Phys 774: Electron Spectroscopy

Photoelectron Spectroscopy

and Electron Diffraction

Fall 2007

Lecture 14

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:

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

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

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

Small penetration depth (few tens of Å) – surface analysis

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

Surface

Neutrons

X-rays

Electrons

Need UHV system for Electron Spectroscopy

OUTLINE

1. ESCA (Electron Spectroscopy for Chemical Analysis) which measures the chemical shift and thereby probes the local environment and ionicity 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.


7. STM (Scanning Tunneling Microscopy) which is used to obtain atomic resolution of atoms and molecules on surfaces.
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 ionizations 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.
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 Langmuir-Hectomode filament and field emission gun.

**Electron Energy Analyzers**

Surface plasmons:

Maximum condition:

Can be used to measure conductivity \( \sigma_k(\omega) \)
High Resolution Electron Energy Loss Spectroscopy (HREELS)

Surface vibrations:

The upper curve shows the energy spectrum of electrons scattered from the (111) surface of silicon, with the 7 x 7 reconstruction pattern present. One sees a background that varies roughly as \((h\nu)^{-2}\). When hydrogen is adsorbed on the surface (lower curve), one sees loss peaks from the hydrogen vibrational modes, but the background disappears.

Electron Energy Loss Spectroscopy (EELS)

Interband transitions:

Fig. 3.8: An energy loss spectrum of a cleaved (111)(2 x 1) silicon surface at an angle of incidence \(\theta_1 = 78.7^\circ\). The data are compared with the theory (---) using bulk optical constants. \(E_{1S} = 50\) eV.

Example of Electron Energy Loss Spectroscopy (EELS)

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

Si dots on Ag surface

Ag surface

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

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 SiO2 are shown for comparison with open squares and solid lines, respectively.

Electron diffraction
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).

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.

Features of High Energy Electron Diffraction

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

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

\[ 2d \cdot \theta_B = \lambda \]

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

The geometry of an electron diffraction experiment is shown here.

The Bragg Law for small angles approximates to:

\[ \lambda = 2d \theta \]

From the diagram:

\[ \frac{r}{L} = 2d \]

Therefore:

\[ \frac{r}{L} = \frac{\lambda}{d} \]

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.
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.

\[
g_{\text{diff}} = g_1 + g_2
\]

focused beams and Electron Diffraction

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, $\theta_b$, to a set of planes.

2. Two sets of electrons will be able to do this - those at $\theta_a$ and those at $\theta_b$.

3. The diffraction results in intensity changes in the background. Because there are more electrons at $\theta_a$ than $\theta_b$ (since electrons passing through $\theta_a$ are closer to the incident direction than those though $\theta_b$) 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.

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.

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

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

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

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

Small penetration depth (few tens of Å) – surface analysis

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