Comparative analysis of nanostructured diblock copolymer films

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Future generations of microelectronic devices will require both, ever-decreasing critical dimensions and shrinking tolerance on those dimensions. The rising costs and complexity associated with lithographically created structures at the nanometer length scale opened opportunities for alternative techniques. Following this track, self-assembly in physical systems might play a key role in future technological applications. Self-assembling materials are characterized by spontaneous formation of nanometer-scaled structures. In addition long-range order or domains are installed.

The self-assembly based nanofabrication process is especially attractive because of its simplicity. The basic preparation procedures involve only a few preparation steps: substrate cleaning, thin film creation and nanostructure creation. Despite all the efforts in creating new types of surface structures, the quality of the self-organized nanostructures is rather limited due to the currently applied experimental analysis techniques [1]. Mostly, experiments are based on local techniques such as atomic force microscopy (AFM) or scanning electron microscopy (SEM). As compared to the desired large scales to be structured these techniques probe only very limited surface areas. To obtain a statistically significant information scattering is a helpful tool. With the advanced scattering technique of grazing incidence small-angle scattering (GISAS) lateral lengths from molecular to micrometer-size are covered. Thus the addressed range is quite comparable to AFM or SEM, but the probed surface area is macroscopic instead of microscopic [2]. In the applied gazing incidence geometry the beam footprint is strongly increased due the extremely small angle of incidence.

Based on the example of dewetted poly(styrene -block- paramethylstyrene) diblock copolymer (molecular weight 230k, symmetric block ratio and narrow molecular weight distribution 1.08) P(Sd-b-pMS) films the possibilities and limitations of GISAXS are enlightened within this investigation. Research is directed towards the host surface structures created by dewetting, because this enables a direct comparison with real space analysis techniques such as AFM or SEM. This opens the opportunity to test modelling of the scattering data. The internal contrast between the styrene and paramethylstyrene block is very low and thus in a good approximation the diblock copolymer can be understood as a simple homopolymer with respect to the scattering signal using x-rays. The grazing incidence small angle x-ray scattering (GISAXS) measurements were performed at the BW4 USAX beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. The selected wavelength was 0.138 nm. The scattered intensity was recorded with a two-dimensional detector which consists of a 512x512 pixel array. Due to the sample-detector distance of 12.1 m a high resolution was achieved. The beam divergence in and out of the plane of reflection was set by two entrance cross-slits. At one fixed angle of incident the two-dimensional intensity distribution can be cut in several vertical and horizontal slices with respect to the sample surface. Vertical slices contain mainly scattering information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions with an in-plane information. Figure 1a shows a typical two-dimensional GISAXS scattering pattern as measured in case of a sample stored for 4 hours under toluene vapour. Since an incident angle \(\alpha_i=0.534^\circ\) larger than the critical angle of the polymeric material was chosen, the specular and the diffuse scattering contributions are well separated along the vertical detector direction and thus easily separated. The specular peak in the top of figure 1a is shielded by a beam stop (resulting in a staggered looking intensity) to protect the array detector, because the specular scattering is orders of magnitude larger compared to the diffuse scattering.
In many cases the data analysis is restricted to a comparison with other experimentally determined data, based on a statistical interpretation of the data [2]. Care has to be taken, because either the reflection-refraction effects in the simple Born approximation or the interplay between interference function and form factor or the particle size distributions might be of importance. Reflection-refraction effects will become significant in the region of total external reflection, e.g. if the incident angle of the GISAXS experiment is chosen close to the critical angle. Moreover, concerning particle size, the coupling between the interference function and form factor greatly increases the complexity of the analysis and prevents the use of classical Guinier or Porod approaches. Therefore, direct modelling of the data can provide further insights. With the program IsGISAXS [3] the simulation of off-specular scattering in the GISAXS geometry is accessible. A detailed description of the possibilities offered by this program can be found in reference [3]. For the modelling basically the form and structure factor have to be chosen.

![Figure 1: a) Typical two-dimensional GISAXS scattering pattern measured at BW4 in case of 4 h storage under toluene vapour atmosphere. b) Calculated two-dimensional GISAXS scattering patterns using the program IsGISAXS as described in the text. Both two-dimensional intensity mappings cover a range of -0.48°<ψ<0.48° in horizontal direction and 0.0°<α<0.55° in vertical direction. The intensity is shown on a logarithmic scale. The colour coding was chosen to emphasize on the features in the diffuse scattering (blue=low and red=high intensity). [4] Because the polymeric material probed within this investigation is placed on top of the solid support the model of supported particles is well suited. In first approximation the form factor of the host structure is chosen to obey a cylinder type and the structure factor to behave like a one-dimensional paracrystal [5]. To elucidate the possibilities and limits of the modelling based on IsGISAXS we restrict us to this model assumption [6]. The two-dimensional intensity mappings shown in figure 1 cover exactly the same angular range. The colour coding was adapted to match. Since only the diffuse scattering is modelled, no specular peak is present in figure 1b. As a consequence the comparison can mainly focus to the region around the Yoneda peaks. On a first view, basic features of the measured two-dimensional intensity mapping are captured by the modelling. In general, the agreement covers the split-up Yoneda peaks in their positions and shapes. Most deviations are originated from a missing background in the modelled data and effect the regime of large ψ (or qy) values [4, 6].

References