Chapter 2

Grazing Incidence Small Angle X-Ray Scattering as a Tool for In-Situ Time-Resolved Studies

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Additional information is available at the end of the chapter

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Abstract

With the advent of third-generation synchrotron sources and the development of fast two-dimensional X-ray detectors, X-ray scattering has become an invaluable tool for in-situ time-resolved experiments. In the case of thin films, grazing incidence small angle X-ray scattering (GISAXS) constitutes a powerful technique to extract morphological information not only of the thin film surface but also of buried structures with statistical relevance. Thus, recently in-situ GISAXS experiments with subsecond time resolution have enabled investigating the self-assembly processes during vacuum deposition of metallic and organic thin films as well as the structural changes of polymer and colloidal thin films in the course of wet deposition. Moreover, processing of thin films has also been investigated in-situ employing GISAXS. In this chapter, we review the current trends of time-resolved GISAXS studies. After an introduction to the GISAXS technique, we present exemplary results of metallic and organic thin film preparation, wet deposition of polymer thin films and self-assembly of colloidal thin films, as well as examples of thin film modification in, e.g., microfluidic channels and within working devices. Finally, an overview of the future perspectives in the field is provided.

Keywords: GISAXS, thin films, time-resolved experiments, kinetics, processing

1. Introduction

Nanostructures have become commonly used in our daily lives because of the novel properties arising at the nanoscale. These are mainly associated to the object size offering a higher surface-to-volume ratio than macroscopic entities and, thus, surface processes become more and more crucial as the material size is reduced. Furthermore, during the last half century several ways of manipulating the materials at the nanometer scale have been developed to control the nanostructure morphology on demand via either building up the nanostructures by atomic manipulation or exploiting self-assembly concepts. The latter presents clear advantages over atomic manipulation such as less demanding fabrication steps and easier scale-up for industrial production. Nevertheless, much is yet to be understood concerning self-assembly. In this sense, apart from the manipulation of materials at the nanoscale, an appropriate and accurate characterization of nanostructures is crucial, especially for studying the kinetics both during fabrication and processing of the nanostructures.

To properly characterize nanostructures, two questions need to bear in mind: what is the size/shape of the nanostructure and how do they separate from each other. The former is critical since nanostructure geometry strongly influences, e.g., the geometric confinement of the electronic structure [1], the catalytic activity [2, 3] or the optical properties [4, 5]. The latter is important since different physical properties may arise from particular nanostructure arrangement or in the space confined between the nanostructures, e.g., highly ordered arrays of plasmonic nanostructures present a collective plasmonic behavior [6], an efficient arrangement of the nano-objects may expose higher surface area on a macroscopic level for catalysis applications [7] or polymers within nanostructured media may show different glass transition temperatures and chain mobility due to confinement [8].

Within a non ideal material system, the size of the nanostructures and the spatial arrangement present a distribution over micro/macroscopic regions. Thus, the collective effects of nanostructured objects call for sound statistic evaluation. In this respect, grazing incidence small angle X-ray scattering (GISAXS) is nowadays one of the most interesting techniques for studying the morphology of nanostructured thin films. As its counterpart, transmission SAXS [9], it is sensitive to the size and shape of the nanoparticles and to the correlation distances between them, being capable of resolving objects and distances ranging from few nanometers to several hundreds of nanometers, in real space. In contrast to SAXS, GISAXS inherently presents high surface sensitivity as a consequence of the measurement geometry employed. In GISAXS, the incident X-ray beam impinges the sample at shallow angles, thus total external reflection on the surface may take place. In addition, this implies that the beam footprint on the sample probes macroscopic areas which, together with the nature of reciprocal space techniques, ensure that high sampling statistics is achieved.

GISAXS was first demonstrated by Levine et al. using a lab source [10]. However, the full potential of GISAXS is realized when a synchrotron is used as X-ray source. This is due to several reasons. First, a high photon flux is required to probe the surface structures, which may be only present in small amount in comparison to the bulk substrate, thus presenting a weak scattering signal; second, highly collimated beams are demanded to improve the reciprocal space resolution, thus the low emittance, small divergence, and partially coherent beams provided by synchrotron radiation sources are in great favor; third, synchrotron sources provide tunable X-ray wavelength, which may be used to probe the chemical composition in parallel to exploring the morphology.

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