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COMMUNICATION

Probing structural changes of spin-coated polystyrene film after swelling and precipitation by synchrotron GIUSAXS and AFM

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Polystyrene film of about 50 nm in thickness on silicon wafer was obtained by spin-coating in tetrahydrofuran solution. The film exhibits a rough surface as shown by atomic force microscopy images and ellipsometry data. Furthermore, such surface roughness produced a characteristic lateral correlation peak in an "out-of-plane" scan in the synchrotron grazing incidence ultra-small angle X-ray scattering pattern. The film was treated with liquids of solvent and non-solvent sequentially, resulting in a process of swelling and precipitation of the polystyrene film. Such a solvent/non-solvent treatment completely changed the original surface structure of the film. Aggregates of polystyrene of different sizes were observed both in atomic force microscopy and synchrotron grazing incidence ultra-small angle X-ray scattering measurements. The results demonstrate that synchrotron grazing incidence ultra-small angle X-ray scattering is a unique means to investigate large area micro-structural features of thin films supported on smooth surfaces.

Keywords thin film, polystyrene, grazing incidence small angle X-ray scattering, morphology

1 Introduction

Polymeric films of thicknesses below 100 nm are of great interest in academic research, due to some fundamental aspects concerning their structure and stability. The most widely considered system could be polystyrene (PS) thin films. Using the spin-coating technique, PS films of different thickness can be easily produced. The structure of a polymeric thin film is normally characterized by atomic force microscopy (AFM) measurements. However, two factors might limit the application and interpretation of AFM data, namely the small sampling area and inaccessibility of the structural features beneath the surface. To address these points, grazing incident small angle X-ray scattering (GISAXS) is used to investigate the structure of thin films. The technique was explored in *in-situ* studies of the structural evolution of metallic nanoparticles, relying on the strong scattering intensity that could be obtained [1–3]. Although the contrast in structured polymeric films is not as strong as that in metallic hybrid materials, synchrotron GISAXS has also been successfully applied to polymeric thin films [4–7]. With structures of larger length scale up to a few micrometers, GIUSAXS must be performed to achieve adequate resolution [8].

In this short paper, we intend to demonstrate how GIUSAXS measurements can be utilized to study the structure of polymeric thin films. Spin-coated polystyrene was used as an example. As will be shown in the following sections, GIUSAXS data represents structural features previously observed under AFM within a relatively small sample area.

2 Experiments

2.1 Sample preparation

PS used in this study was supplied by BASF SE. It has a molecular weight (Mw) of 275000 g/mol. PS films supported on oxidized silicon wafers were prepared by spin-coating a 5.0 mg/mL tetrahydrofuran (THF) solution. In order to remove residual solvent, the films were annealed in a vacuum oven first at 333 K for 120 min and then at 383 K for 90 min. The thus obtained PS film was referred as the initial film. The initial film was then immersed into N, N-Dimethylformamide (DMF) for 2 s followed by a rapid transfer into ethanol for 3 min. As DMF is a solvent of PS while ethanol is a non-solvent, such treatment induced first a swelling of the film and then a precipitation process.

2.2 Instruments and methods

Synchrotron GIUSAXS measurements were performed using the beamline BW4 at HASYLAB, DESY, Hamburg, Germany [8]. The energy of the X-ray radiation was 8.979 keV, resulting in a wavelength of 0.13808 nm. The size of the primary X-ray beam at the sample position was 0.4 mm×0.4 mm. The sample to detector distance was 13037 mm causing

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GIUSAXS geometry. The scattering vector $\boldsymbol{q}$ was decomposed as $\boldsymbol{q} = \boldsymbol{q}_y + \boldsymbol{q}_z$ (where $\boldsymbol{q}_y$ and $\boldsymbol{q}_z$ are the horizontal and vertical components, respectively) and $|\boldsymbol{q}| = q = \frac{4\pi}{\lambda}\sin\theta$ (where 2θ is the scattering angle and λ the wavelength). The GIUSAXS experiments were performed in a vacuum chamber equipped with a sample holder mounted on a goniometer. The scattered intensity was recorded at a fixed angle of incidence ($\alpha_i = 0.4°$) of the X-ray beam with respect to the sample surface. The specular peaks were always kept at the same position on the detector. GIUSAXS data were recorded with an exposure time of 10 minutes and with a two-dimensional detector array (2048×2048 pixels, pixel size: 79.1 μm). The AFM measurements were carried out using a scanning probe microscope (SPA-300HV, Seiko Instruments Inc., Japan). The ellipsometry measurement was performed with a UVISEL ER Ellipsometer (Jobin Yvon S.A.S, France).

3 Results and discussion

The surface structure of spin-coated PS films on the top of the silicon wafer is known to be related to the solvent used. In our case, THF was used to prepare a 5 mg/ml PS solution for spin-coating. Under this condition, one expects a rough surface of the final film due to the low boiling point of THF and thus, fast evaporation of the solvent during spin-coating [9,10]. Before conducting AFM measurements, the initial untreated sample was analyzed in ellipsometry experiments. The ellipsometry data cannot be fitted with a model concerning only a homogenous layer, but can be well described by a model comprising of two layers having different optical properties and thickness. Best fit was achieved when the thickness of the two layers was (2.58±0.16) and (44.9±0.17) nm, respectively. This implies that after spin-coating the initial PS film possessed a rough layer of a few nanometers in thickness on top of a homogenous PS layer of about 45 nm in thickness. To further verify this structural feature, AFM measurements using tapping mode were performed. Figure 1 shows the obtained AFM images of both the initial spin-coated film and a film after solvent/non-solvent treatment. It must be mentioned that for the film after treatment, no meaningful ellipsometry data could be obtained due to the strong light scattering on the surface. The AFM image for the initial film presents a wrinkle-like surface morphology of typical dimension of several hundred nanometers. The amplitude/thickness of this wrinkle-like structure, in the surface normal direction, is within a few nanometers in accordance with the structural model obtained via ellipsometry measurements. A solvent/non-solvent treatment completely changed the initial structure of the PS film, as shown by the AFM image on the right side of Figure 1. The final cluster-like surface structure implies drastic changes during the swelling and precipitation process, also possibly dewetting of the thin PS film from the surface of the silicon wafer when swelling was followed by precipitation. The detailed mechanism is beyond the scope of the current work and will not be further discussed. It was noted that the PS clusters are smaller in size and broader in size distribution compared to the initial wrinkle-like structure. The two different morphologies shown in Figure 1 are common for many other polymeric films and thus were selected to illustrate the capability of synchrotron GIUSAXS technique. For comparison, patterns obtained via a two-dimensional Fourier transformation of the AFM images were also included in Figure 1. The scattering vector in the Fourier transformed patterns is defined as $s = \frac{q}{2\pi}$.

Figure 2 presents the GIUSAXS patterns for the initial spin-coated and solvent/non-solvent treated PS films. For the initial film, most of the scattering intensity in the GIUSAXS pattern was concentrated around a plane defined by the incidence X-ray and the normal of the film, which is a typical reflection behavior of thin film. On the other hand, for the treated film, we observed a greater spread in the intensity distribution. In view of the reciprocal principle of scattering experiments, the GIUSAXS patterns of the initial and the treated films imply structural features of different length scales. A straightforward conclusion drawn from the GIUSAXS patterns is that the initial film possessed much larger structures than the treated one. Quantitative evaluations could be performed by considering the scattering intensity distribution along a horizontal slice parallel to the wave vector component $\boldsymbol{q}_y$ ("out-of-plane scan"). This intensity distribution $I(\boldsymbol{q}_y)$ represents the lateral structural features of the film. Figure 3 shows such an out-of-plane scan at $q_z = 0.28\ \mathrm{nm}^{-1}$ (Yoneda Peak [11]). $I(\boldsymbol{q}_y)$ of the initial film clearly shows a correlation peak around $q_y = 0.01\ \mathrm{nm}^{-1}$, indicating a structure of correlation length of about 600 nm in the lateral direction of the film. This result is in good agreement with the one obtained via AFM. A Fourier transformation of the AFM image yields a similar correlation peak (Figure 1). From the data of the treated film, one finds a broad correlation peak located around $q_y = 0.06\ \mathrm{nm}^{-1}$, indicating a correlation length of about 100 nm. Again, this behavior is in accordance with the data obtained via a Fourier transformation of the AFM image of the treated film. Obviously, after solvent/non-solvent treatment, the scattering data indicates a much broader size and correlation distance distribution compare to that of the initial film.

It must be mentioned that in a GIUSAXS measurement, the footprint of the X-ray beam on the sample is several orders of magnitude larger than that of an AFM investigation due to the very small incidence angle. Therefore, results obtained from

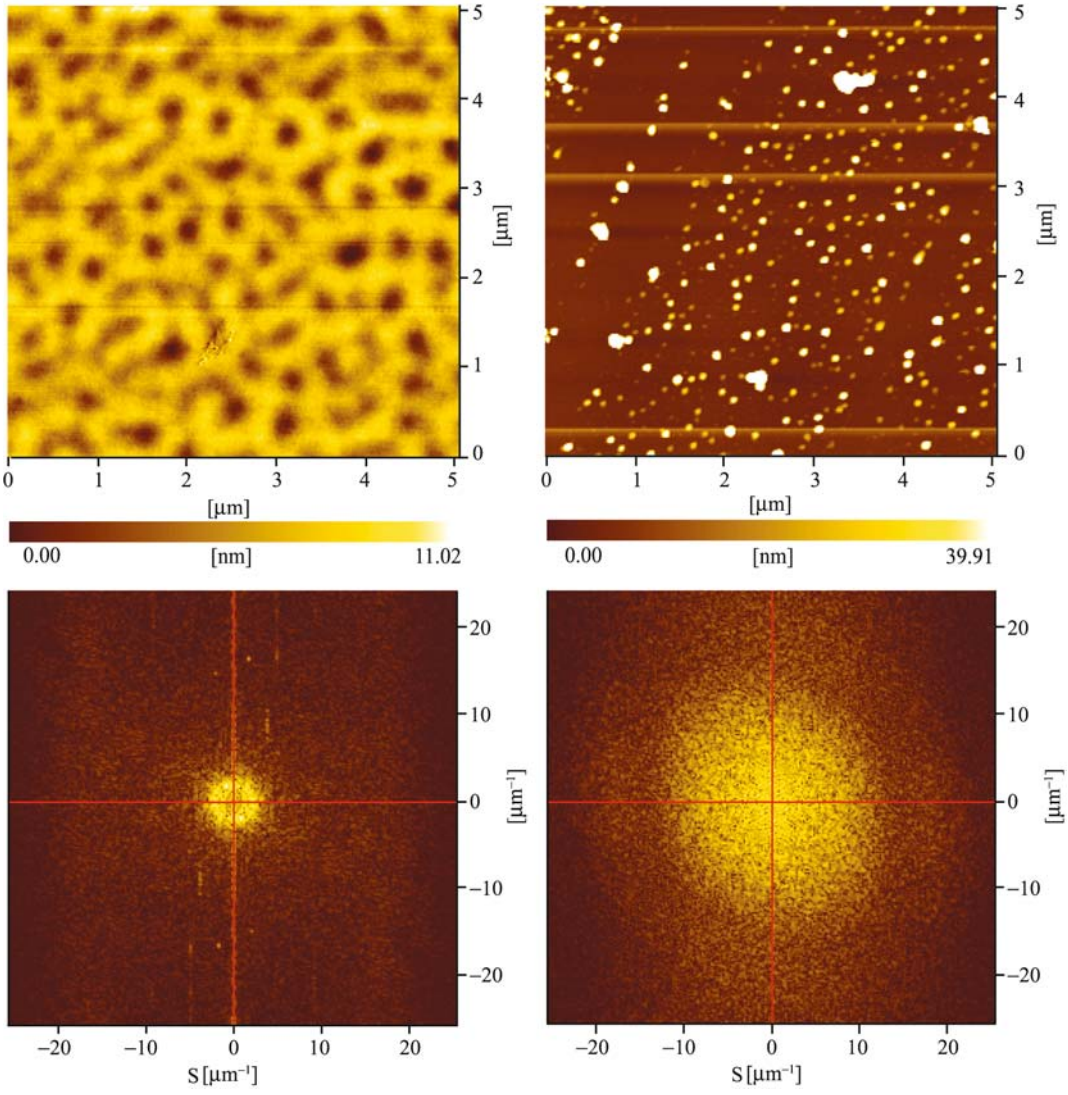

Figure 1 AFM height images (top) and corresponding patterns (bottom) obtained via two-dimensional Fourier transformation: the initial spin-coated PS film (left) and the PS film after solvent/non-solvent treatment (right).

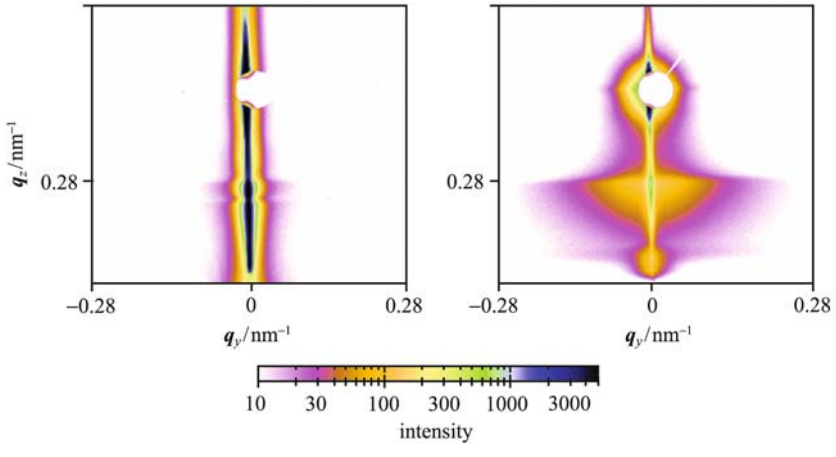

Figure 2 GIUSAXS patterns: the initial spin-coated PS film (left) and the PS film after solvent/non-solvent treatment (right).

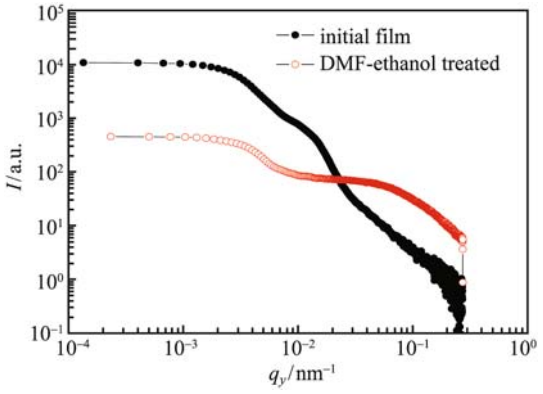

Figure 3 The one dimensional GIUSAXS data obtained by an out-of-plane cut of the two dimensional patterns shown in Figure 2 at q_z= 0.28 nm^{-1}.

GIUSAXS measurements average over a macroscopic volume/area of the sample. In the case presented here, we were not able to demonstrate other qualitative differences between the two techniques, namely the ability of detecting buried structures beneath the surface from GIUSAXS measurements. Examples illustrating such differences can be found elsewhere [12].

4 Conclusion

In summary, we demonstrated that the wrinkle-like surface structure of PS thin film spin-coated from its THF solution is limited on the top few nanometers. It also has a uniform distribution across a large length-scale. Results from AFM, ellipsometer and GIUSAXS agree with each other although the observation windows of those techniques are largely different (5 μm×5 μm for AFM, ϕ = 1 mm for the ellipsometer and 0.4 mm×40 mm for GIUSAXS). The wrinkle-like structure exhibiting about 600 nm lateral correlation length could be completely changed after solvent/non-solvent treatment, resulting in a cluster-like surface structure with a wide size distribution.

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