Chapter 2

Experimental Methods

2.1 X-Ray Diffraction Measurement

As described in 1.1.2, constructive interference of incoming and scattered X-rays may give insight in the symmetry of exposed crystal structures. This can be utilized for thin film investigation and is called X-ray diffraction (XRD). The XRD device used for this work, namely an *X'Pert Pro* (*Malvern Panalytical Ltd.*), as well as the applied scanning techniques will be presented in the following.

A sample with surface normal parallel to the z-axis of the laboratory system is exposed with X-rays at an angle ω between sample surface and incident radiation. The diffracted radiation is measured at an angle α_{out} between sample surface and detector. 2θ is used to describe the angle between outgoing beam and the extension of the incoming beam, which both span the scattering plane. It follows that $2\theta = \omega + \alpha_{out}$. Note that θ in Equ. (1.9) is the same angle as half of 2θ. The scattering plane is depicted in Fig. 2.1a. The sample can be rotated by ϕ ("azimuth") and ψ around an axis parallel to the surface normal and parallel to the intersection of sample surface and scattering plane, respectively.

2.1.1 2ϑ-ω-scans

When probing for lattice plane distances using the Bragg condition in its simplest form, it is assumed that the scattering planes are parallel to the sample surface (cf. Fig. 2.1a). It is necessary that $\omega = \alpha_{out}$ which implies $2\theta = 2\omega$. So the angle of incidence ω is coupled to 2θ which represents the distance between lattice planes (cf. Equ. (1.9)). Measuring the diffracted X-ray intensity while varying 2θ and maintaining the condition $2\theta = 2\omega$, is called a 2ϑ-ω-scan. This results in a so-called 2ϑ-ω diffraction pattern, where peaks correspond to constructive interference and thus to certain lattice plane distances.

When analyzing 2ϑ-ω diffraction patterns, one usually compares to predicted peak positions of the expected phase of the compound which is investigated. This reference diffraction pattern stems from powder samples of the respective compound, containing all crystal orientations during one 2ϑ-ω-scan. When a peak is identified, a possible peak shift is determined and the shape of the peak is investigated. Peak shifts may be due to residual stress, substrate induced strain or compositional gradients in the thin film [1]. A minimum amount of peak broadening is always present due to convergence of
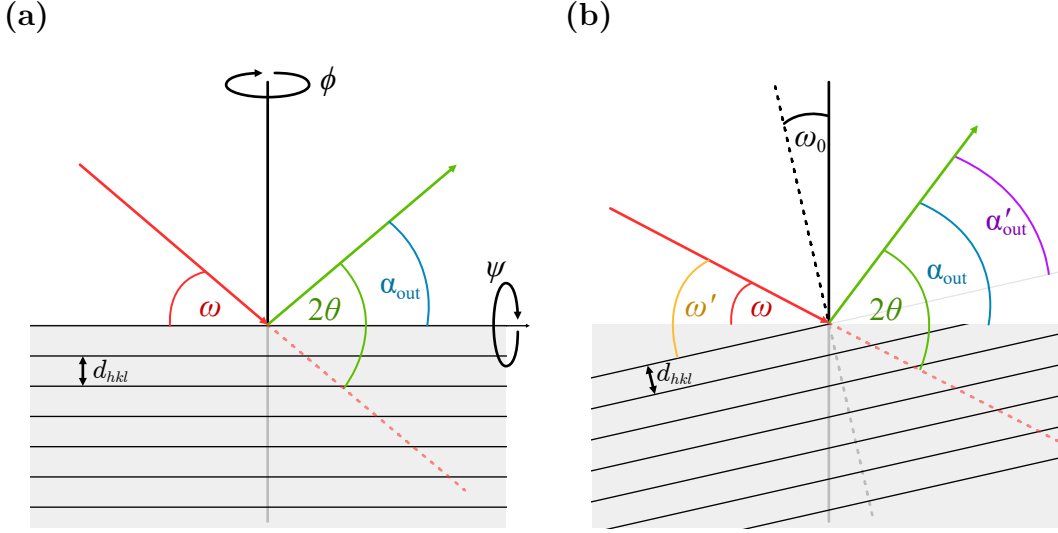
(a)   **(b)**

Figure 2.1: (a) Geometry for a 2ϑ-ω-scan without offset. **(b)** Scattering geometry containing an offset ω_0. Angle of incidence and angle of diffraction decrease and increase, respectively. Note that 2θ is not affected by this offset.

the incident beam as well as convolution of $K\alpha_1$- and $K\alpha_2$-radiation (cf. 1.1.2), which is called instrumental broadening [1]. The Full Width at Half Maximum (FWHM) of the highly crystalline substrate peaks may give a reference for broadening of peaks in 2ϑ-ω diffraction data.

This method can be extended to measure lattice planes which are not parallel to the sample surface but tilted by ω_0. This is done by rotating the reference frame of the sample in such a way that the BRAGG condition is fulfilled again. Note that 2θ does not change upon rotation, as can be seen in Fig. 2.1b. When probing for plane distances of the rotated lattice, one finds for the coupling between 2θ and ω:

$$\omega' = \alpha'_{\text{out}}$$
$$\omega + \omega_0 = \alpha_{\text{out}} - \omega_0$$
$$\omega + \omega_0 = (2\theta - \omega) - \omega_0$$
$$\Rightarrow 2\theta = 2(\omega + \omega_0) = 2\omega'\,.$$

This coupling is equivalent to a 2ϑ-ω-scan but with an offset ω_0 applied to the angle of incidence. There are several use cases for applying an offset ω_0:

(i) It is assumed that ω denotes the angle between incident X-ray beam and the sample surface. But a perfect alignment between sample and sample holder is not always possible. So to correct this tilt between expected sample position and it's real inclination, the offset ω_0 can be set to really probe for lattice planes parallel to the sample surface. This is done before measuring a 2ϑ-ω-scan to achieve preciser results.

(ii) When probing for lattice planes which are not parallel to the sample surface ("asymmetric reflections"), one can apply the expected inclination angle as an offset ω_0. This is the case in Fig. 2.1b.

(iii) When 2θ is fixed, but ω_0 is varied, a so-called ω-scan is performed, which enables quantification of mosaicity (cf. 2.1.2).

2.1.2 ω-scans

Thin films may exhibit a distribution of lattice plane inclination, called mosaicity. This results in an observation of diffraction peaks for several offsets ω_0. The mosaicity can thus be quantified by fixing 2θ, representing a certain lattice plane distance, and then vary ω_0 and measure the X-ray intensity. This is called an ω-scan, and the FWHM of the observed diffraction pattern (also called "Rocking curve") is a measure for the mosaicity [1]. ω-scans are particularly useful when comparing a set of thin films of varying deposition parameters to optimise growth conditions. In particular, recording Rocking curves of symmetric and asymmetric lattice planes allows the calculation of dislocation densities in the thin film [2].

2.1.3 φ-scans

A 2ϑ-ω-scan is not capable of resolving in-plane rotations of crystal domains, because the distance of lattice planes parallel to the surface are not affected. Those rotational domains can be detected by probing for lattice planes which are inclined with respect to the surface, i.e. by fixing 2θ to the expected lattice plane distance and ω_0 to the inclination angle (cf. Fig. 2.1b). Depending on the symmetry of the inspected material, constructive interference should only appear for distinct values of ϕ. So by rotating the sample by 360° and simultaneously recording the X-ray intensity, a so-called φ-scan (also called "Azimuth-scan") can yield information about the existence of rotational domains. If the number of observed peaks in the φ-scan diffraction pattern exceeds the theoretically expected number for a single crystal, rotational domains are present [1]. Furthermore, comparing the φ-scan diffraction data of thin film and substrate reveals whether the film has grown with an in-plane rotation with respect to the substrate. Finally, if the thin film grows in a tilted manner on the substrate, a φ-scan prior to an ω-scan can ensure the correct positioning bevor alignment. Then, the BRAGG condition is fulfilled for performing a 2ϑ-ω-scan.

2.1.4 Reciprocal Space Maps

Because the BRAGG condition is equal to the description of diffraction with $\mathbf{k}' - \mathbf{k}$ and reciprocal space vectors $\mathbf{K}_{hkl}$ (cf. 1.1.2), both can be used depending on context. Henceforth, $\mathbf{k}' - \mathbf{k}$ will be denoted by the "scattering vector" $\mathbf{q}$. Note that $\mathbf{k}$ and $\mathbf{k}'$ are parallel to incoming and outcoming beam, respectively. From the definition of angles, it follows that

$$\mathbf{q} = \begin{pmatrix} q_\parallel \\ q_\perp \end{pmatrix} = \mathbf{k}' - \mathbf{k} \tag{2.1}$$

$$= \frac{1}{\lambda} \begin{pmatrix} \cos\alpha_{\text{out}} \\ \sin\omega \end{pmatrix} - \frac{1}{\lambda} \begin{pmatrix} -\cos\alpha_{\text{out}} \\ \sin\omega \end{pmatrix} \tag{2.2}$$

$$= \frac{1}{\lambda} \begin{pmatrix} \cos(2\theta - \omega) - \cos(\omega) \\ \sin(2\theta - \omega) + \sin(\omega) \end{pmatrix} . \tag{2.3}$$

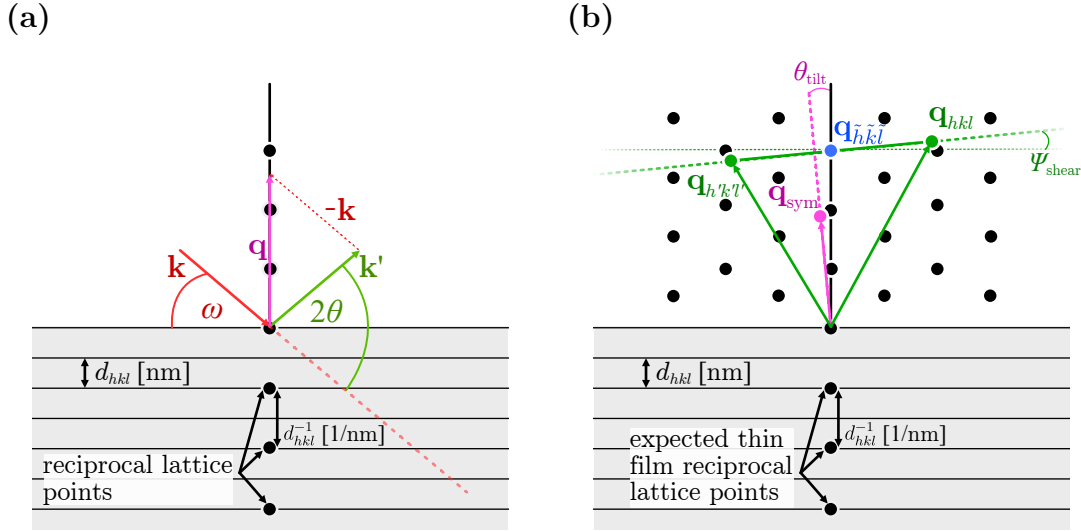**(a)**   **(b)**

Figure 2.2: (a) Construction of the scattering vector (magenta) from incoming (red) and outgoing (green) beam, according to Equ. (2.3). The reciprocal lattice points are visualized together with the lattice planes. It has to be noted that the distances between lattice planes and between reciprocal lattice points have different dimensions. **(b)**

From Equ. (2.3), two properties follow for the scattering vector:

$$-q_{\parallel}/q_{\perp} = -\tan\left(\omega - \frac{2\theta}{2}\right) = \tan\omega_0 \, , \tag{2.4}$$

$$|\mathbf{q}| = \sqrt{q_{\parallel}^2 + q_{\perp}^2} = \frac{1}{\lambda}2\sin\theta \stackrel{\text{Bragg}}{=} \frac{1}{d_{hkl}} \, , \tag{2.5}$$

where the last equality of Equ. (2.5) holds, if $\mathbf{q}$ is a reciprocal lattice vector $\mathbf{K}_{hkl}$. The scattering vector, together with the corresponding XRD geometry is depicted in Fig. 2.2a. Because 2θ and ω can simultaneously be represented by $\mathbf{q}$, it is possible to measure intensities for several $\mathbf{q}$, such that a part of the reciprocal space $Q \ni \mathbf{q}$ is mapped. Consequently, this is called a Reciprocal Space Map (RSM). According to Equ. (1.8), a peak in 2D reciprocal space Q should be observed if $\mathbf{q}$ is a reciprocal space vector. In this case, $\mathbf{q} = \mathbf{K}_{hkl}$ is called a "reflection". With Equ. (2.4) one can determine ω_0 – the direction of the corresponding lattice planes[1], and with Equ. (2.5) the lattice plane distance d_{hkl} can be calculated.

A 2ϑ-ω-scan corresponds to a set of $\mathbf{q}$ with fixed direction in reciprocal space, but varying length. For scanning symmetric reflections, $\mathbf{q}$ is parallel to the surface normal (as in Fig. 2.2a). On the other hand, an ω-scan corresponds to a set $\mathbf{q}$ with fixed length but varying direction. The mosaicity can therefore approximately be quantified by the broadening of a reflection perpendicular to the direction of $\mathbf{K}_{hkl}$. Because anisotropic strain has an effect on direction and length of inclined lattice planes, asymmetric reflections, i.e. $\omega_0 \neq 0$, can be deconvoluted into an in-plane and out-of-plane component. By this means, RSMs enable the calculation of lattice constants. To precisely calculate

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[1]Note that the "$-$" in $-q_{\parallel}/q_{\perp}$ is necessary, such that this fraction is the tangens the angle between $\mathbf{q}$ and surface normal with correct sense of rotation.

the latter, several corrections are applied to the recorded RSMs, as proposed in Kneiß et al. (2021) [3]:

1. High-quality sapphire substrates are used for deposition of thin films. It can be assumed that they have the expected crystal structure of bulk α-Al_2O_3 (cf. Tab. 1.1). So any deviation of the observed reflection $\mathbf{q}_{hkl}^{Al_2O_3,obs}$ from the expected peak position $\mathbf{q}_{hkl}^{Al_2O_3,lit}$ is corrected by a rotation $\mathbf{R}$ and scaling ρ of reciprocal space Q:

$$\mathbf{q}^{cor} = \rho\mathbf{R} \cdot \mathbf{q}^{obs} \quad , \quad \mathbf{q}^{obs} \in Q \,, \tag{2.6}$$

with

$$\mathbf{R} = \begin{pmatrix} \cos\gamma & -\sin\gamma, \\ \sin\gamma & \cos\gamma \end{pmatrix} \quad , \quad \gamma = \arccos\left(\frac{\mathbf{q}_{hkl}^{Al_2O_3,lit} \cdot \mathbf{q}_{hkl}^{Al_2O_3,obs}}{\left|\mathbf{q}_{hkl}^{Al_2O_3,lit}\right| \cdot \left|\mathbf{q}_{hkl}^{Al_2O_3,obs}\right|} \right) \tag{2.7}$$

$$\rho = \frac{\left|\mathbf{q}_{hkl}^{Al_2O_3,lit}\right|}{\left|\mathbf{q}_{hkl}^{Al_2O_3,obs}\right|} \,. \tag{2.8}$$

2. If the thin film grows tilted (e.g. due to slip systems, cf. 1.3.2), a symmetric reflection – having scattering vector parallel to the surface normal in theory – will exhibit an in-plane component $q_{\parallel,hkl}^{film} \neq 0$. The tilt angle can be calculated by Equ. (2.4):

$$\theta_{tilt} = \arctan\left(-\frac{q_{\parallel,hkl}^{film}}{q_{\perp,hkl}^{film}} \right) \,. \tag{2.9}$$

To determine the lattice constants from asymmetric peaks, the reciprocal space is again rotated as in Equ. (2.7) but with rotation angle $-\theta_{tilt}$. This scenario is depicted in Fig. 2.2b, where the magenta colored reflection deviates from the expected symmetric position.

3. If the thin film is sheared, a symmetric reflection $\mathbf{q}_{\bar{h}\bar{k}l}^{film}$ will be unaffected. On the contrary, an asymmetric reflection with both in- and out-of-plane component is affected. To get reliable results for the lattice constants, this shear angle Ψ_{shear} has also to be corrected, and can be calculated from two inclined lattice planes (hkl) and $(h'k'l')$, i.e. scattering vectors with non-zero in-plane component. Those vectors must have symmetry of a mirror plane perpendicular to the scattering plane[2]. The geometry is depicted in Fig. 2.2b, with the blue and green reflections representing the symmetric and asymmetric reflections, respectively. The shear angle can be calculated with

$$\Psi_{shear} = \arctan\left(\frac{q_{\perp,hkl}^{film} - q_{\perp,h'k'l'}^{film}}{q_{\parallel,hkl}^{film} - q_{\parallel,h'k'l'}^{film}} \right) \,. \tag{2.10}$$

To correct the shear, a rotation around the corresponding symmetric reciprocal lattice point $\mathbf{q}_{\bar{h}\bar{k}l}^{film}$ with the same expected out-of-plane component must be applied.

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[2]This can be achieved by probing for a plane (hkl) and then rotate the sample around ϕ by $180°$.

Table 2.1: Configurations for the applied XRD scans.

scan type	detector mode	step size (°)	active channels	effective width
2ϑ-ω-scan	1D Scanning Line	0.005	255	2.51°
ω-scan	0D Receiving Slit	0.005	55	3.025 mm
ω-optimization	0D Receiving Slit	0.02	37	2.035 mm
φ-scan	0D Receiving Slit	0.05	55	3.025 mm
φ-optimization	0D Receiving Slit	0.5	55	3.025 mm
RSMs	1D Frame Based	0.005	255	2.51°

2.1.5   Technical Aspects

The radiation is produced by an copper anode, resulting in a wavelength of $\lambda = 1.5406\,\text{Å}$ for Cu-Kα_1 radiation. Note that Cu-Kα_2 and Cu-Kβ radiation is not filtered out, resulting in additional low-intensity peaks in the diffractograms. Furthermore, contamination of the anode with tungsten results in an observable W-Lα_1 contribution with energy between Cu-Kα- and Cu-Kβ-radiation. During the course of the conducted experiments, the contaminated anode has been replaced, so the peaks corresponding to W-Lα_1-radiation are not present in every diffractogram.

The diffracted radiation is detected with a *PIXcel^{3D}* (*Malvern Panalytical Ltd.*) detector. For 2ϑ-ω-scans (cf. 2.1.1), the detecor is operating in "Scanning Line" mode. For scans fixing the 2ϑ position, i.e. ω- (cf. 2.1.2) and φ-scans (cf. 2.1.3), the detector is operated in "Receiving Slit" mode. RSMs are recorded with the "Frame Based" mode. The settings for the various scans are listed in Tab. 2.1. Note that it is distinguished between scans and optimizations. The latter were applied for aligning the sample correctly, depending on the measurement. For example, before a 2ϑ-ω-scan of *m*-plane oriented rhombohedral samples, a φ-scan has been applied for the inclined (30.6) reflection to find the correct azimuth of the *c*-axis, which is called φ-optimization. Afterwards, a Rocking curve has been recorded and ω set to the maximum of the peak to compensate for the expected lattice tilt (cf. 1.3.2).

Bibliography

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