Grazing-Incidence Wide-Angle X-ray Scattering

X-ray scattering techniques play a key role in the field of modern material science. In our group, X-rays are used as a powerful tool to obtain information about chemical phases, crystal structures and material morphology on different length-scales, which we usually combine with imaging techniques such as optical or atomic-force microscopy or scanning electron microscopy to obtain detailed morphological pictures of thin films. In the fast-progressing field of functional soft-matter, thin films have attracted great attention for many applications such as stimuli-responsive polymers or organic or hybrid photovoltaics and electronics. The thin-film geometry poses its special challenges on the organization of the X-ray experiment: a grazing-incidence reflection geometry is chosen to lengthen the X-ray path inside the thin film. This increases the scattering cross-section and the probed volume to obtain an enhanced scattering signal with good statistics. By tuning the angle of incidence and hence the penetration depth of the X-rays, we can decide to focus on structural information of the film surface or the bulk film.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) is a powerful tool to investigate crystalline structure and molecular orientation in thin films (Müller-Buschbaum 2014; Hexemer und Müller-Buschbaum 2015) [1] Similar as for X-ray diffraction (XRD), the physical ground of this technique is based on coherent interference of elastically scattered photons, which is known as Bragg or Laue diffraction. In contrast to XRD, a two-dimensional detector collects multiple distinct Bragg reflexes of (poly-)crystalline samples within one single exposure frame. By reflex indexing, the crystallographic hkl-indices can be assigned to the individual reflexes and existent material phases are identified. Each single reflex comprises significant crystallographic information, which can be analysed to quantify the molecular or crystalline orientation and texture, i.e. preferred orientation within crystallographic orientations. Texture can have a great influence on the physical and chemical material properties and is largely controlled by the process of material formation in the thin film. Therefore, analysing and optimizing the film morphology is essential to achieve high quality films with favorable properties for the desired application.

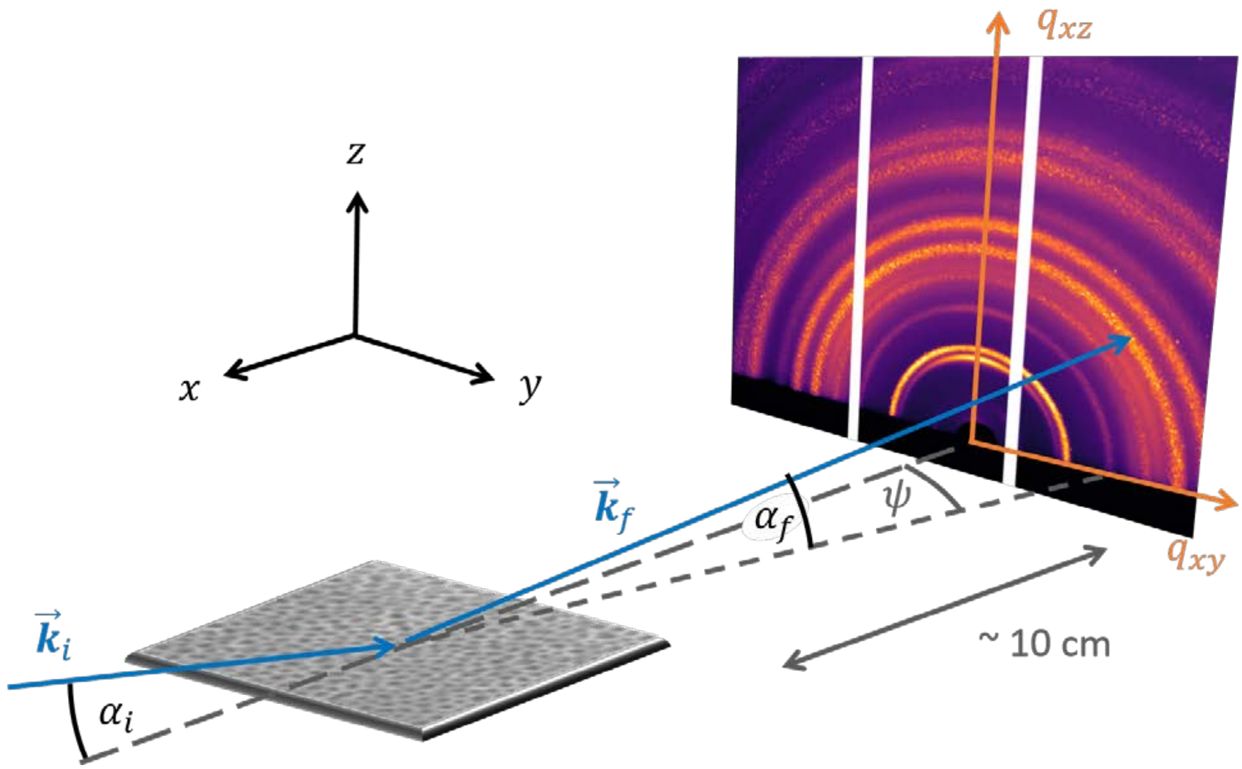

Figure 1. Schematic illustration of the GIWAXS geometry. The incident X-ray beam $\overrightarrow{k_i}$ strikes the sample under shallow angle α_iThe scattered wave $\overrightarrow{k_f}$ reaching the area detector can be described by the real-space in-plane exit angle α_f and the out-of-plane angle ψ (with respect to the scattering plane), and by q_{xy} and q_{xz} in reciprocal space (where the subscript x indicates a non-negligible momentum transfer in x-direction).

GIWAXS as a non-destructive techqnique with short acquisition times down to milliseconds at brilliant synchrotron sources offers the unique opportunity to investigate fast processes. This can be done in real time by following phase formation or degradation and crystal growth or ordering (e.g. during print or spray deposition) *in-situ*, or by relating device performance (e.g. in solar cells, thermoelectrica or smart surface coatings) to structural changes *in-operando* (link to the respective articles here)

Here is a comprehensive selection of work related to GIWAXS of our group within the last years:

Organic and hybrid solar cells attracted a high level of attention within the last years. The degree of crystallinity and crystalline orientation has been shown to be linked directly to the device performance.

- Moseguí González et al. measured P3HT:PCBM solar cells *in-operando* and found a high degree of correlation between the solar cell performance and the crystallinity of P3HT. In particular, they relate radiation-induced aging mechanisms, which decrease the crystallinity, to the decline of open-circuit Voltage caused by changes of electronic material properties.(Moseguí González et al. 2017) [2]
- Li et al. investigated the crystallization of a low band-gap polymer PffBT4T-2OD in printed titania mesoporous scaffolds for the application in hybrid solar cells. They found a correlation between scaffold pore size and polymeric crystallinity, where larger pores increase the polymer stacking density and decrease crystal sizes, except for the face-on orientation of PffBT4T-2OD, where

crystal sizes grow. This increases the desired face-on to edge-on ratio which is beneficial for an enhanced photovoltaic performance (Li et al. 2020) [3].

- Yang et al. see a higher crystallinity and degree of crystalline face-on orientation by adding a third component to Fullerene-based organic solar cells which improved the device performance and stability (Yang et al. 2020) [4].
- Wienhold et al. achieved around 9% efficient printed non-fullerene organic solar cells by optimizing the morphology. Based on studying the positive effect of solvent additives, an improved performance and crystallinity could be realized(Wienhold et al. 2019) [5] (Jiang et al. 2022).

Towards high efficiency hybrid solar cells, the organic-inorganic compound material perovskite gained increasing attention in the last years due to unique material properties and high solar cell efficiencies.

- Oesinghaus et al. compared five different typical perovskite deposition methods and find a strong relation to the morphology and crystallite orientation. The results provide direct evidence for different perovskite conversion mechanisms, and pave the way toward tailored film morphologies (Oesinghaus et al. 2016) [6].
- Filonik et al. followed the crystallization of the perovskite layer in printed mesoscopic solar cells *in-situ. The processing additive of 5-aminovaleric acid iodide suppresses the formation of large crysta*lline grains early in the crystallization process, resulting in improved backfilling and improved device performance (Filonik et al. 2019) [7].

Current and future projects aim towards deeper understanding of mechanisms during film formation (e.g. of printed films) and towards exploring further the pathways leading to device degradation in our thin film solar cells, in order to learn how to improve the thin-film morphology and device stability (Guo et al. 2021).

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