Lesson 8

Diffraction from finite size crystals

In the previous lesson we found that, in the kinematic approximation, the amplitude scattered in the direction of the wave vector ***k'*** is given by:

$$A = \sum_{j=0} f_j(\theta)\cdot e^{ik.r_j}\cdot e^{ik'(r-r_j)} = e^{ik'r}.\sum_{j=0} f_j(\theta)\cdot e^{i(k-k')r_j} = e^{ik'r}.S(\Delta k).\sum_{r_j=Crystal} e^{i\Delta k.r_j}$$

$$\text{Structure factor } S(\Delta k) = \sum_{r_j=u.cell} f_j(\theta)\cdot e^{i\Delta k.r_j}$$

We write $\mathbf{r}_j$ as a function of the unit cell vectors **a** and **b**:

$\mathbf{r}_j = m.\mathbf{a} + n.\mathbf{b}$, and the index j is now determined by m and n

Inserting this in the summation we get: $\displaystyle\sum_{r_j=crystal} e^{i\Delta k.\vec{r}_j} = \sum_{m=1}^{M} e^{i\Delta k.m\vec{a}}.\sum_{n=1}^{N} e^{i\Delta k.n\vec{b}}$

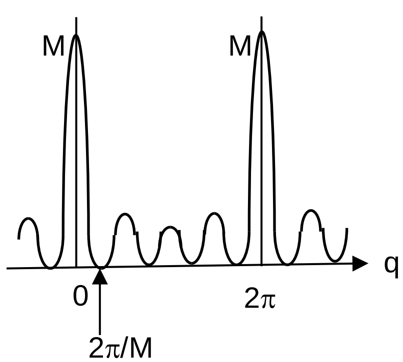
M and N are the number of cells in the a and b directions.

$$A(\Delta k) = S(\Delta k).\frac{e^{iM\Delta k.\vec{a}}-1}{e^{i\Delta k.\vec{a}}-1}.\frac{e^{iN\Delta k.\vec{b}}-1}{e^{i\Delta k.\vec{b}}-1} = S(\Delta k).\frac{e^{i\frac{1}{2}M\Delta k.\vec{a}}}{e^{i\frac{1}{2}\Delta k.\vec{a}}}.\frac{e^{i\frac{1}{2}M\Delta k.\vec{a}}-e^{-i\frac{1}{2}M\Delta k.\vec{a}}}{e^{i\frac{1}{2}\Delta k.\vec{a}}-e^{-i\frac{1}{2}\Delta k.\vec{a}}}.\frac{e^{i\frac{1}{2}N\Delta k.\vec{b}}}{e^{i\frac{1}{2}\Delta k.\vec{b}}}.\frac{e^{i\frac{1}{2}N\Delta k.\vec{b}}-e^{-i\frac{1}{2}N\Delta k.\vec{b}}}{e^{i\frac{1}{2}\Delta k.\vec{b}}-e^{-i\frac{1}{2}\Delta k.\vec{b}}}$$

The important quantity is the intensity. The modulus square eliminates all the exponential terms of the form exp(ika). So we obtain:

$$I(\Delta k) = \left|A(\Delta k)\right|^2 = \left|S(\Delta k)\right|^2.\frac{\sin^2(\frac{1}{2}M\Delta k.\vec{a})}{\sin^2(\frac{1}{2}\Delta k.\vec{a})}.\frac{\sin^2(\frac{1}{2}N\Delta k.\vec{b})}{\sin^2(\frac{1}{2}\Delta k.\vec{b})}$$

Whenever $\Delta\mathbf{k.a}=2\pi h$ ($h=0, \pm1, \pm2, \ldots$), i.e., in the direction of the diffracted beams for the infinite surface, both numerator and denominator become zero. The limiting value is $(1/2M\,\Delta k\text{ a})^2/(1/2\,\Delta k\text{ a})^2 = M^2$, and similarly N^2 for the b term. The zeros of $I(\Delta k)$ are the zeros of the numerators, which occur for:



$\frac{1}{2}.M.\Delta\mathbf{k.a} = m\pi$, $m = 0, \pm1, \pm2, \ldots$
$\frac{1}{2}.N.\Delta\mathbf{k.b} = n\pi$, $n = 0, \pm1, \pm2, \ldots$

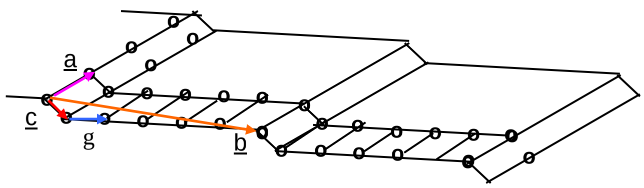
$\Delta k_x = 2\pi m/aM$, $\Delta k_x = 2\pi m/aM$

The graph of $I(\Delta k_x)$ looks like in the figure.

The diffraction spots are no longer sharp delta functions but instead are broad, with a width at half maximum of 2π/aM. The size of the domains can be measured from the spot size. The simple rule is: the ratio of spot separation to spot width is equal to the number of unit cells in the domain. If a domain is large in the a direction and short in the b direction, the LEED pattern will show spots elongated in the b^* direction and narrow in the a^* direction.

Stepped surfaces

Stepped surface is a special case of a large but infinite unit cell with a finite periodic structure inside the cell (the terrace), which acts as a small crystal. Lets consider the surface consisting of terraces n-atoms wide separated by one atom high steps, as in the following sketch:



The unit cell has unit vectors a and b; c is the step vector and g is the vector position inside the terrace. The scattering amplitude is proportional to (Δk ≡ q):

$$A(\vec{q}) = \sum_{m}^{\infty} e^{i\vec{q}.m\vec{a}} . \sum_{n}^{\infty} e^{i\vec{q}.n\vec{b}} . \sum_{j \in cell} \vec{f}_j(\theta) e^{i\vec{q}.\vec{\rho}_j}$$

The two infinite sums give the Laue conditions q.a = 2πh (h = 0,1,2, …,-1,-2,…), and q.b = 2πk (k = 0,1,2, …etc). So the LEED pattern will have lines of closely spaced spots (~1/b), separated by a larger distance (~1/a). As we will see now, not all the spots in the lines are visible. This is due to the unit cell structure factor S(Δk), the last term in *A(q)*. Lets write it down explicitly (*q, c* and *g* are vectors):

$$S(\vec{q}) = f(\theta).\left\{e^{iqc} + e^{iq(c+g)} + e^{iq(c+2g)} + e^{iq(c+3g)} + ...e^{iq(c+ng)}\right\}$$

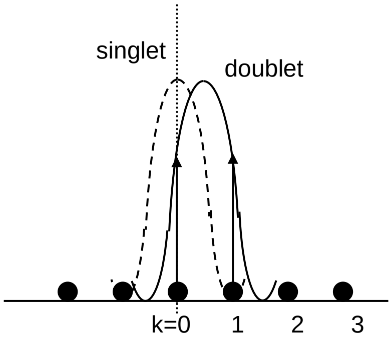
The intensity is:

$$|S(q)|^2 = f^2 . \frac{\sin^2 \frac{(n+1)}{2} \vec{q}.\vec{g}}{\sin^2 \frac{1}{2} \vec{q}.\vec{g}} = f^2 . \frac{\sin^2 \frac{n+1}{2n}(2\pi h - \vec{q}.\vec{c})}{\sin^2 \frac{1}{2n}(2\pi h - \vec{q}.\vec{c})}$$

we have used the relation: q.ng = q.(b - c) = 2πh –q.c. Like before, the zeros of the denominator determine the intense diffraction maxima. This occurs when

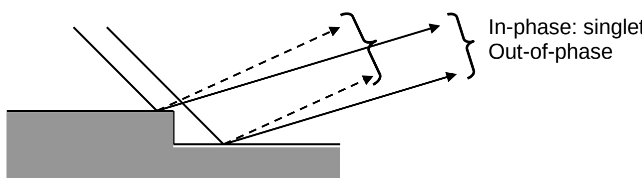
$$\frac{1}{2n}(2\pi h - \vec{q}.\vec{c}) = l\pi\,, \qquad \text{with } l = 0, 1,2 \ldots \qquad (1)$$

The term **q.c** produces a shift of the maxima. If we momentarily put it = 0, we get $h = n.l$. Since n is the terrace width, the large maxima occur whenever h is a multiple of n, i.e. they are separated by the number of cells in the terrace. If n = 5 for example, only the spots at 0, 5, 10, 15 etc, are intense. In fact the intensity scales as $(n+1)^2 = 36$ over the secondary maxima. Notice that the first zero of the numerator (determining the width of the intensity envelope) occurs at



$$\frac{n+1}{2n} 2\pi h_{zero} = \pi$$

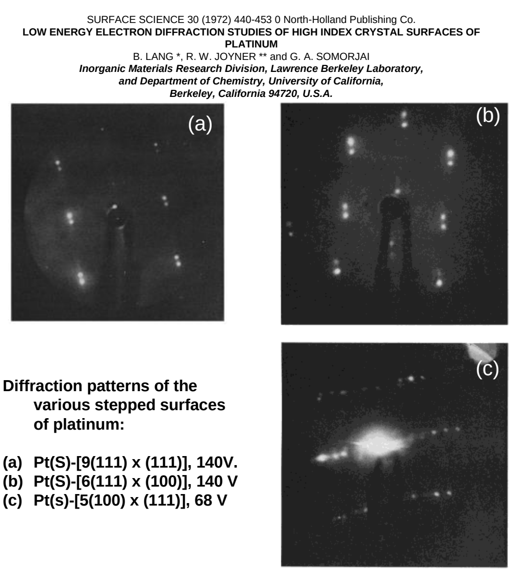
so that $h_{zero} = n/(n+1) < 1$. So even the first secondary maximum is outside the main envelope, at least for the special case assumed here of **q.c** = 0. This will occur for special values of the energy E. As E changes, so does **q** and **q.c** shifts the position of the principal maxima. For example, if qc = 2π, then putting this into (1) we get $h\text{-}1 = l.n$, so that now the principal maxima are centered in the spots h = 1, 6, 11, 16, …, and for qc = π, the maxima are centered on $h - 0.5 = l.n$, i.e., on h = 0.5, 5.5, 10.5, …. In this case we



will have a doublet of spots.

The LEED pattern is similar to that of the infinite terrace, i.e., it shows an hexagonal arrangement of spots (for the 111 surface), except that the spots are doublets, or singlets, depending on the energy.

The formation of doublet spots can also be seen as the result of interference between reflections on the upper and lower terrace. When the conditions (incident energy and angles) are such that there is constructive interference in the direction of one "terrace" spot, we will have a singlet. If the interference is destructive, there will be extinction. However by deviating a little the



Diffraction patterns of the various stepped surfaces of platinum:

(a) Pt(S)-[9(111) x (111)], 140V.
(b) Pt(S)-[6(111) x (100)], 140 V
(c) Pt(s)-[5(100) x (111)], 68 V

scatering direction the interference will be constructive again and a doublet (one on each side) will form.

Determination of step heights and terrace widths

From the above discussion we see that we can determine step heights and terrace widths from the beam energies at which doublets appear and dissappear. The important relation is $\underline{q}.\underline{c} = h\pi$. For simplicity lets consider the specular beam. If $\underline{u}_z$ is a unit vector perpendicular to the surface

$$\underline{q} = \underline{u}_z.2k\cos\phi$$

Where ϕ is the angle of incidence and k the incident wavevector. The step height is: $c_z = \underline{c}.\underline{u}_z$, so that

$$\underline{q}.\underline{c} = c_z.\ 2k\cos\phi = h\pi$$

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

The relation we need is:

$$\sqrt{E} = \sqrt{\frac{\hbar^2}{2m}}\frac{h\pi}{2c_z\cos\phi}\ ,$$

for h = even we have a singlet

for h = odd, doublet

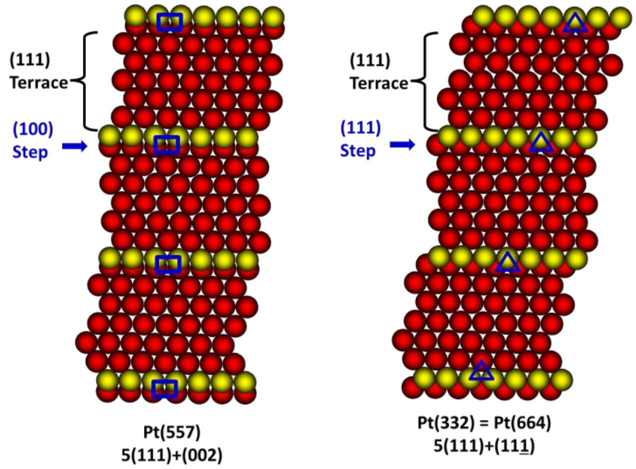
The slope of a plot of the $E^{1/2}$ values determined experimentally, giving doublets or singlet spots versus h is a straight line. From the slope of this line we get c_z. This immediately tells us whether the steps are mono- or multi-atomic high.

Miller indices of stepped surfaces

Michel Van Hove developed a new and useful way of interpreting Miller indices of stepped surfaces …:

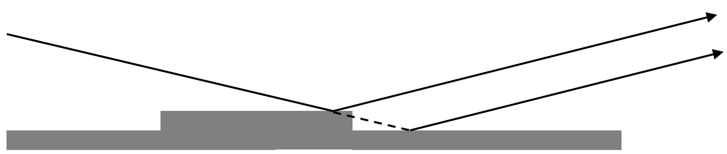
(557) = 5(111) + (002)
(332) = (664) = 5(111) + (11-1)

The Miller indices have to correspond to allowed reflections, which for fcc means that all must be of the same parity (even or odd)



Using scattering to monitor growth

One very useful application of electrons and atom scattering is to study epitaxial growth, for example metals on metals or semiconductors in molecular beam epitaxy (MBE). The idea is very simple: one monitors the intensity of the specularly reflected



beam of electrons or atoms as a function of the evaporation time. If a fraction of a monolayer of material has formed an island on the surface or the substrate we have for the scattered amplitude

$$A = \theta e^{i\vec{k}'\vec{r}} + (1-\theta)e^{i\vec{k}\vec{c}}e^{i\vec{k}'(\vec{r}-\vec{c})} = e^{i\vec{k}'\vec{r}}\left\{\theta + (1-\theta)e^{i\vec{q}\vec{c}}\right\}$$

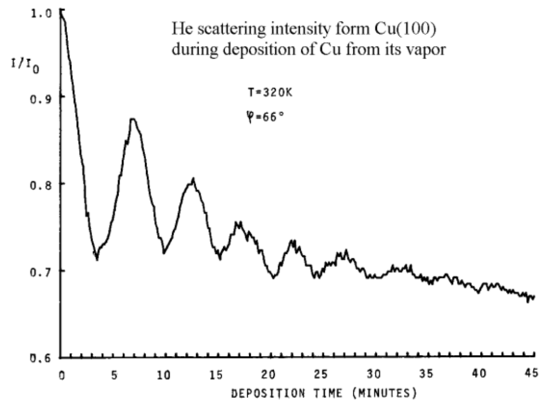
where θ is the coverage, i.e., the fraction of second layer grown over the surface. The intensity is

$$I = 1-4\theta(1-\theta)\sin^2(\underline{q}.\underline{c}/2)$$

If the angle of incidence is such that the interference is constructive, i.e., qc = 0, 2π, 4π, …, then I =1 and stays constant. This makes sense, since if the phase difference is a multiple of the wavelength, the electrons or atoms don't see the island steps. If however, the interference is destructive, i.e., if qc = π, 3π, 5π, …, then ideally

$$I = 1-4\theta(1-\theta)$$

Which is a strongly oscillating function of θ. Minima are reached at $\theta = ½$.
Example: Cu grown on Cu(100) by evaporation, studied with He scattering:

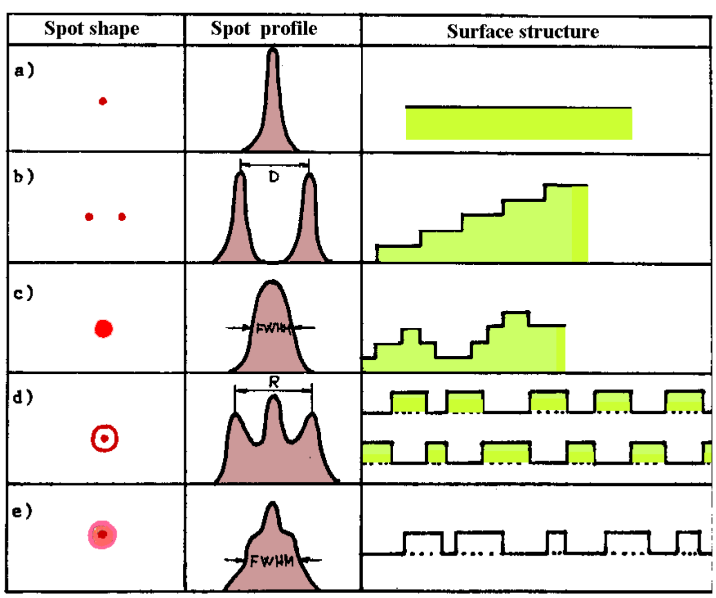


In this example the intensity oscillations do not recover to 1 after each monolayer completion indicating that the growth is not perfect, and defects, holes etc. are left behind in the growing film.

Similar osicllations are observed using RHEED (= reflection high energy electron diffraction), in specular reflection to monitor growth. RHEED is more extensively used since it is much easier to implement than atom scattering.

Spot profiles

The distribution of intensity around a diffraction spot contains interesting information about the structure of the domains or islands that produce them on the surface. We have already seen that small domains broaden the spots in specific directions.



The following spot profiles can be produced by different arrangements and sizes of islands:

a) flat surface: sharp point-like spot
b) periodically stepped surface: doublet/singlet
c) random height steps: broad spot
d) equal-size terraces randomly distributed: central sharp spot with volcano-like ringrandom distribution of islands: sharp spot with shoulders on broad base