

Phys 774: Electron Spectroscopy Photoelectron Spectroscopy and Electron Diffraction

Fall 2007

Lecture 14

1

Interaction of Electrons, X-rays, and Neutrons with matter

Need UHV system for Electron Spectroscopy

2

Doing Spectroscopy with Electrons

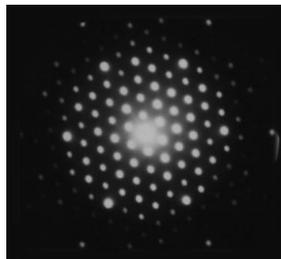
- > Most electron diffraction is performed with high energy electrons whose wavelengths are orders of magnitude smaller than the inter-planar spacing in most crystals. For example, for 100 keV electrons $\lambda < 3.7 \times 10^{-12}$ m. Typical lattice parameters for crystals are around 0.3 nm.
- > Electrons are charged, light particles and their penetration into solids is **very** limited.
- > LEED and RHEED are therefore considered to be surface science techniques.
- > A typical electron diffraction pattern for a crystalline specimen is shown here:

$$\lambda = h/p = h/(2mE)^{1/2}$$

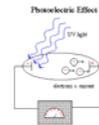
$$E = 20 \text{ eV} \rightarrow \lambda \approx 2.7 \text{ \AA};$$

$$100 \text{ keV} \rightarrow 0.037 \text{ \AA}$$

Small penetration depth (few tens of \AA)
– surface analysis



OUTLINE

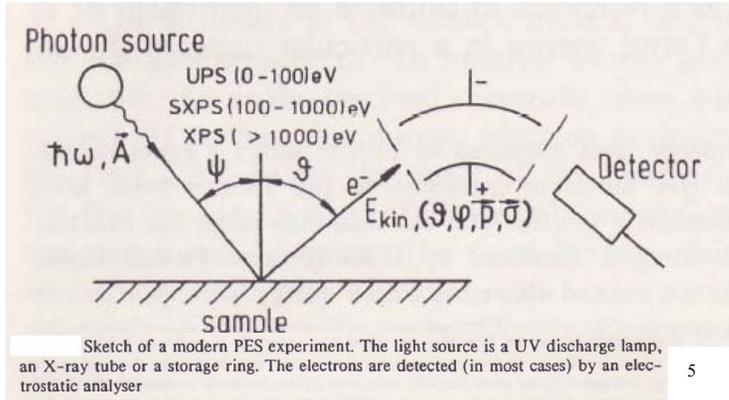
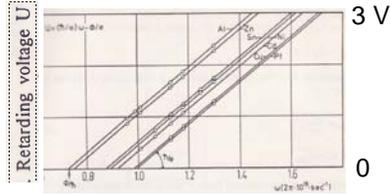
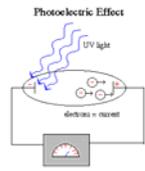


1. ESCA (Electron Spectroscopy for Chemical Analysis) which measures the chemical shift and thereby probes the local environment and oxidation state of the compound – also called x-ray photoelectron spectroscopy (XPS)
2. AES (Auger Electron Spectroscopy) is a two electron process mainly used for elemental analysis of surface constituents
3. X-ray Fluorescence again is mainly used for elemental (chemical) analysis
4. ELS (Electron Loss Spectroscopy) which like optical spectroscopy gives the dielectric function of the material – also called electron energy loss spectroscopy (EELS)
5. LEED (Low Energy Electron Diffraction) mainly used for structural analysis.
6. RHEED (Reflection High Energy Electron Diffraction) mainly used for in situ characterization of superlattices during layer-by-layer growth.
7. STM (Scanning Tunneling Microscopy) which is used to obtain atomic resolution of atoms and molecules on surfaces.

elastic

4

Photoelectron spectroscopy



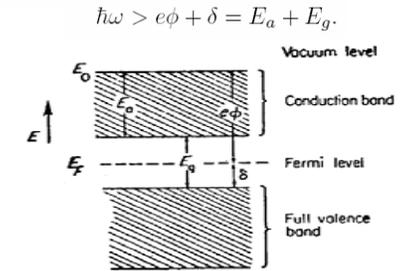
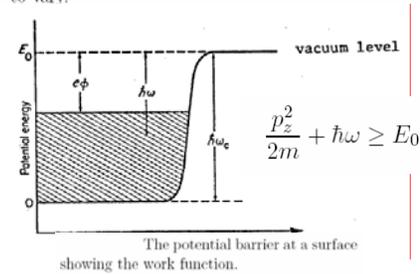
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Photoemission spectroscopy

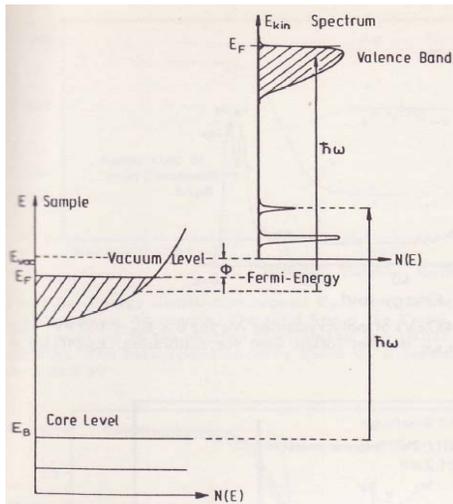
$$I = I(E, \theta_e, \phi_e, \vec{\sigma}; \hbar\omega, \vec{\rho}_p, \theta_p, \phi_p)$$

where $E, \theta_e, \phi_e, \vec{\sigma}$ are respectively the kinetic energy, polar angle, azimuthal angle, and spin of the electron, and $\omega, \vec{\rho}_p, \theta_p, \phi_p$ are respectively the frequency, polarization, polar angle, and azimuthal angle of the photon.

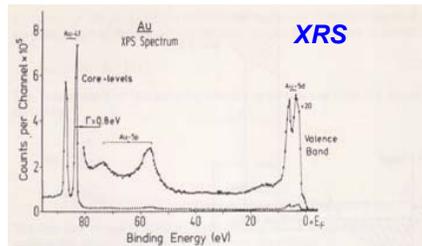
1. EDC (Energy Distribution Curves) where the photoelectron current is observed as a function of electron energy $I = I(E)$ with all other parameters held constant
2. CIS (Constant Initial State Spectroscopy) where $\hbar\omega - E$ is kept constant, and the photoelectron current is measured as a function of electron energy and photon energy $I = I(E, \hbar\omega)|_{E-\hbar\omega=\text{const}}$
3. CFS (Constant Final State Spectroscopy) where $I = I(\hbar\omega)$ is measured
4. ARPS (Angular Resolved Photoemission Spectroscopy) where the angles are allowed to vary.



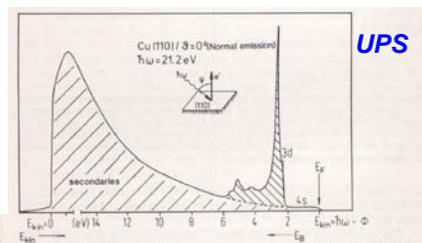
Photoemission spectroscopy



Relation between the energy levels in a solid and the electron energy distribution produced by photons of energy $\hbar\omega$. The natural abscissa for the photoelectrons is the kinetic energy with its zero at the vacuum level of the sample ($E_{kin} = \hbar\omega - |E_B| - \phi$). Experimenters generally prefer to use E_B as the abscissa. E_B is the so-called binding energy of the electrons, which in solids is generally referred to the Fermi level and in free atoms or molecules to the vacuum level



XPS spectrum ($\hbar\omega = 1487\text{eV}$) of polycrystalline Au for $0 \leq E_B \leq 100\text{eV}$. The 5d valence band and the $4f_{7/2,5/2}$ doublet (often used for calibration: $E_B(4f_{7/2}) = 84.0\text{eV}$) are clearly seen



UPS (He I, $\hbar\omega = 21.2\text{eV}$) spectrum from a (110) face of Cu (normal emission, $\theta = 0, \phi$ being the polar angle with respect to the surface normal). The flat 4s band and the structured 3d band are seen. The cutoff marks the point where $E_{kin} = 0$ and via (1,2) the work function can then be derived

Photoemission spectroscopy

In the photoemission process, three basic things must happen: (3-step model)

1. optical excitation of an electron from an occupied state
2. transport of the photo-excited electron to the surface
3. the electron must escape from the surface and into the vacuum region

$$I_p(E, \omega) = P(E, \omega) \cdot T(E) \cdot D(E)$$

Electron excitation probability:

$$P(E, \omega) \sim \sum_{n,n'} \int d^3k \delta(E_{n'}(\vec{k}) - E_n(\vec{k}) - \hbar\omega) \delta(E_{n'}(\vec{k}) - E)$$

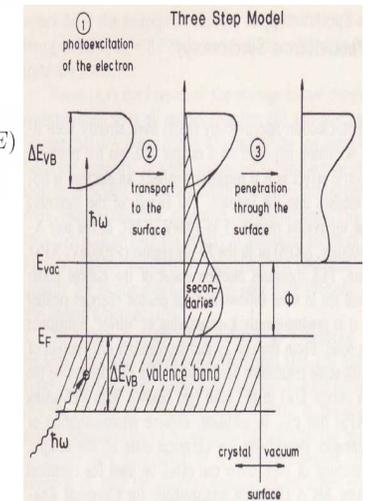
The first δ function represents the joint density of states for optical absorption and the second δ function selects out the energy that is set by the energy analyzer.

Transmission function:

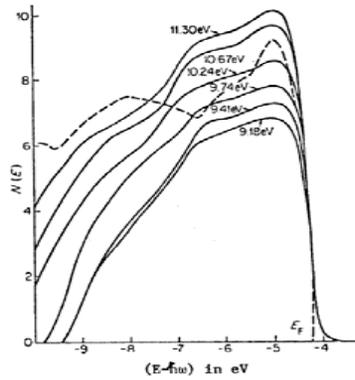
$$T(E) = \frac{\lambda_e(E)/\lambda_{ph}(\omega)}{1 + \lambda_e(E)/\lambda_{ph}(\omega)}$$

Escape function:

$$D(E) = \begin{cases} \frac{1}{2} \left[1 - \left(\frac{E_F + \phi}{E} \right)^{\frac{1}{2}} \right] & \text{for } E > E_F + e\phi \\ 0 & \text{otherwise} \end{cases}$$



Photoemission spectroscopy



Energy distribution curves for photoelectrons in aluminum for various photon energies. The dashed curve shows the density of states over a wide energy region.

9

Photoelectron spectroscopy

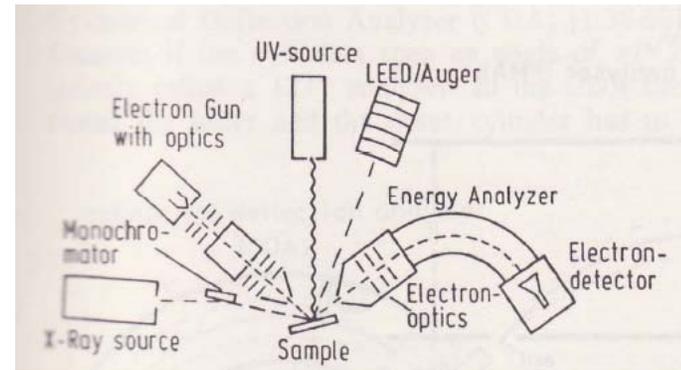
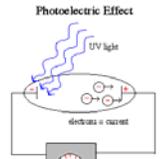
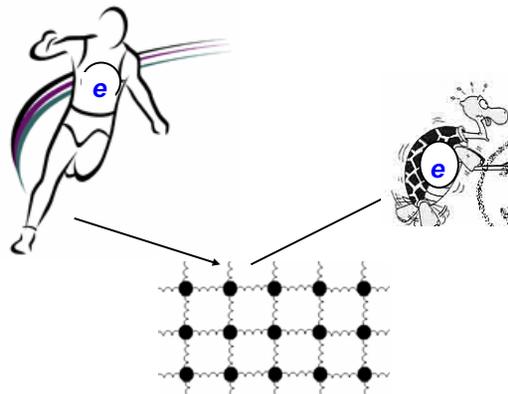


Diagram of a typical modern setup used for PES experiments involving UV source, monochromatic X-ray source, LEED-Auger facility, and electron-energy analyser usable for PES, Auger analysis and EELS (electron energy-loss spectroscopy)



10

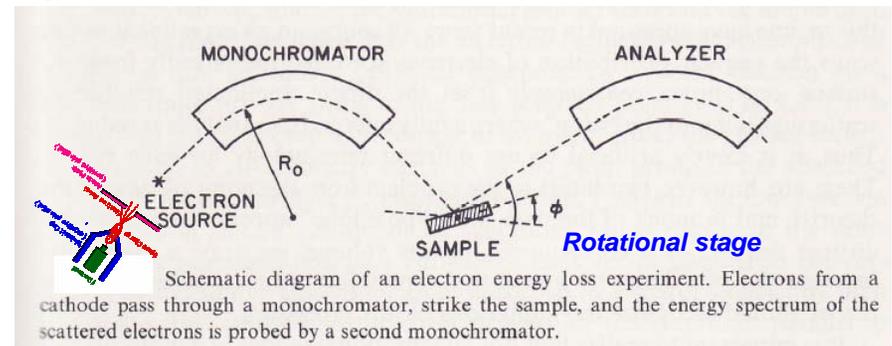
Electron Energy Loss Spectroscopy (EELS)



11

Electron Energy Loss Spectroscopy (EELS)

In **electron energy loss spectroscopy** (EELS) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations, inner shell ionisations, and Cherenkov radiation. The inner shell ionisations are particularly useful for detecting the elemental components of a material. For example, one might find that a larger-than-expected number of electrons comes through the material with 285 eV (electron volts, a unit of energy) less energy than they had when they entered the material. It so happens that this is about the amount of energy needed to remove an inner-shell electron from a carbon atom. This can be taken as evidence that there's a significant amount of carbon in the part of the material that's being hit by the electron beam. With some care, and looking at a wide range of energy losses, one can determine the types of atoms, and the numbers of atoms of each type, being struck by the beam. The scattering angle (that is, the amount that the electron's path is deflected) can also be measured, giving information about the dispersion relation of whatever material excitation caused the inelastic scattering.



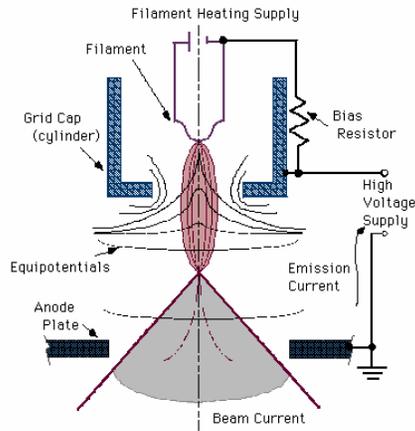
Schematic diagram of an electron energy loss experiment. Electrons from a cathode pass through a monochromator, strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.



Electron Energy Loss Spectroscopy (EELS)

The Electron Source

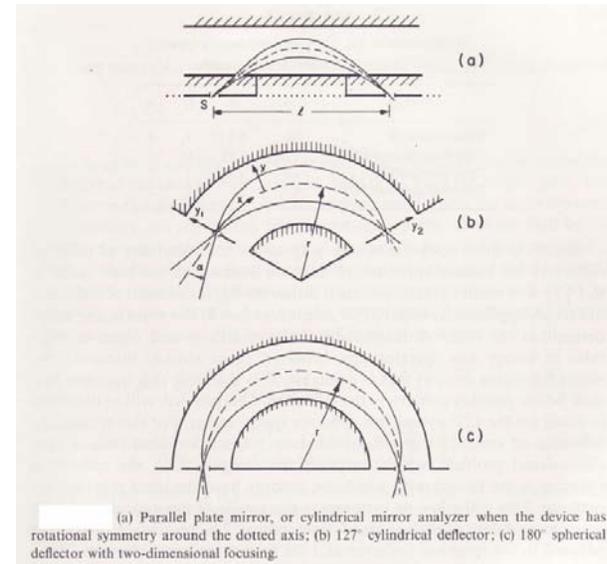
The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten which functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. Some accelerate right by the anode and on down the column, to the sample. Other examples of filaments are Lanthanum Hexaboride filaments and field emission guns.



13

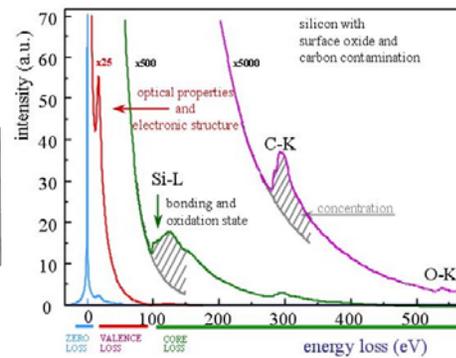
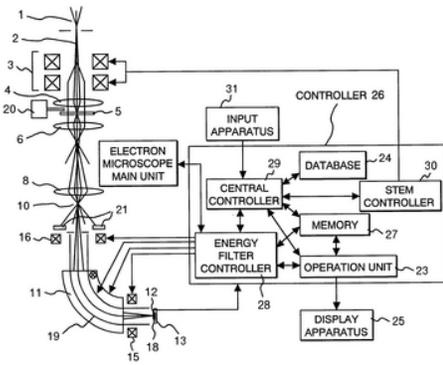
Electron Energy Loss Spectroscopy (EELS)

Electron Energy Analyzers



14

Electron Energy Loss Spectroscopy (EELS)



15

Electron Energy Loss Spectroscopy (EELS)

Surface plasmons:

$$\epsilon_b(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + [i/\tau(\omega)])} \equiv \epsilon_\infty + \frac{4\pi i\sigma(\omega)}{\omega}, \quad \text{loss function } \text{Im}\{-1/(1 + \epsilon_b(\omega))\}$$

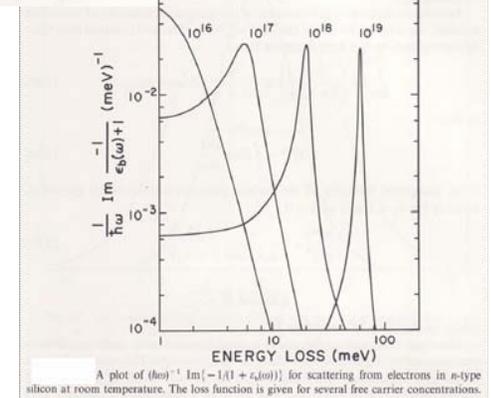
$$\text{Im}\left\{\frac{-1}{1 + \epsilon_b(\omega)}\right\} = \frac{\omega\omega_{sp}^2}{(1 + \epsilon_\infty)\tau(\omega) [(\omega_{sp}^2 - \omega^2)^2 + \omega^2/\tau^2(\omega)]^{-1/2}}, \quad \text{Maximum condition: } \omega_{sp}^2 = 4\pi ne^2/m^*(1 + \epsilon_\infty)$$

$\omega_{sp} = \omega_p/(1 + \epsilon_\infty)^{1/2}$ is the frequency of the surface plasmons

$$\omega \ll \omega_{sp},$$

$$\text{Im}\left\{\frac{-1}{1 + \epsilon_b(\omega)}\right\} = \frac{\omega}{\omega_p^2} \frac{1}{\tau(\omega)} \equiv \frac{\omega}{4\pi\sigma_R(\omega)}$$

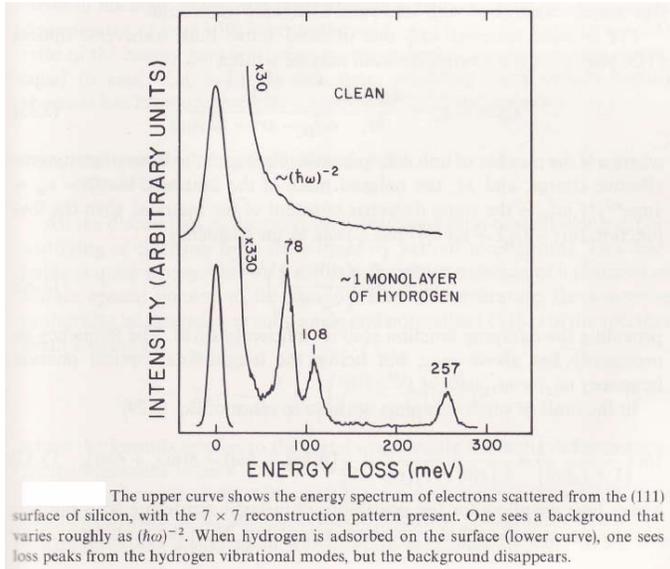
Can be used to measure conductivity $\sigma_R(\omega)$



A plot of $(\hbar\omega)^{-1} \text{Im}\{-1/(1 + \epsilon_b(\omega))\}$ for scattering from electrons in n-type silicon at room temperature. The loss function is given for several free carrier concentrations.

High Resolution Electron Energy Loss Spectroscopy (HREELS)

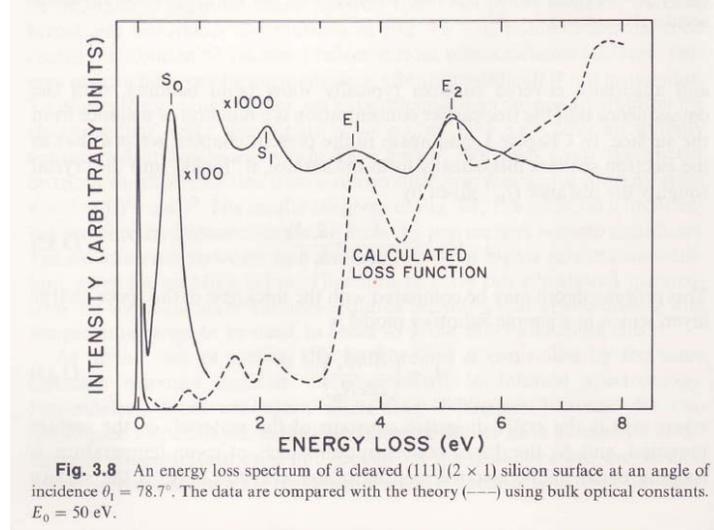
Surface vibrations:



17

Electron Energy Loss Spectroscopy (EELS)

Interband transitions:



18

Example of Electron Energy Loss Spectroscopy (EELS)



Solid State Communications 113 (2000) 553-558

solid state communications
www.elsevier.com/locate/ssc

In situ Raman scattering studies of the amorphous and crystalline Si nanoparticles

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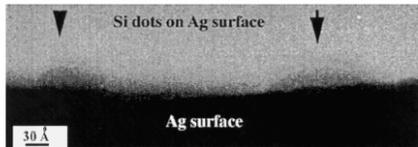
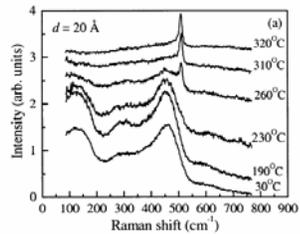


Fig. 1. TEM cross-section image of the recrystallized 30 Å sample grown on Ag buffer.



19

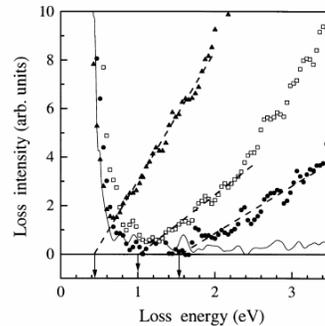
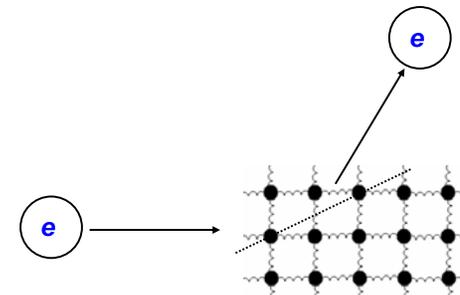


Fig. 6. EELS spectra of the 5 Å sample before (triangles) and after the annealing (circles). Dashed lines guide the eye to the onset of the electronic transitions indicated with arrows. Spectra for polycrystalline Si and SiO_2 are shown for comparison with open squares and solid line, respectively.

Electron diffraction



20

Electron diffraction vs. x-ray

The two techniques are complementary. In general, though, electron diffraction is more sensitive than x-ray diffraction (electrons are charged), and can give more information about surfaces (you can see defects on surfaces, etc.)

This shows a picture of diffraction from a powder (which is why you get rings rather than spots).

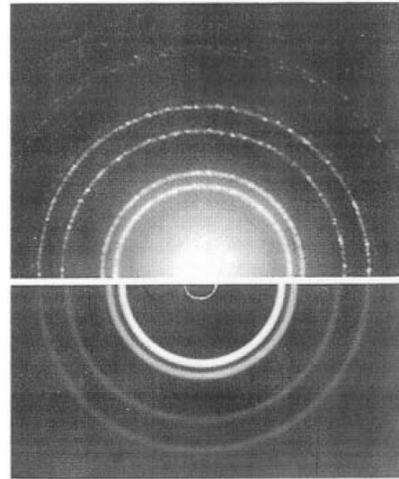
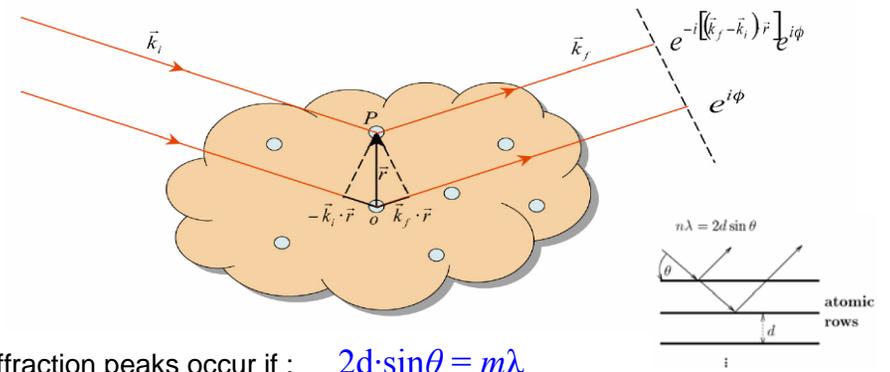


FIGURE 4.3 Comparison of X-ray diffraction and electron diffraction. The upper half of the figure shows the result of scattering of 0.071 nm X rays by an aluminum foil, and the lower half shows the result of scattering of 600 eV electrons by aluminum. (The wavelengths are different so the scales of the two halves have been adjusted.)

41

Interaction of Electrons, X-rays, and Neutrons with matter

Adding up phases at the detector of the wavelets scattered from all the scattering centers in the sample:



Diffraction peaks occur if : $2d \cdot \sin \theta = m\lambda$

Or: $\vec{k}_f - \vec{k}_i = \vec{G}$ where \vec{G} is a reciprocal lattice vector of the crystal

22

Features of High Energy Electron Diffraction

There are three particularly important features of diffraction using **high energy electrons**:

(1) Since λ is very small, Bragg angles are also small, so the Bragg Law can be simplified to:

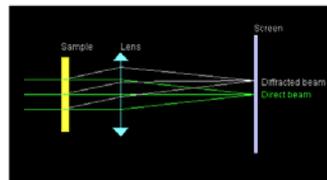
$$2d \cdot \theta_B = \lambda$$

Electron energy / keV	Wavelength / pm	Diffracting planes	θ_B
50	5.355	Cu ₁₁₁	0.75
100	3.701	Al ₂₀₀	0.54
300	1.969	Si ₂₀₀	0.32

(2) The diameter of the *Ewald sphere* is very large compared to the size of the unit cell in the reciprocal lattice.



(3) Lenses are able to focus the diffraction pattern and to change the camera length, which is equivalent to moving the film in an x-ray experiment



Geometry of Electron Diffraction

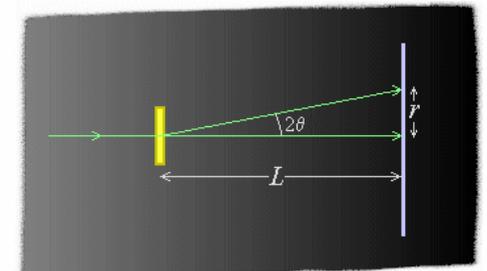
Geometry

The geometry of an electron diffraction experiment is shown here.

The Bragg Law for small angles approximates to:

From the diagram: $\frac{r}{L} = 2\theta$

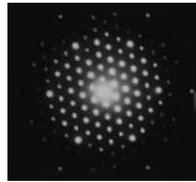
Therefore: $\frac{r}{L} = \frac{\lambda}{d}$ or $r = \lambda L \times \frac{1}{d}$



The distance, r , of a diffraction spot from the direct beam spot on the diffraction pattern, varies inversely with the spacing of the planes, d , that generate that spot.

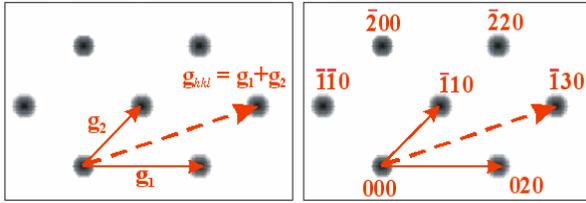
24

Geometry of Electron Diffraction



Indexing Electron Diffraction Patterns

If we know the index for two diffraction spots it is possible to index the rest of the spots by using vector addition. Every diffraction spot can be reached by a combination of these two vectors.



BCC pattern 1



BCC pattern 2



BCC pattern 3

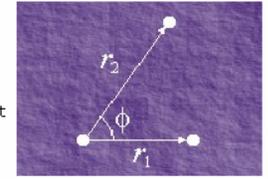


Geometry of Electron Diffraction

Indexing the pattern

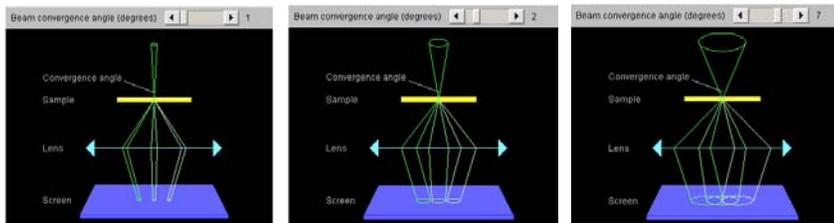
Any 2-D section of a reciprocal lattice can be defined by two vectors so we only need to index 2 spots. All others can be deduced by vector addition.

If the crystal structure is known, the ratio procedure for indexing is:



- Choose one spot to be the origin. **Note:** it does not matter which spot you choose.
- Measure the spacing of one prominent spot, r_1 . **Note:** for greater accuracy measure across several spots in a line and average their spacings.
- Measure the spacing of a second spot, r_2 . **Note:** the second spot must not be collinear with the first spot and the origin.
- Measure the angle between the spots, ϕ .
- Prepare a table giving the ratios of the spacings of permitted diffraction planes in the known structure.
- Take the measured ratio r_1/r_2 and locate a value close to this in the table.
- Assign the more widely-spaced plane (usually with lower indices) to the shorter r value.
- Calculate the angle between pair of planes of the type you have indexed.
- If the experimental angle ϕ , agrees with one of the possible values - accept the indexing. If not, revisit the table and select another possible pair of planes.
- Finish indexing the pattern by vector addition.

Focused beams and Electron Diffraction



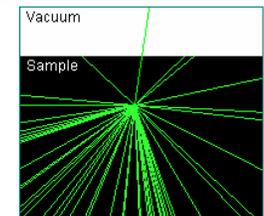
Conventional electron diffraction techniques use a parallel beam of incident radiation, these techniques are called Selected Area Diffraction (SAD). In contrast Convergent Beam Electron Diffraction (CBED) uses a convergent beam of electrons to limit the area of the specimen which contributes to the diffraction pattern.

Each spot then becomes a disc within which variations in intensity can usually be seen. Such patterns initially seem more difficult to interpret but they contain a wealth of information about the symmetry and thickness of the crystal and are widely used in TEM.

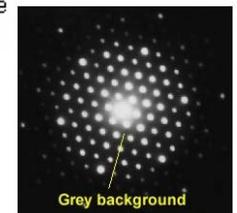
The big advantage of CBED over SAD techniques is that most of the information is generated from small regions beyond the reach of other techniques.

Inelastic Scattering and Electron Diffraction

Conventional high energy electron diffraction relies on elastic scattering. However, in a thick enough specimen, **inelastic** scattering will also take place. Inelastically scattered electrons travel in all directions but their distribution **peaks in a forward direction**.



More electrons are scattered forward than sideways. This contributes a grey background around the central spot of the diffraction pattern, as shown here.

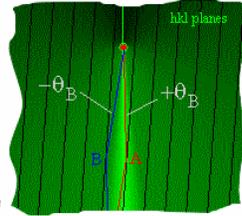


Kikuchi lines in Electron Diffraction

(1) Electrons which have been inelastically scattered can subsequently be diffracted, but only if they are now travelling at the Bragg angle, θ_B to a set of planes.

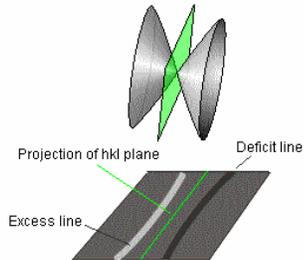
(2) Two sets of electrons will be able to do this - those at $+\theta_B$ and those at $-\theta_B$.

(3) This diffraction results in intensity changes in the background. Because there are more electrons at A than B (since electrons passing through A are closer to the incident direction than those through B) one bright line is developed (the excess line) together with one dark line (the deficit line).



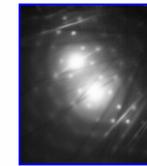
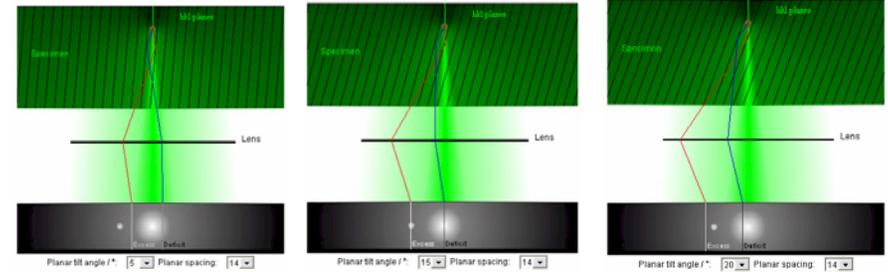
(4) Because the electrons are inelastically scattered in **all** directions, the diffracted electrons will form a **cone**, not a beam. Hence we observe Kikuchi **lines** - not Kikuchi spots!

(5) The spacing of the pair of Kikuchi lines is the same as the spacing of the diffracted spots from the same plane. However, the position of the lines is very sensitively controlled by the orientation of the specimen and Kikuchi lines are often used to set the orientation of a crystal in the TEM to an accuracy of 0.01 degrees.

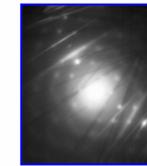


29

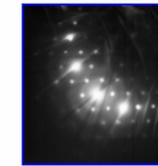
Kikuchi lines in Electron Diffraction



The Kikuchi lines pass straight through the transmitted and diffracted spots. The diffracting planes are therefore tilted at **exactly** the Bragg angle to the optic axis



The crystal has now been tilted **slightly away** from the Bragg angle, so that the Kikuchi lines no longer pass through the transmitted and diffracted spots.



Here the crystal is tilted so that **more than one set of planes** are diffracting. Each set of diffracting planes has its own pair of Kikuchi lines.

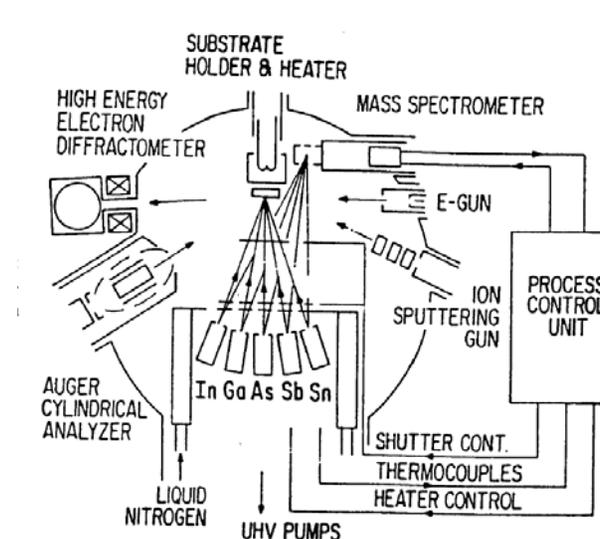
30

Reflection High Energy Electron Diffraction (RHEED)

- Glancing incidence: despite the high energy of the electrons (5 – 100 keV), the component of the electron momentum perpendicular to the surface is small
- Also small penetration into the sample – surface sensitive technique
- No advantages over LEED in terms of the quality of the diffraction pattern
- However, the geometry of the experiment allows much better access to the sample during observation of the diffraction pattern. (important if want to make observations of the surface structure during growth or simultaneously with other measurements)
- Possible to monitor the atomic layer-by-atomic layer growth of epitaxial films by monitoring oscillations in the intensity of the diffracted beams in the RHEED pattern.

31

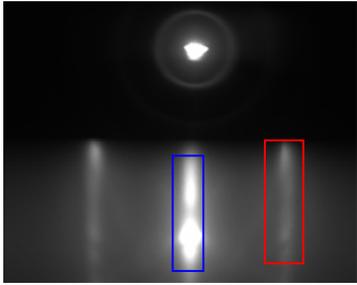
MBE and Reflection High Energy Electron Diffraction (RHEED)



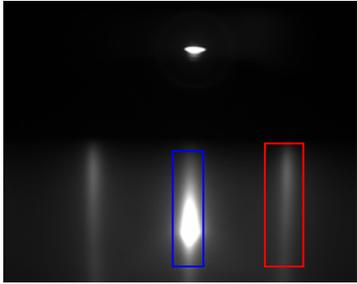
32

Real time growth control by Reflection High Energy Electron Diffraction (RHEED)

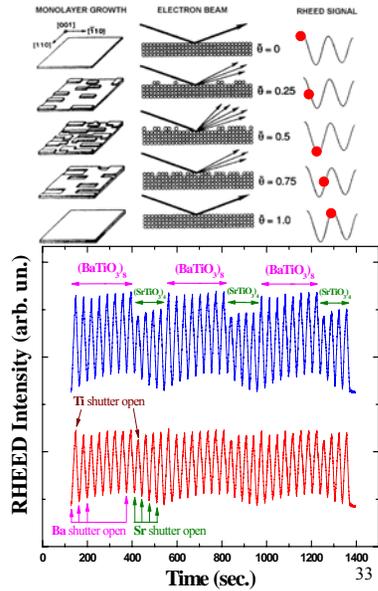
Growth start



Growth end



110 azimuth



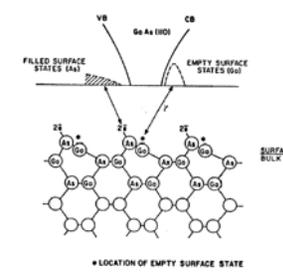
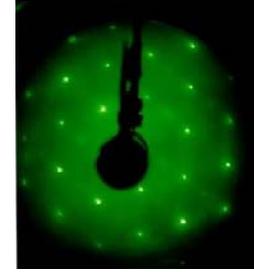
Low Energy Electron Diffraction (LEED)

$$\lambda = h/p = h/(2mE)^{1/2}$$

$$E = 20 \text{ eV} \rightarrow \lambda \approx 2.7 \text{ \AA}$$

$$200 \text{ eV} \rightarrow 0.87 \text{ \AA}$$

Small penetration depth (few tens of \AA)
– surface analysis



Because electrons are light, charge particles, they interact with the electrons within the lattice and do not penetrate far.

