEED Intensities

Positions of LEED spots give information only about surface geometry (unit cell)
Need <u>intensity</u> analysis for determining positions of overlayer atoms

<u>Kinetic Theory</u> – "single scattering" theory

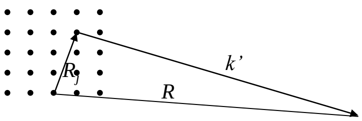
Basic assumption: electron undergoes only a <u>single</u> scattering event when interacting with ion cores

Other assumptions:

Incident wave can be described by plane wave: $\psi_i = \psi_o e^{i\vec{k}\cdot\vec{r}}$

After scattering, the wave from a single atom is $\psi_S = \left(\psi_o \frac{e^{i\vec{k}\cdot\vec{r}}}{R}\right) \cdot f\left(\vec{k},\vec{k}'\right) \cdot e^{i\cdot(\vec{k}-\vec{k}')\cdot\vec{R}_j}$

Spherical wave — Atomic scattering factor — Phase shift caused by path difference between atom and origin



For a 2D array: $I \propto |\psi|^2$

$I \propto |F|^2 \cdot |G|^2$ — Interference function

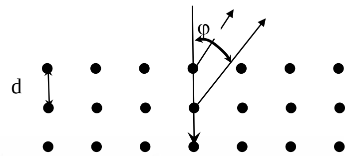
Structure factor: $F = \sum_{j=1}^{S} f_j \cdot e^{i(\vec{k}'-\vec{k})\cdot\vec{R}_j}$

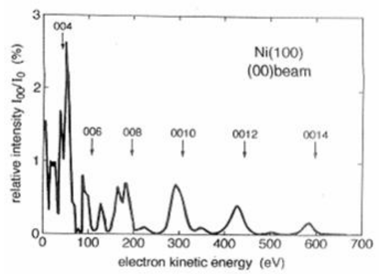
(sum over unit cell)

Results of Kinematic Theory

<u>How does intensity vary?</u>

- need to fulfill "Bragg condition"
- no explicit E dependence, except for atomic scattering factor ⇒slow ↓ as E↑
- theory <u>predicts</u> Bragg peak positions, but <u>poorly</u> estimates relative intensity



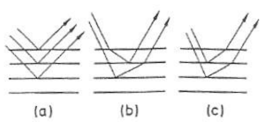


<u>Example</u>: get interference because of

(i) in-plane (2D) scattering

(ii) between-plane scattering

$\Delta = d\,(1 + \cos\varphi) = n\,\lambda$



Need multiple scattering approach!!!

Fig.4.10a-c. Schematic representation of single and multiple scattering processes in LEED. (a) single-scattering events at the "lattice planes" cause a regular Bragg reflection. (b) Double-scattering events with forward- and subsequent back-scattering contribute to the (00) Bragg spot. (c) Double-scattering event with back-scattering and subsequent forward-scattering

Multiple Scattering Theory

Highly computational; includes
- **ion core scattering**
- **multiple scattering**
- **inelastic scattering**
- **temperature effects**

Each atom experiences a flux that includes the incident flux and contributions from the other atoms

- Direct (transform of diffr. int.) – highly debatable?!
- Assume a trial structure, do multiple scattering calculations, use R-factor analysis

(or Pendry factor; the smaller the better!!!)

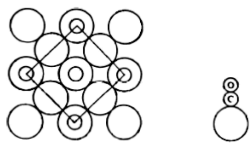


Fig. 2.26 Schematic plan and sectional view of the structure determination for the Ni{100}($\sqrt{2} \times \sqrt{2}$)$R45°$–CO surface.

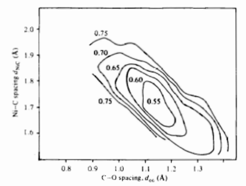
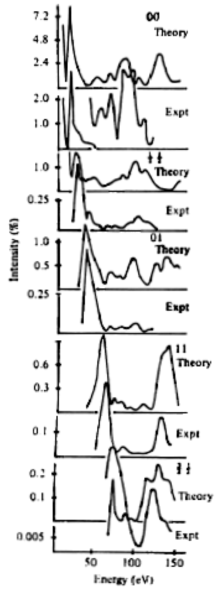


Fig. 2.24 Pendry *R*-factor contour map for a study of the Ni{100}($\sqrt{2} \times \sqrt{2}$)$R45°$–CO structure using the Ni–C and C–O spacings as parameters but assuming a CO molecule perpendicular to the surface and **directly above** a top layer Ni atom (see fig. 2.26 – after Andersson & Pendry, 1980).



3.7 Reflection High-Energy Electron Diffraction (RHEED)

Elements of RHEED: high energy electrons (5-50keV); grazing incidence on crystalline sample; often in Molecular Beam Epitaxy (MBE) setups

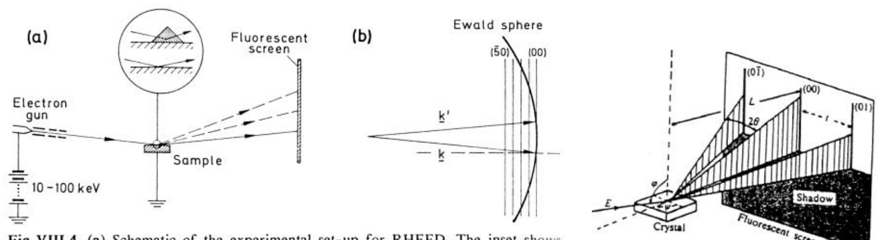


Fig. VIII.4. (a) Schematic of the experimental set-up for RHEED. The inset shows two different scattering situations on a highly enlarged surface area: surface scattering on a flat surface (below) and bulk scattering by a three-dimensional crystalline island on top of the surface (above). (b) The Ewald sphere construction for RHEED. **k** and **k'** are primary and scattered wavevectors, respectively. The sphere radius k = k' is much larger than the distance between the reciprocal lattice rods (hk). For more details, see Sect.4.2 and Figs.4.2,3

cf. Luth, pp.201-209

RHEED pattern consists of streaks and spots (some controversy about causes of streaks)

- streaking: diffraction from perfect planes, and nearly “flat” Ewalds sphere;

- spots: surface roughness

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Example RHEED patterns

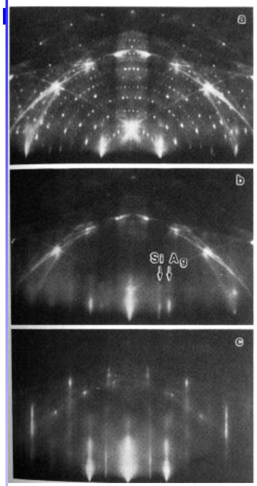
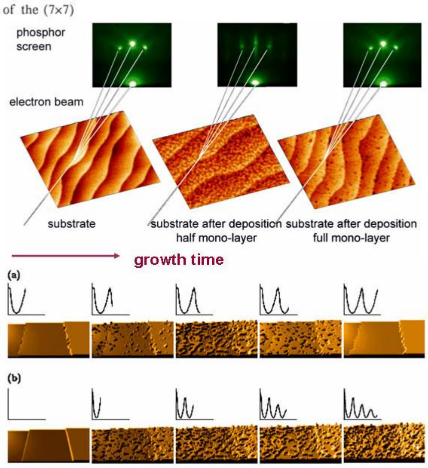


Fig. VIII.5a–c. RHEED patterns taken with a primary energy of E = 15 keV and a direction of incidence of [112] on a Si(111) surface: (a) Clean Si(111) surface with a (7×7) superstructure. (b) After deposition of nominally 1.5 monolayers (ML) of Ag streaks due to the Ag layers are seen on the blurred (7×7) structure. (c) After deposition of 3ML of Ag the texture structure due to the Ag layers develops in place of the (7×7) structure [VIII.3]



Important use:

RHEED oscillations for MBE to monitor growth conditions

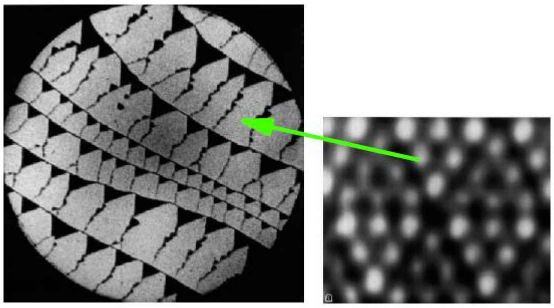
Comparison of Experimental Specs for LEED and RHEED

Range of elements:	all, but not element specific both
Destructive:	no, except in special cases of electron-beam damage both
Depth probed:	4-20Å (LEED) 2-100Å (RHEED)
Detection limits:	0.1ML; atomic positions to 0.1Å both
Resolving power:	typically 200Å; best systems 5μm both
Lateral resolution:	typically 0.1mm; best systems ~10μm (LEED)
	200μm x 4mm; best systems 0.3nm x 6 nm (RHEED)
Imaging capability:	no; need special instruments – LEEM
Main uses:	analysis of surface crystallography (LEED)
	monitoring surface structure, in-situ growth (RHEED)
Cost:	<75K (LEED) 50k-200k (RHEED)

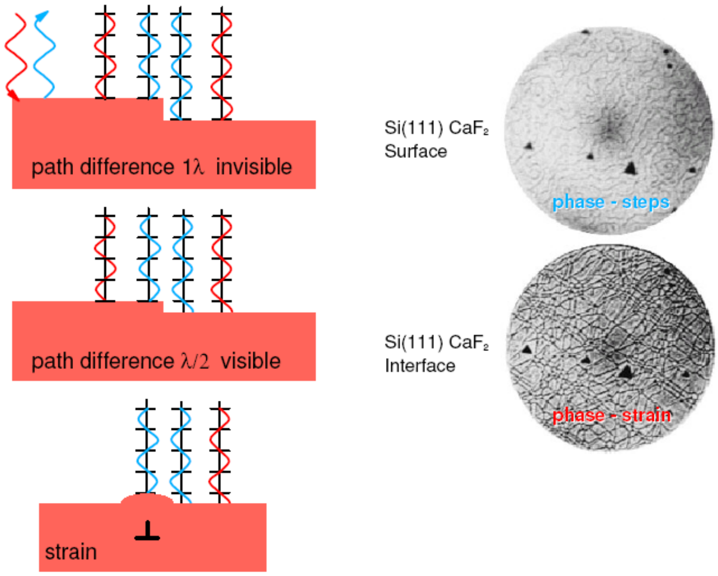
3.8 Low Energy Electron Microscope (LEEM)

LEEM history

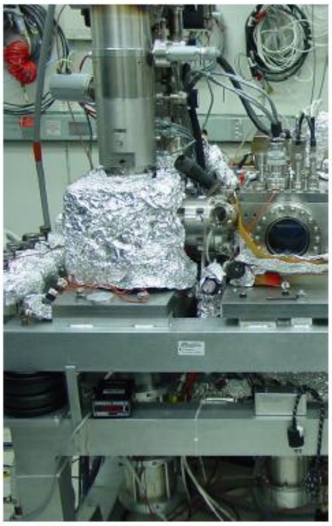
- 1962 Invention by Ernst Bauer
- 1985 Operational LEEM instrument (Telieps and Bauer)
- 1991 IBM LEEM-I (Tromp and Reuter)
- 1998 IBM LEEM-II
- 2006 SPECS FE-LEEM P90



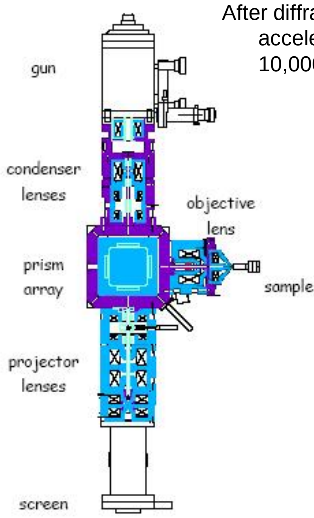
Phase contrast



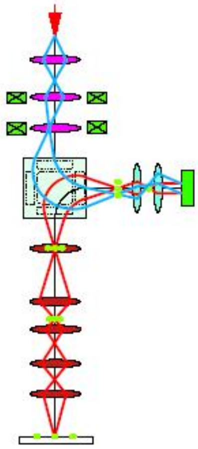
IBM LEEM II



Surf. Reviews and Lett. 5 (1998) 1189



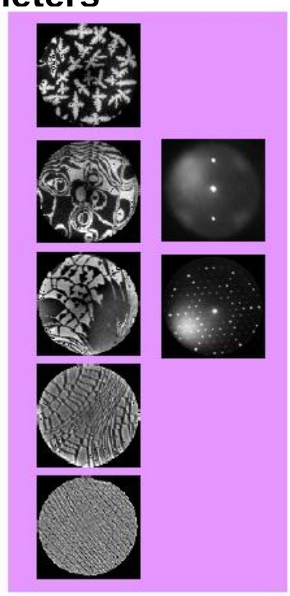
After diffraction, electrons are accelerated from ~ 1 eV to ~ 10,000 eV



LEEM operating parameters

- 0 - 100 eV electron energy
- field of view 1 - 100 µm
- 5 nm resolution in plane
- vertical resolution: atomic steps, 0.1 nm
- in situ growth, etching
- RT – 1200ºC

⇒ extremely useful tool to study crystal growth in situ



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

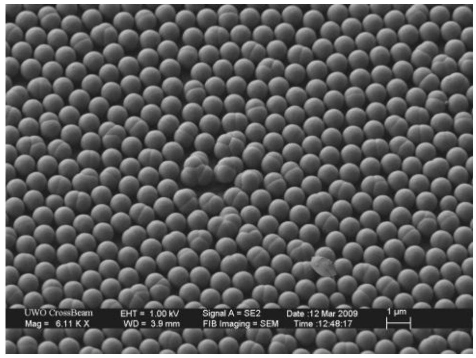
* From R.M Tromp

3.9 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM)

- topology, morphology, chemical information (BSE and EDX)

- 0.5-1000keV electron energy
- field of view 0.1 - 100 μm
- 5 nm resolution in plane
- Magnification 10x – 300,000x
- Typical operating pressure <1atms
- Non-destructive nature: though sometimes electron beam irradiation can cause sample damage

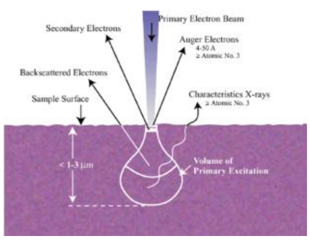


by Eric Barbagiovanni

- **Advantages**: surface, common technique
- **Disadvantages**: vacuum compatibility; coating non-conductive specimens, typical cost: US$50,000 to 300,000

Electron beam-solid interactions

Secondary electrons (SEs): are produced by the interactions between energetic e's and weakly bonded valence e's of the sample



Backscattered electrons (BSEs): are primary e's leaving the specimen after a few large angle elastic scattering events

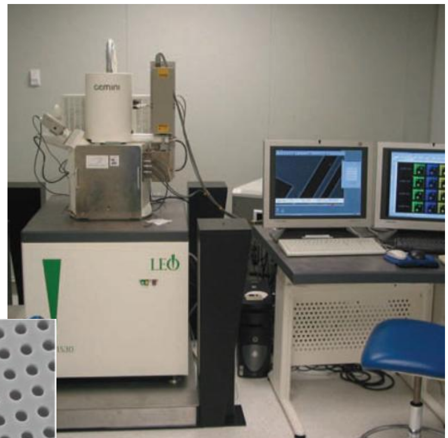
Auger electron: incident e^- kicks out an inner shell e^-, a vacant e^- state is formed; this inner shell vacant state is then filled by another e^- from a higher shell, and simultaneously the energy is transferred to another e^- that leaves the sample

Characteristic X-rays: emitted when a hole is created in the inner shell of an atom in the specimen due to inelastic e^- scattering, as it can recombine with an outer shell e^- (EDX)

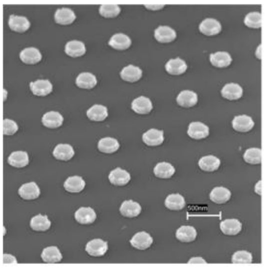
Cathodoluminescene (CL): light emission arising from the recombination of e-h pairs induced by excitation of e's in the valence band during inelastic scattering in a semiconducting sample

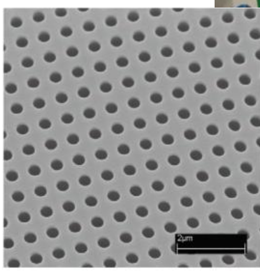
SEM/e-beam lithography in the Nanofab

The e-beam lithography system (right) is a LEO 1530 field emission scanning electron microscope (FE-SEM) fitted with a laser interferometer controlled stage (middle right).



The micrograph (bottom right) shows a square array of 300nm holes on 700nm pitch written in PMMA on Si. Also shown is an array of Cr dots on Si patterned by e-beam lithography and liftoff (below).





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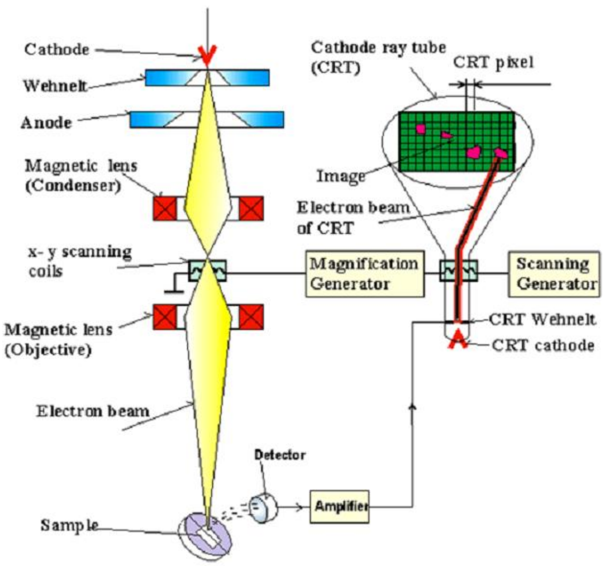
Schematic diagram of SEM



Filament (cathode): free e's by thermionic emission of W, LaB_6

Wehnelt Cylinder: focuses the e-beam and stabilizes beam current

Anode Plate: maintains the HV difference between the anode and the cathode, and accelerates the free electrons down the column

Condenser Lens: reduces the diameter of the electron beam to produce a smaller spot size

Scan Coils: electromagnetically raster the e-beam on the surface

Final Objective Lens: focuses the e-beam on the surface; the smallest spot is about 5 nm (~ 1nm with a FI source)

Detectors: within the scope chamber, but not part of the column are the detectors

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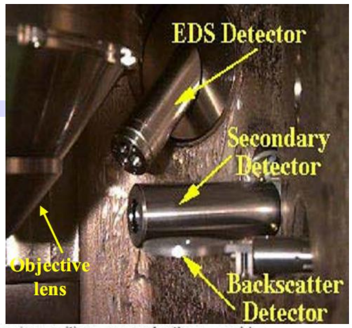
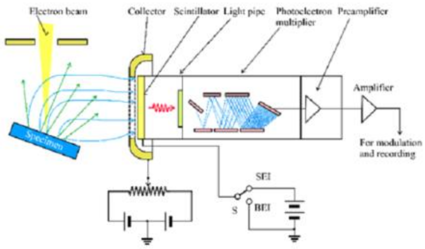
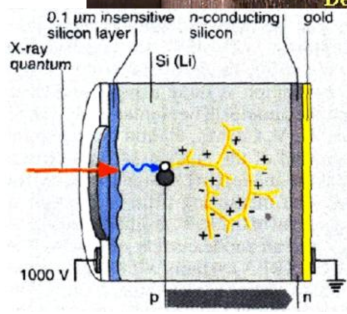
SEM Detectors





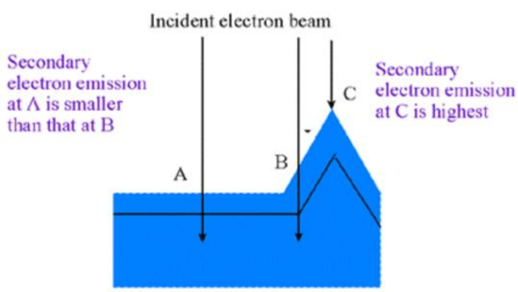
Everhart-Thornley (E-T) detector

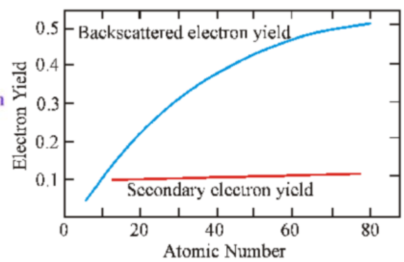


EDX spectrometer

Contrast of secondary electron micrograph

Contributions from (a) sample topography and (b) compositional contrast





Q: Why do the backscattered electron micrographs, rather than secondary electron micrographs reveal the compositional contrast?