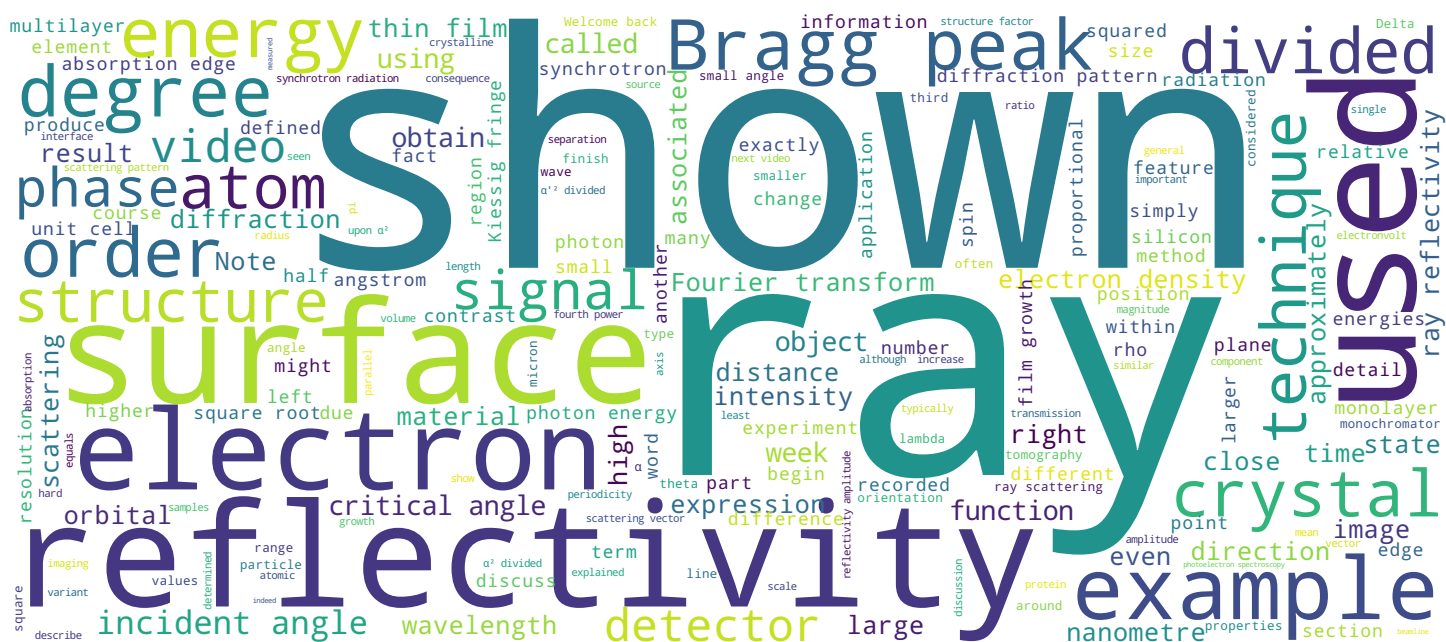


X-ray reflectometry

Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



Search MOOC



Video



Contents and objectives of this video



- Introductory comments
- Fresnel equations
- Roughness
- Kiessig fringes
- Multilayers
- Monitoring film growth

Hello again. Welcome back to this, the last video of Week 2, in which we discuss X-ray reflectivity, a particular form of small-angle X-ray scattering. We begin with some introductory remarks and the Fresnel equations for reflectivity, which provide insights as to the behaviour of reflectivity in the X-ray regime. We consider how this signal is impacted by surface or interface roughness and also by the presence of one or more interfaces below the surface when investigating thin films and multilayers, which results in interference in the form of Kiessig fringes. We finish with the application of X-ray reflectivity in monitoring thin film growth, which can feature both roughness and Kiessig fringe signal.

Notes

Summary



0m 05s

Introductory comments



- Determination of properties of surfaces, interfaces, thin films, multilayers
 - Thickness
 - Roughness
 - Density profiles
- XRR measures specularly reflected x-ray intensity as a function of α , the grazing incidence angle, typically up to approximately 2°
 - Intensity drops $\propto \alpha^{-4} \Rightarrow$ need for SR
 - Start measurement a little below α_c

X-ray reflectivity does exactly what it says on the can. One measures the specular reflectivity of X-rays as a function of incident angle. The range of angles typically lies between a little below the critical angle for total external reflection, normally around 0.1-0.2 degrees, and a few degrees. From this data, diverse information can be extracted, including the electron density profile perpendicular to the surface, down to the penetration depth of the sample, surface roughness, and in the case of layered systems, the interface roughness, layer thickness, and layer density as well. The properties of multilayered structures can be discovered and even real-time kinetic experiments monitoring thin film growth down to picometres per second growth rates, or even slower. The rapid drop off in reflectivity intensity above the critical angle, which closely follows an inverse fourth power dependence, means that synchrotron radiation is highly advantageous, although X-ray reflectivity using lab sources is not uncommon.

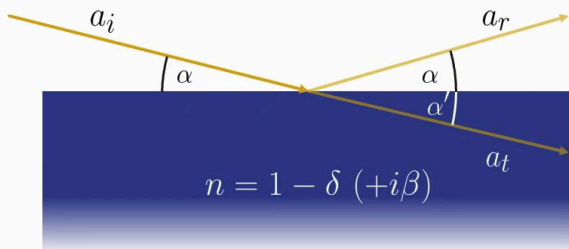
Notes

Summary



0m 52s

The Fresnel equations for reflectivity



$$a_i = a_r + a_t$$

▪ Snell's law

$$\frac{\cos \alpha}{\cos \alpha'} = 1 - \delta$$

▪ But

$$\cos x \approx 1 - x^2/2 \text{ (for } x \ll 1\text{)}$$

$$\Rightarrow \frac{1 - \alpha^2/2}{1 - \alpha'^2/2} = 1 - \delta$$

$$\Rightarrow 1 - \alpha^2/2 = 1 - \alpha'^2/2 - \delta + \delta \alpha'^2/2$$

$$\Rightarrow \alpha^2 \approx \alpha'^2 + 2\delta$$

We begin with Snell's law and its simplification for shallow incident angles, which we will then use in our handling of the Fresnel equations for reflectivity. For an X-ray beam impinging on a surface at an angle α , which is greater than the critical angle, and the electric field amplitude a_i , there will be a specularly reflected beam with amplitude a_r and a transmitted beam at an angle α' , which is determined by Snell's law. This angle α' is shallower than α . We now make the approximation that for small angles, cosine x is accurately given by 1 minus x squared divided by 2, and hence we obtain 1 minus α^2 divided by 2, divided by 1 minus α'^2 divided by 2 is equal to 1 minus δ . We multiply both sides by 1 minus α'^2 divided by 2 to obtain 1 minus α^2 divided by 2 is equal to 1 minus $\alpha^2 \alpha'^2$ divided by 2 minus δ plus $\delta \alpha'^2$ divided by 2. This last term is several orders of magnitude smaller than the next smallest term and is therefore ignored. This leads us to the simple expression that α^2 is equal to α'^2 plus 2δ .

Notes

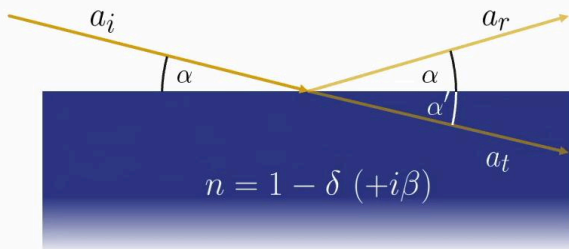
Summary



2m 02s

The Fresnel equations for reflectivity

$$r = a_r / a_i$$



$$a_i = a_r + a_t$$

- Reflection amplitude

$$\begin{aligned} r &= \frac{\alpha - \alpha'}{\alpha + \alpha'} \\ &= \frac{\alpha - \sqrt{\alpha^2 - 2\delta}}{\alpha + \sqrt{\alpha^2 - 2\delta}} \\ &= \frac{1 - \sqrt{1 - 2\delta/\alpha^2}}{1 + \sqrt{1 - 2\delta/\alpha^2}} \end{aligned}$$

- But

$$\begin{aligned} (1 - x)^n &\approx 1 - nx \\ \Rightarrow r &= \frac{1 - (1 - \delta/\alpha^2)}{1 + (1 - \delta/\alpha^2)} \end{aligned}$$

The reflectivity amplitude, now remember, we actually measure the intensity, which is proportional to the amplitude squared, is given by the Fresnel equations for reflectivity and transmission, and is equal to the difference in incident and transmitted angles across the surface divided by their sum. Exactly at the critical angle, therefore, α' is equal to zero, and the reflectivity is unity, as we would expect. We should also recognise, qualitatively, that the reflectivity will drop off thereafter, extremely rapidly with increasing incident angle, as the difference in angle between the instant and transmitted beam rapidly becomes extremely small. We use our expression from the previous slide to express α' in terms of α to obtain this expression for the reflectivity amplitude r . We divide both top and bottom of the right-hand side by α to obtain r is equal to 1 minus the square root of 1 minus 2δ upon α^2 divided by 1 plus the square root of 1 minus 2δ upon α^2 . We now make the approximation that 1 minus x to the n is equal to 1 minus nx for small x and obtain a reflectivity amplitude r is equal to 1 minus 1 plus δ upon α^2 divided by 1 plus 1 minus δ upon α^2 .

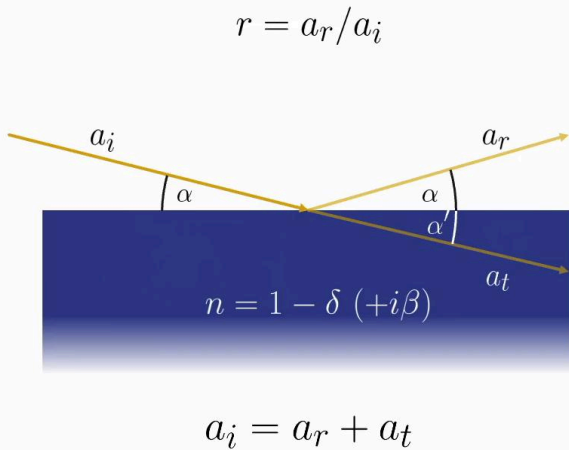
Notes

Summary



3m 41s

The Fresnel equations for reflectivity



- Reflection amplitude

$$r = \frac{\alpha - \alpha'}{\alpha + \alpha'}$$

$$= \frac{\alpha - \sqrt{\alpha^2 - 2\delta}}{\alpha + \sqrt{\alpha^2 - 2\delta}}$$

$$= \frac{1 - \sqrt{1 - 2\delta/\alpha^2}}{1 + \sqrt{1 - 2\delta/\alpha^2}}$$

- But

$$(1 - x)^n \approx 1 - nx$$

$$\Rightarrow r = \frac{1 - (1 - \delta/\alpha^2)}{1 + (1 - \cancel{\delta/\alpha^2})}$$

$$= \frac{\delta}{2\alpha^2}$$

- Reflection intensity: $R = r^2 = \frac{\delta^2}{4\alpha^4}$

This last term in the denominator is insignificantly small compared to two and is therefore dropped. This results in the extremely simple expression that the reflectivity amplitude is equal to δ divided by two α^2 and the reflectivity intensity or simply reflectivity is equal to δ^2 divided by four α to the fourth. This inverse fourth power dependence of the reflectivity on the incident angle that we mentioned earlier means that the reflectivity drops off extremely quickly.

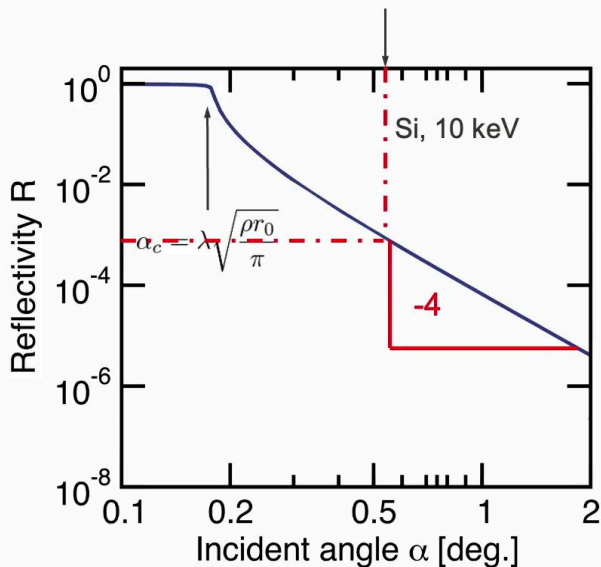
Notes

Summary



5m 22s

The Fresnel equations for reflectivity



- Reflectivity (perfectly smooth surface)

$$R = r^2 = \frac{\delta^2}{4\alpha^4}$$

- But

$$\alpha_c = \sqrt{2\delta}$$

$$\Rightarrow R = \left(\frac{\alpha_c}{2\alpha}\right)^4; \alpha \gg \alpha_c$$

- $\alpha_c \Rightarrow$ electron density, material type

$$\alpha_c = \lambda \sqrt{\frac{\rho r_0}{\pi}}$$

- Rule of thumb:

$$\alpha_c [\text{deg.}] = \left(\frac{Z^{1/2}}{30}\right) \lambda [\text{\AA}]$$

A double logarithmic plot of the reflectivity against incident angle thus has a gradient of minus four, as shown here for silicon at 10 keV. Note also that because the critical angle equals the square root of 2δ , we can also express the reflectivity in terms of the ratio of the critical angle to the incident angle. For example, an incident angle that is three times larger than α_c will be reflected with an intensity which is six to the fourth times smaller, that's almost 1,300 times weaker. In this example of silicon and 10-keV x-rays, the critical angle is 0.18 degrees and the reflectivity at 0.54 degrees is 8.3 times 10 to the minus four, very close to that predicted by our equation. Note also that the critical angle depends on the wavelength and the square root of the electron density. Hence the reflectivity is proportional to the fourth power of the wavelength and approximately proportional to Z^2 .

Notes

Summary



Surface and interface roughness

- Roughness $\gtrsim \lambda$?
 - Reflectivity impacted

We're all familiar with rough surfaces in the visible regime being poor reflectors. Think of the bathroom mirror directly after taking a shower. In an analogous manner, reflectivity of X-rays drops off even more rapidly than it does from an atomically smooth surface if the surface has a roughness that is comparable to or larger than the wavelength of the X-rays being used.

Notes

Summary



7m 16s

Surface and interface roughness

- Roughness $\gtrsim \lambda$?

- Reflectivity impacted
- Model roughness as a Gaussian function that is convoluted with a perfectly flat surface:

$$S_R = S_F \otimes f_R(z)$$

- Reflectivity:

- FT of surface function S_R
- Convolution theorem

$$\begin{aligned} R_R &= R_F \cdot \mathcal{F}\{f_R(z)\} \\ &= R_F \cdot \exp\left[-(2k\alpha\sigma)^2\right] \end{aligned}$$

R.M.S. roughness σ

$$f_R(z) = e^{(-z^2/2\sigma^2)}$$



- Example

- $\lambda = 1 \text{ \AA}, \sigma = 5 \text{ \AA}, \alpha = 1^\circ$
- $\exp[-(2k\alpha\sigma)^2] = 0.300$
- Reflectivity reduced by 70%

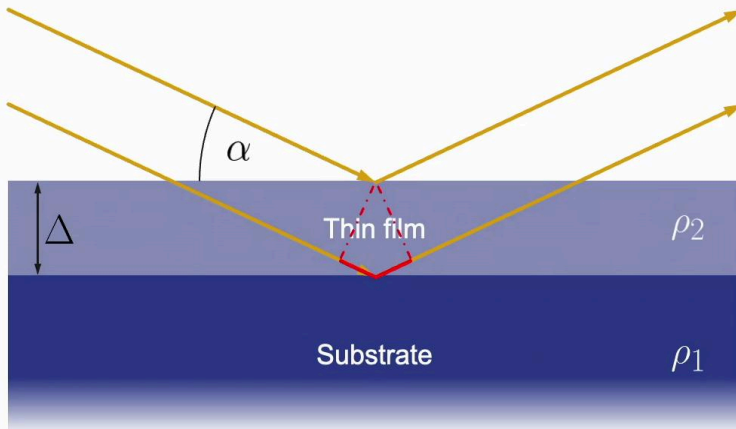
If we describe the average roughness as a Gaussian distribution with a roughness standard deviation sigma, the reflectivity above the critical angle drops off as the perfectly flat surface multiplied by the Fourier transform of the roughness function, that is the exponent of minus $2k\alpha\sigma$ all squared. For the more maths-adept student, it is briefly mentioned that this can be explained by the convolution theorem. The surface is the convolution of a flat surface with a Gaussian roughness function, and therefore, the scattering pattern is the Fourier transform of this convolution, in other words, the reflectivity curve at the perfectly flat surface multiplied by the Fourier transform of the roughness function. As an example, a surface roughness standard deviation of five angstroms being probed with one-angstrom radiation will reduce the reflectivity at an incident angle of one degree as compared to that for a perfectly smooth surface by 70%.

Notes

Summary



Thin films and Kiessig fringes



$$\text{OPD} = m\lambda \approx 2\Delta\alpha$$

When investigating thin films, the X-rays will not only be reflected from the top surface, but also from the interface between the film and substrate, assuming that they have distinct electron densities, that is, ρ_1 is not equal to ρ_2 . The optical path difference between the rays reflected from the bottom and top is equal to $2\delta \sin \alpha$, where δ is the film thickness. For almost all instances, α is sufficiently small that $\sin \alpha$ can be accurately approximated by α , given in radians. For constructive interference, therefore, $2\delta \alpha$ should equal an integer number of wavelengths. Such interference fringes are called Kiessig fringes.

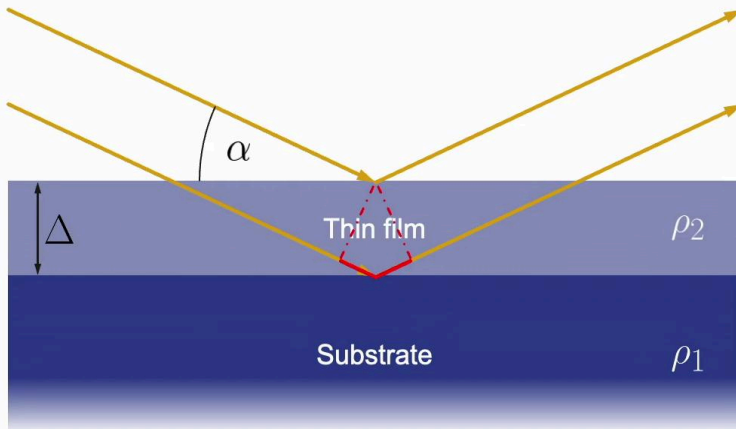
Notes

Summary

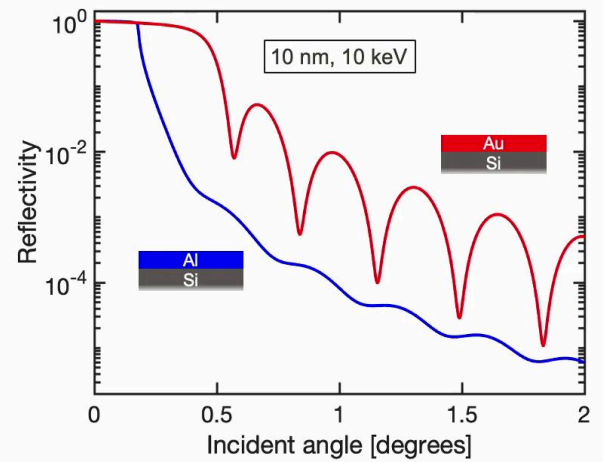


8m 53s

Thin films and Kiessig fringes



$$\text{OPD} = m\lambda \approx 2\Delta \sin \alpha$$



$$\begin{aligned}\rho_{\text{Si}} &= 0.699 \text{ e}/\text{\AA}^3 \\ \rho_{\text{Al}} &= 0.783 \text{ e}/\text{\AA}^3 \\ \rho_{\text{Au}} &= 4.666 \text{ e}/\text{\AA}^3\end{aligned}$$

Two examples are shown here. For 10 keV radiation reflectivity curves from 10 nanometres of aluminium and 10 nanometres of gold deposited on silicon. Note that the oscillation amplitude for aluminium on silicon is much less pronounced than that for gold on silicon, and this is due to the two elements, aluminium and silicon, having a similar electron density. The separation between fringes is equal to λ divided by 2δ .

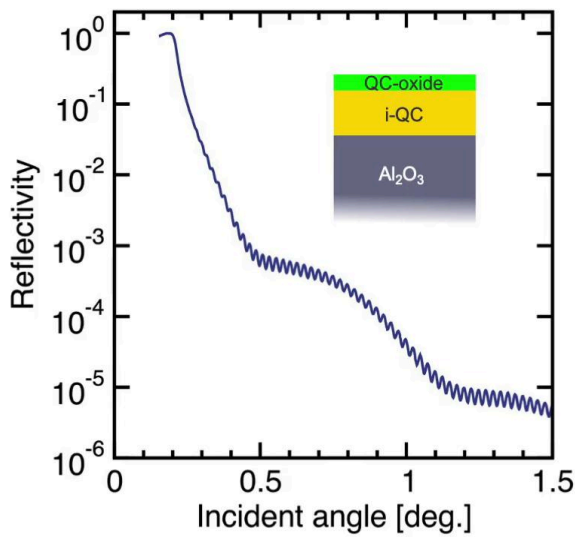
Notes

Summary



9m 46s

Thin film example – quasicrystal TiNiZr on Al_2O_3



- TiNiZr alloy icosahedral quasicrystal thin film deposited on sapphire(0001)
 - 120 nm thick
 - 1-Å radiation
 - Slow oscillation: $\Delta\theta = 0.72^\circ$
 - $\Delta = \lambda/(2\Delta\theta) = 3.98 \text{ nm}$
 - Oxidized in air \Rightarrow 4 nm QC-oxide

An example is shown here of a real system consisting of 120 nanometre thick film of an icosahedral quasicrystal formed by the alloy of titanium, nickel, and zirconium grown on an atomically flat sapphire substrate. This was then measured some days after its fabrication, whereby in the intervening time, the film had been exposed to air. The rapid Kiessig oscillations associated with the film itself were further modulated by a much slower oscillation, which was associated with the upper four nanometres of the film being oxidised during its exposure to air.

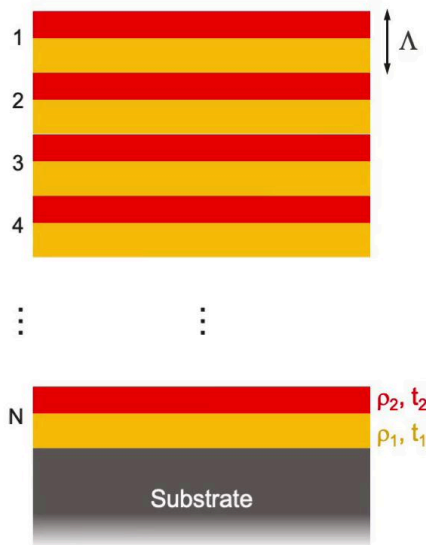
Notes

Summary

10m 20s



Multilayers



- ML defined by:
 - Two sublayers of differing electron density
 - One low density ρ_1 , thickness t_1
 - One high density ρ_2 , thickness t_2
 - Periodicity $\Lambda = t_1 + t_2$
 - Ratio of t_1 sublayer thickness to $\Lambda = \Gamma$
 - Number of periods N
 - Substrate type
 - Interfacial interdiffusivity/roughness

The next level of complexity after thin films is the fabrication of periodic stacks of normally two distinct materials; one with a low electron density, the other with a high electron density. These are used in so-called multilayer monochromators as high bandwidth devices that deliver more photons on the sample and are interesting for those techniques for which the best monochromaticity is not required, such as in computed tomography or some flavours of protein crystallography. Such multilayers are defined by the densities of each sublayer, their thickness, the periodicity, which is simply the sum of the thicknesses, the ratio of the thicknesses, which is called Gamma, the number of periods, the substrate type, and any interfacial diffusivity or roughness that there may be.

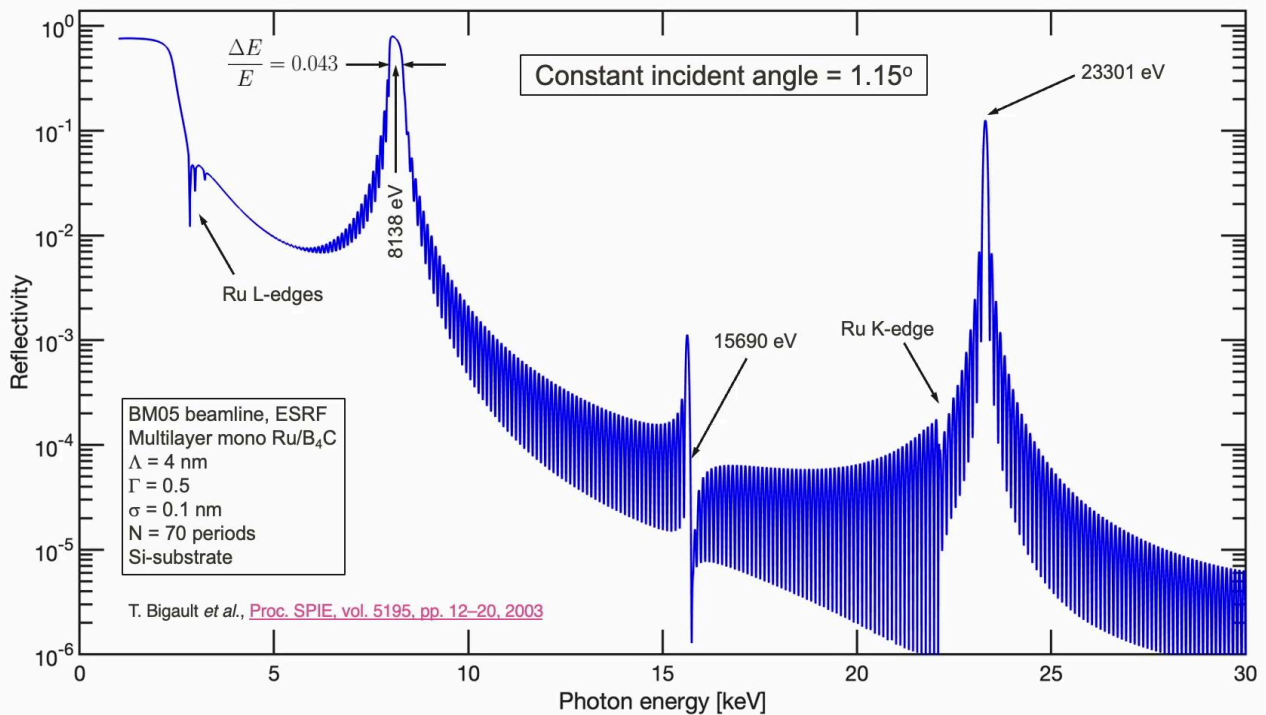
Notes

Summary



11m 02s

Multilayers



The properties of the multilayers can be summarised in this plot of reflectivity as a function of photon energy at a fixed incident angle of 1.15 degrees. This is a simulation of a multilayer, which is used in a multilayer monochromator at the BM05 beam line at the ESRF, and consists of alternating layers of ruthenium and boron carbide of equal thickness of two nanometres, repeated 70 times. The standard deviation interfacial roughness is estimated to be one angstrom. More details of this multilayered structure can be found in the provided link. There are several features which should be explained. First, there are both L and K absorption edges to be found around 3 keV and 22.117 keV. The K-edge causes the Kiessig fringes at energies above that edge to reduce in amplitude due to the fact that the absorption edge results in the X-ray seeing a lower electron density. Next, the bandwidth of a single multilayer is approximately 4%, well over two orders of magnitude greater than that for a silicon 111 crystal. The next feature is especially interesting, namely the energies of the three features highlighted here. The first and third are clearly diffraction peaks associated with the multilayer periodicity.

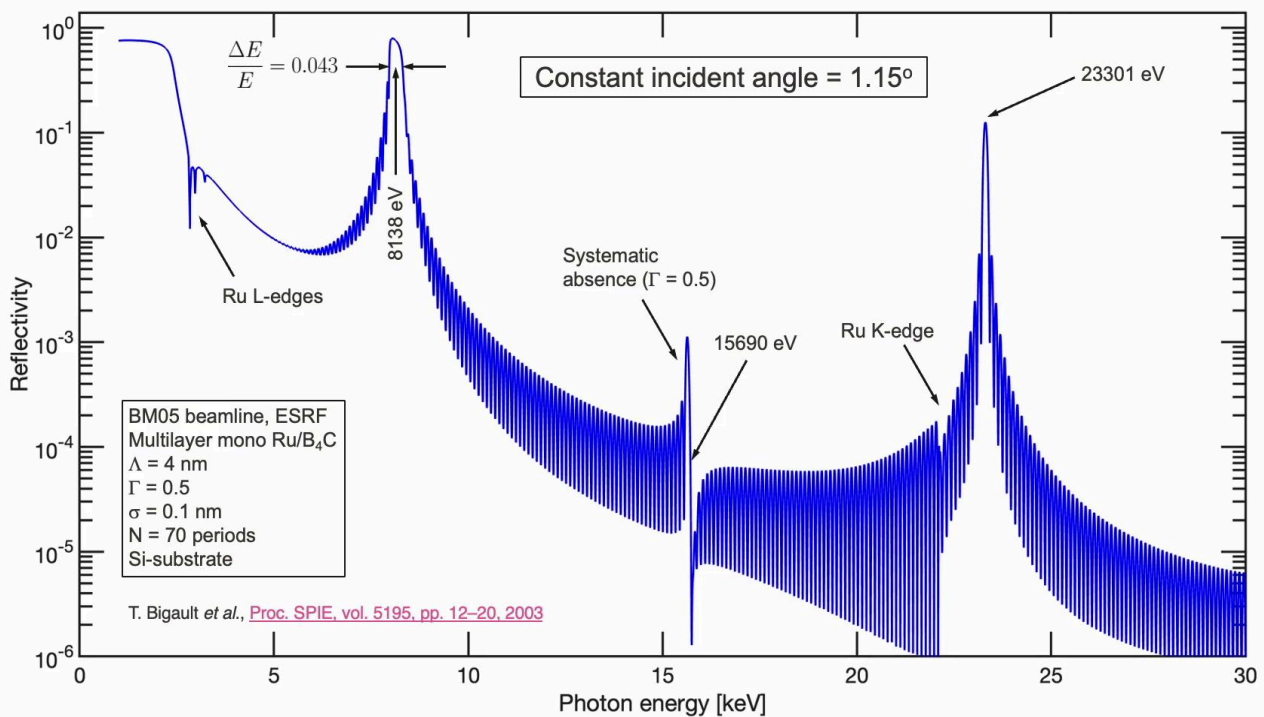
Notes

Summary

11m 56s



Multilayers



They are, in fact, the first and third Bragg peaks. The odd appearance of the second feature is, in fact, the second Bragg peak. Why it looks like this will be explained in just a moment. Here, I want to show that although the energies are close to being in a ratio of 1-2-3, they are not exactly so. Importantly, the first Bragg peak at 8,138 eV is significantly higher in energy than a third of the energy of the third peak, which is 23,301 eV divided by three, which is equal to 7,767 eV. The reason for this is that the first Bragg peak has a critical angle that is close to the fixed incident angle of 1.15 degrees. As a consequence, the beam transmitted within the multilayer is significantly refracted to a new angle, which changes the Bragg condition. This is an advantage, as it means that the harmonics from an undulator, which do perfectly have integer-multiple energies of the fundamental, can be effectively suppressed using multilayers. Now, the odd appearance of the second Bragg peak is a consequence of the fact that the two sublayers have equal thicknesses. Interference effects cause the even harmonics to be forbidden in this specific system.

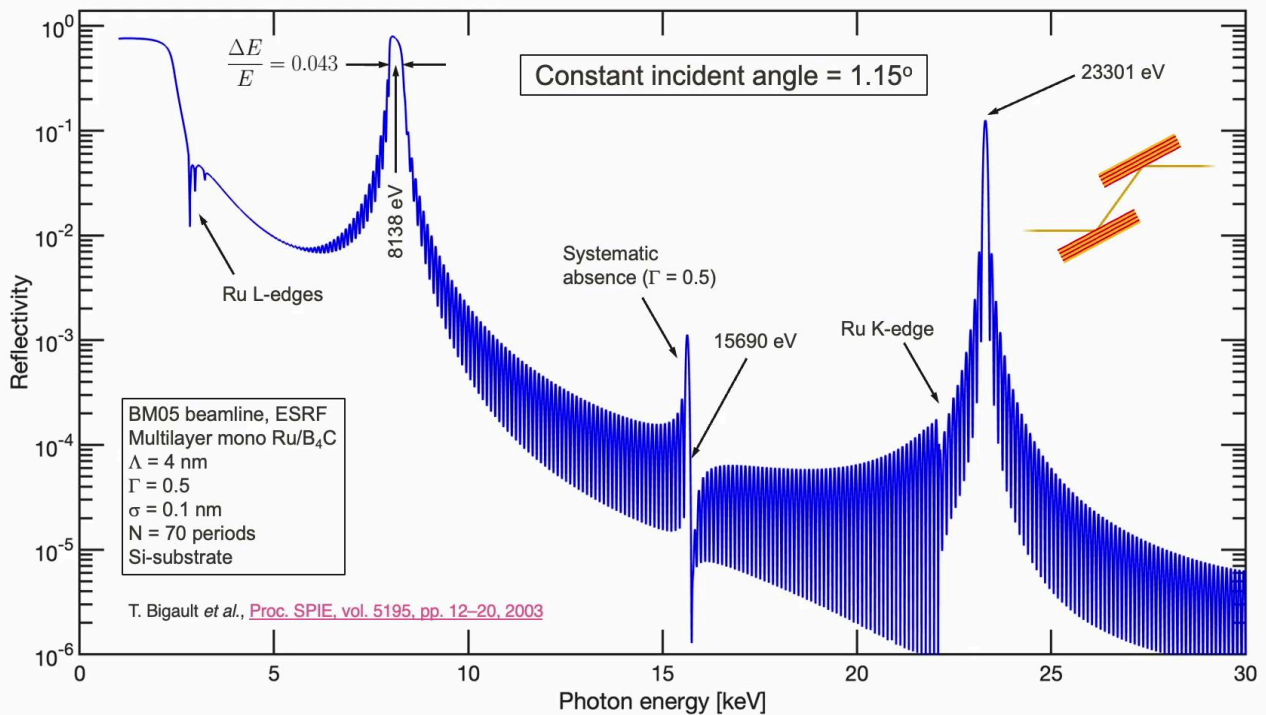
Notes

Summary



13m 35s

Multilayers



Hence the second Bragg peak, which should otherwise be seen at approximately 16 keV, is almost completely suppressed. In more general terms, if the thickness ratio of the reflection, high-density sublayer, and the spacer-low density sublayer can be expressed as a simple integer ratio, a divided by b, reflections which are integer multiples of a plus b, are suppressed. This is simply the phenomenon of systematic absences discussed in more detail in Week 1 in video 1.3.1 for the case here of the one dimensional artificial crystal that is a multilayer. Lastly, it should be noted that multilayers, at least those used in monochromators, are most commonly found as pairs. This is in order to ensure that the monochromatised beam emerging from the monochromator is parallel to the polychromatic incident beam. Hence, the reflectivity curve of a monochromator is the square of the reflectivity of a single multilayer.

Notes

Summary

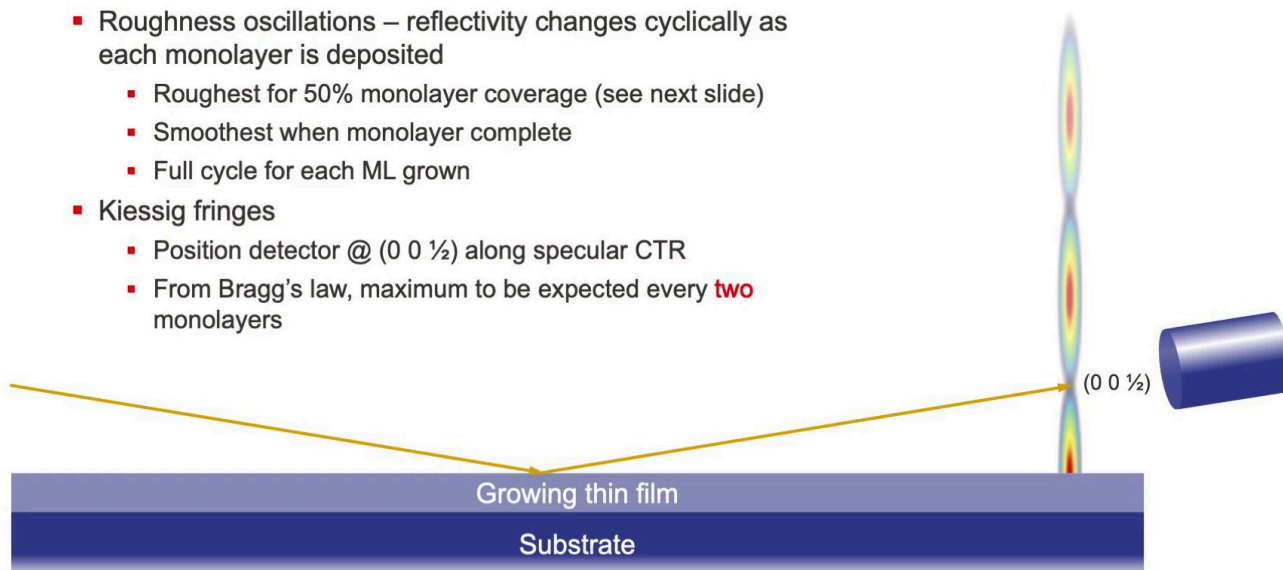
15m 12s



Monitoring thin film growth with XRR

Two effects

- Roughness oscillations – reflectivity changes cyclically as each monolayer is deposited
 - Roughest for 50% monolayer coverage (see next slide)
 - Smoothest when monolayer complete
 - Full cycle for each ML grown
- Kiessig fringes
 - Position detector @ $(0\ 0\ \frac{1}{2})$ along specular CTR
 - From Bragg's law, maximum to be expected every **two** monolayers



X-ray reflectivity can be used to monitor film growth. If the film grows in a layer-for-layer manner, this is called Frank-van der Merwe growth, then the roughness will vary periodically, being maximally rough when each new monolayer is 50% complete. By monitoring the reflectivity during growth, the film growth can be followed monolayer for monolayer. If the material is crystalline, a good angle to choose to monitor growth is halfway between the direct beam at zero degrees and the first Bragg peak in the specular direction. In other words, at the $(0\ 0\ \frac{1}{2})$ position of a CTR. Here, the reflectivity is at a minimum, but also varies most strongly with roughness. Because of the weakness of the signal, the use of synchrotron radiation is important. Moreover, every second rough oscillation is stronger due to Kiessig fringes passing through the point of observation as the film grows.

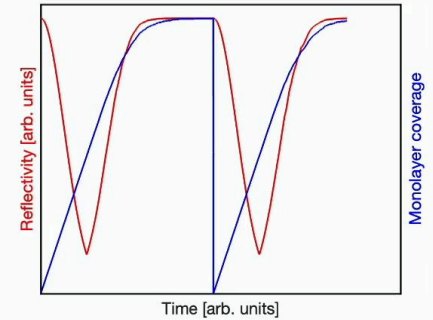
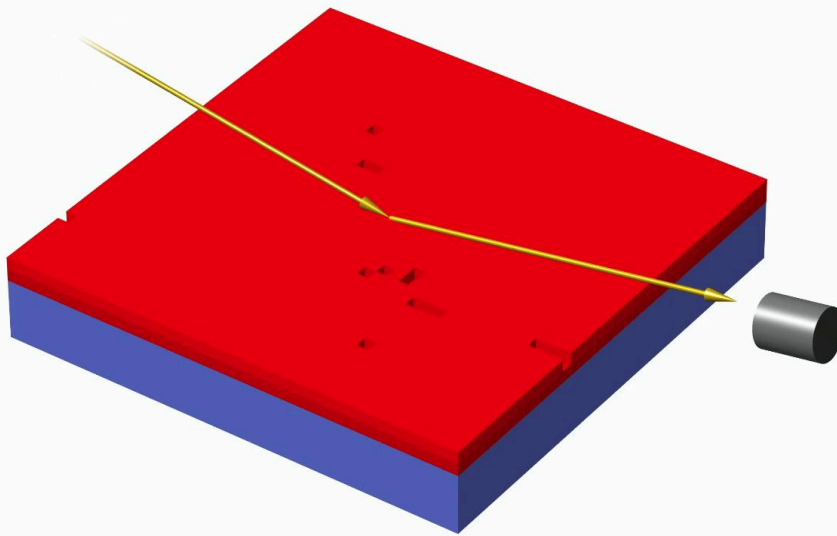
Notes

Summary



16m 27s

Monitoring thin film growth with XRR



A cartoon of monolayer for monolayer growth is shown here. Coverage increases rapidly at the beginning of each monolayer, as most sites are unoccupied. But slows down towards it being close to completion, as the incident particles require time to find unoccupied positions. On the right, the monolayer coverage and the reflectivity are shown as functions of time for the deposition of the first two monolayers, and covered. All right.

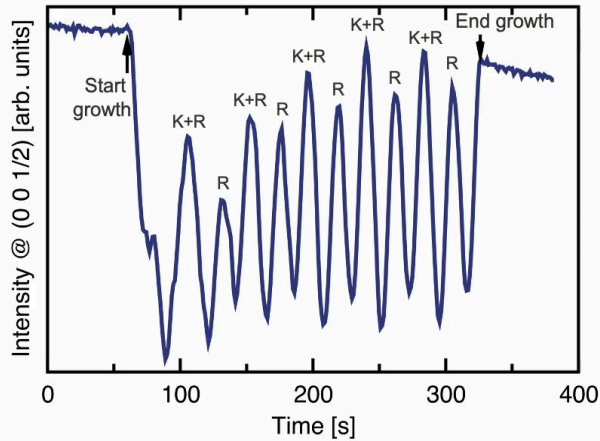
Notes

Summary

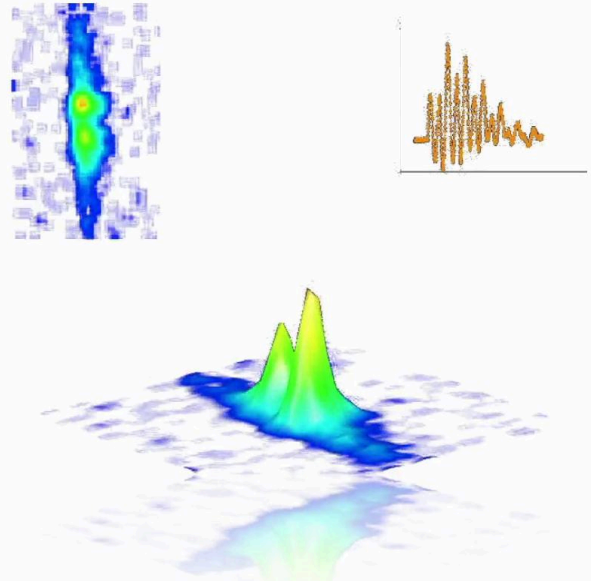


17m 38s

Monitoring thin film growth with XRR



12 ML growth of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$



Movie of YBCO HTSC growth in-situ

Two real examples are shown here. On the left, the growth of twelve monolayers of lanthanum strontium manganate on strontium titanate are shown. Note the alternating high and lower intensity oscillations due to the Kiessig fringes forming every two monolayers, while the roughness fringes have a periodicity of one monolayer. On the right, the growth of yttrium barium copper oxide superconducting thin film on strontium titanate is shown as a video. Note that the intensity initially increases at the start of growth, indicative that the substrate material on which the film grew was not perfectly atomically flat, and that the first part of the growth filled in this incomplete monolayer. Also note that after the first couple of oscillations, there is a general decrease in their amplitude. This is due to an imperfect monolayer for monolayer growth, and as a consequence, an increase in underlying roughness. This is actually called Stranski–Krastanov growth.

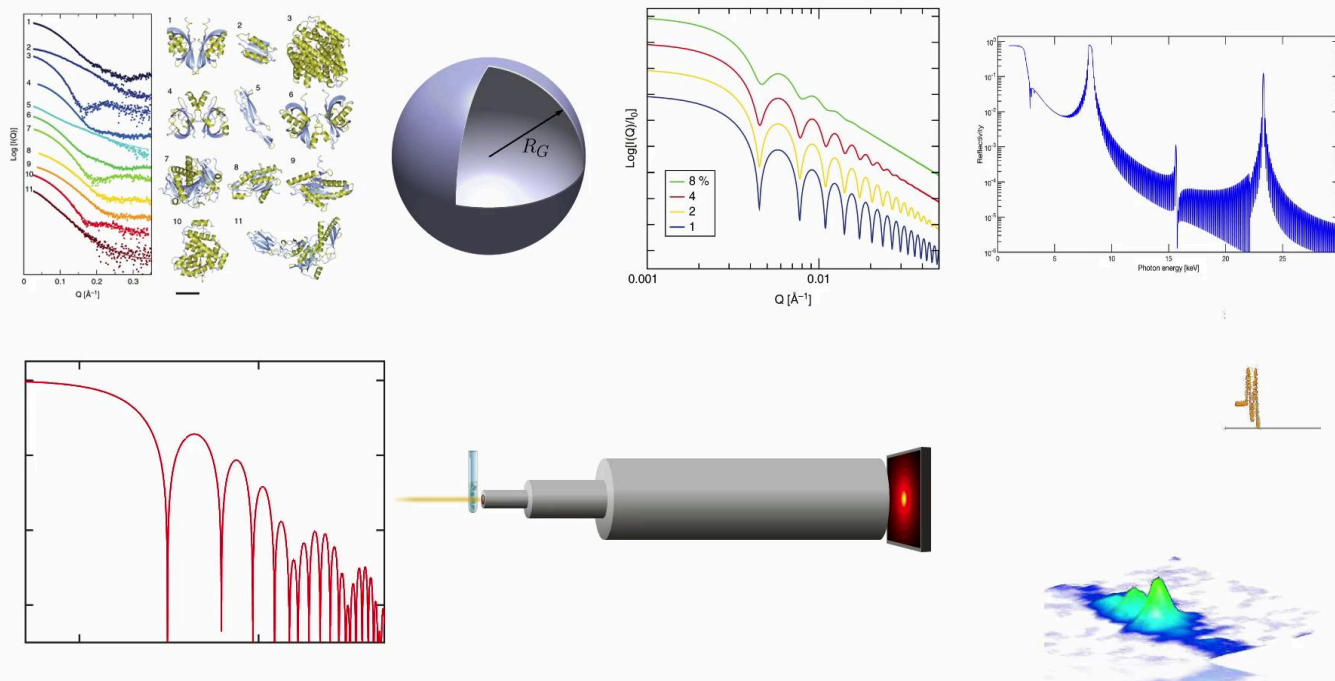
Notes

Summary

18m 25s



Summary of this section



To summarise this section, we have concerned ourselves with small-angle X-ray scattering, which probes samples on the nanometre to hundreds of nanometre scale. We considered idealised objects and their scattering patterns. Information can be extracted in different regions of these curves. At low scattering vectors, the radius of gyration delivers information about the general size of the objects under investigation, while at high Q values, the surface area to volume ratio and types of shapes can be gleaned. We also considered the impact of polydispersity and considered some experimental details. Lastly, we looked at X-ray reflectivity and its application for sample surface quantification, thin films, and multilayers. X-ray reflectivity can also be used to monitor thin film growth with accuracies better than a hundredth of a monolayer coverage.

Notes

Summary



19m 38s

Next week...



Next week is the first of two weeks concerned with X-ray spectroscopies. We'll cover basics of X-ray spectroscopies and look at variants of X-ray absorption spectroscopy.

Notes

Summary



20m 33s