Thin Films, Surfaces and Epitaxy

10 Lectures in course

1. Basic concepts
2. Surface crystallography
3. Surface spectroscopy
4. Adsorption
5. Growth energetics
6. Epitaxy basics
7. Epitaxy models
8. General thin film growth
9. Specialist thin film growth
10. Nanostructures

LECTURE 2: surface crystallography

1. Introduction, definitions,
2. Miller indices
3. Surfaces of fcc and bcc
4. Surface reconstructions
5. Wood's notation of overlayers
6. Surface reciprocal lattice
7. Low energy electron diffraction (LEED)
8. LEED display apparatus
9. LEED pictures
10. LEED patterns
11. Surface domains
12. Reflection high energy electron diffraction (RHEED)
13. Scanning tunneling microscopy (STM)

Figures from McCash, Zangwill, manufacturers websites, TCD researchers, Klaus Hermann and Philip Hoffmann; Epitaxy of Nanostructures by Schcukin et al
Surface structure?

e.g. a typical metal fcc nanoparticle - showing ideal surface structures

Begin with flat surface of mono-atomic simple cubic structure

Simple cubic lattice: low index faces

(100)  (010)  Consider origin as being located at rearmost vertex in each of these sketches

(110)  (111)

(221)  Also (221)

Exercise: determining the Miller indices of a plane?
Recall Miller indices

The most common planes in a cubic primitive (P) lattice are indicated here.

If a plane intercepts all the points on the axis, translate it by one lattice unit normal to the plane (this is an identical position) in order to name it.

Indices for planes within the bulk:
Indices for planes, Miller indices, are the reciprocals of axis intercepts, when a plane does not intercept an axis, the index is zero. The indices are usually written as $h, k, l$ or $(h k l)$ indicating the plane.

Directions and planes in the bulk

Directions and indices within the bulk:
Directions in the unit cell are specified by three integer indices $u$, $v$, $w$ as $[u v w]$ indicating a direction.

e.g. the opposite direction to $[1 1 0]$ is written as $[-T T 0]$ (or as $[-1 -1 0]$ or sometime $[1 1 0]$)

A perpendicular direction (in a cubic lattice) has the product of the indices of the two directions summing to zero... $e.g. [-1 1 0]$ is at right angles to $[1 1 0]$.

These directions are indistinguishable except for the choice of origin and are said to belong to the <110> "family" of directions.

$e.g. [100]$ - denotes the $[100]$ vector direction; for cubic lattice $[100]$ is equivalent to $[010]$ or $[001]$ directions - can refer to <100> "family" of directions.
From simple lattice to face-centred-cubic lattice

<table>
<thead>
<tr>
<th>Simple cubic lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>(essentially no solid is a simple cubic, instead ...)</td>
</tr>
</tbody>
</table>

face-centred-cubic (fcc) lattices

<table>
<thead>
<tr>
<th>(001)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sqrt{2}a )</td>
<td>( \sqrt{2}a )</td>
<td>( \sqrt{3}a )</td>
</tr>
</tbody>
</table>

fcc surface atom densities: “atoms/area”

- (001): \( 2/a^2 = 1.61 \times 10^{15} \text{ cm}^{-2} \) (\( a=3.5\text{Å} \))
- (110): \( 2/\sqrt{2}a^2 = 1.14 \times 10^{15} \text{ cm}^{-2} \)
- (111): \( 4/\sqrt{3}a^2 = 1.86 \times 10^{15} \text{ cm}^{-2} \)

Surfaces, surface normals vector directions

**Surfaces**: ideal surfaces equivalent to bulk planes (hkl) e.g. (100) - denotes the (100) plane or (100) surface; for cubic lattice (100) is equivalent to (010) or (001) - can refer to “family” of equivalent surfaces as (100):

- \{100\}_\text{fcc}
- \{100\}_\text{bcc}

| (100), (010), (001) and [100], [010], [001] for fcc Au and bcc W |

| (110), (111) and [110], [111] for fcc Au and bcc W |

**Surface normals**: In cubic lattices the surface normal to every (hkl) surface is the vector direction [hkl] - because in cubic lattice all axes are equal and orthogonal
Exercise 1: do same for fcc (111) and (110)

Exercise 2: picture equivalent surfaces for bcc

**Reconstruction:** surfaces can “reconstruct” i.e. deviate from the ideal surface plane as it was in the bulk.

Lateral relaxation changing surface atom arrangement can occur as well as relaxation of surface layer inwards (or outwards) compared to bulk.
Reconstructed surfaces

fcc (110) "missing row" 2x1

Differing shadings - different layers

Surface basis vectors and Wood’s notation

Wood’s notation describes the observed surface in terms of the surface basis vectors of the truncated bulk crystal surface $a_1$ and $a_2$, and those of the new top layer or overlayer vectors denoted as $o_1$ and $o_2$. The notation $N$ is either “p” or “c” and $\Theta$ the relative angle of rotation.

Red dots indicate adsorbed atoms in an ordered overlayer.
Surface lattice vectors and Wood's notation

(100) p(2x2) "primitive"

(110) c(2x2) "centred"
or $\sqrt{2} \times \sqrt{2} R 45^\circ$

(111) e.g. an ordered overlayer changes the basis vectors of the (100) surface to $a'$ and $b'$, described in Wood’s notation as $(a'/a) \times (b'/b)$

Surface reciprocal lattice vectors

Reciprocal lattice vectors:

$$a^* = 2\pi (b \times c) / (a \cdot (b \times c))$$

Here $c$ is directed into the surface, $a$ and $b$ within the surface.

Hence $a^*$ and $b^*$ are within the surface and

$$a^* \perp b \text{ and } b^* \perp a$$
Electron diffraction from surfaces

- Fundamentals
- Low energy electron diffraction (LEED)
  - Side note: Discovery
- Display apparatus
- Reciprocal lattices
- LEED pictures
- Real space, reciprocal space and LEED patterns
- Surface domains

- I-V curves - left out

- Reflection high energy electron diffraction (RHEED)

Real space imaging of surfaces

- Scanning Tunneling Microscopy (STM)

Fundamentals of electron diffraction

De Broglie wavelength of electron

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

\[ \lambda = \frac{h}{\sqrt{2meV}} = \sqrt{\frac{150.4}{V}} \text{ Å} \]

Electron beam voltage in range 30-300 V gives \( \lambda \) comparable to lattice spacing!

Also, corresponds to minimum in mean free path, hence surface sensitive!

Electron energy = 20 eV \( \Rightarrow \lambda = 2.7 \text{ Å} \)

Electron energy = 200 eV \( \Rightarrow \lambda = 0.87 \text{ Å} \)
**Low energy electron diffraction**

Diffraction of mono-energetic electrons, elastically reflected (scattered) from the surface “grating”

\[ n\lambda = d(\sin \theta - \sin \alpha) \]

(usually \( \alpha = 0 \), normal incidence)

*Coherence length* determined by spread of energy and parallelism of incident electron beam: pattern is non-coherent sum of patterns from coherence length scales (~100 Å) - thus probes medium range spatial ordering.

**Uses:**
1. Surface order (esp. adlayer) and cleanliness
2. Orient sample w.r.t. polar and azimuthal angles
3. Full real-space structure (in principle)
4. Roughness

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**Discovery of electron diffraction - (& LEED)**

“Diffraction of Electrons by a Crystal of Nickel
The Physical Review 1927

D & G had been working on electron scattering (1921) from polycrystalline nickel: during the accident the target became oxidised; after removing the oxide by heating, the scattering was dramatically altered:

The target was now more crystalline: electrons were diffracted by the crystal, just like x-rays!
LEED display apparatus

Use beam of electrons from gun at well defined energy $E_p$.

Germer: retarding field analyser.
Note polarity of potentials on the grids/screen!

Collected electrons have energy range $0$-$E_p$.

select only those elastically reflected (scattered) by retarding the range by $E_r$, where $E_r = E_p - \Delta E$;
only these pass through the "retarding grid" to be accelerated to ($E_s$~5 keV) screen energy, producing fluorescence on impact.

Reciprocal lattice viewed with LEED

LEED pattern from fcc(111) surface taken with low energy electron beam (~60 eV).

The LEED image directly gives you the reciprocal lattice of the surface. From it one can tell the azimuthal orientation of the surface.
LEED pictures

fcc(111) surface

Spot pattern replicates the surface reciprocal lattice!

E_c > E_b > E_a

λ_c < λ_b < λ_a

As E_p increases, λ decreases:
pattern "shrinks" (reduced θ)

E.g. https://www.youtube.com/watch?v=6uzpGbnrc1c

Spots positions (diffracted beams) determined by
Laue diffraction condition: Δk must be reciprocal lattice vector (or multiple thereof)

2D Laue diffraction condition

(κ_i - κ_s)|_k = Δκ_i = ±G_s

2D version of Ewald sphere (note rods!) illustrates how individual spots derive from reciprocal lattice and incident electron beam energy and direction.

Labeling of spots.
(serious problem of "multiple scattering")

LEED patterns

fcc

real space

diffraction pattern

diffraction (LEED) pattern

(0,0) represents the reflected beam along the surface normal

(100)

(110)

(111)

PY4N07/P07
Surface domains

Ge(100) "2-domain" 2x1

Square shows reciprocal lattice unit cell of ideal (100) surface: "real" surface undergoes 2 x1 reconstruction (dimer-formation). Should see half-size reciprocal unit cell, or extra spot halfway along one direction; actually seen along both directions, evidence of two orthogonal domains on surface (arising from next layer rotation).

RHEED

"reflection high energy": Surface sensitivity by grazing angle reflection; Small incidence angle and large Ewald sphere indicates expect to see narrow "streaks" - spots indication of bumpy surface! (i.e. full of asperities)! RHEED oscillations of intensity in streak during film growth mark the completion of an atomic layer; typically incorporated in MBE or PLD systems.
**RHEED**

Illustration of diffraction of electrons in RHEED by various structures, asperities (i.e. bumps) and of smooth surfaces if electron beam very narrow i.e. hits one point on surface only.

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**STM basics**

"entry level":

Under bias, electrons tunnel across gap; i.e. probability $\approx \exp(-z)$ thus tunnel current strong function of tip-sample distance ($z$):

2 properties:

1. z-sensitivity
2. spatial (x,y) resolution

Microscopy: x-y raster tip "parallel" to surface 2 modes:

1. "constant height" - keep $z$ fixed; measure current; plot $I$
2. "constant current" - change $z$ to keep current fixed; plot required $z$ movement

Reverse polarity, reverse current

Change bias to change the surface states you tunnel "into" or "out of" i.e. selectivity of occupied/unoccupied states
Si(111) 7x7 reconstruction - as observed by STM

Si (111) 7x7: aka "DAS"
Dimer-adatom-stacking fault

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