In situ micro-beam GISAXS investigation during spray deposition of polymer colloidal thin films

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Recently, the novel technique of spray deposition was used in the fabrication of organic-based multilayer devices such as transistors [1], semiconductors [2], electrolyte films [3] and solar cells [4]. This technique allows for performing rapid deposition of organic-based nanostructured layers showing high homogeneity over a large area and is thus of great interest in industrial applications such as sensor coating [5], optical sensor [6] or magnetic recording [7, 8] technology. Understanding of the fast kinetic phenomena that take place during the spray deposition is crucial to optimize the deposition parameters and better control the multilayer device nanostructure and properties. We used the technique of micro-beam grazing incidence small-angle X-ray scattering (μGISAXS) to investigate in situ the formation of polymer thin films during spray deposition and following solvent evaporation.

The μGISAXS experiments were performed at the P03 beamline [9, 10] of the PETRA III storage ring at HASYLAB (DESY, Hamburg). The beam size was reduced to 15 μm x 25 μm (vertical x horizontal) by using an assembly of parabolic beryllium compound refractive lenses. We used a wavelength λ = 0.095 nm, a sample-to-detector distance D_{SD} = 3.95 m and an incidence angle α_i = 0.45^o. Thanks to the high flux available at the P03 beamline and to the use of a fast detector (Pilatus300k from *Dectris*), typical time resolutions ranging from 50 to 100 ms could be achieved. For spray deposition we used a modified automated commercial airbrush from *Harder & Steenbeck* (Grafo T3 model). The sample-to-spray nozzle distance was 100 mm and the gaz pressure 0.1 MPa (1 bar).

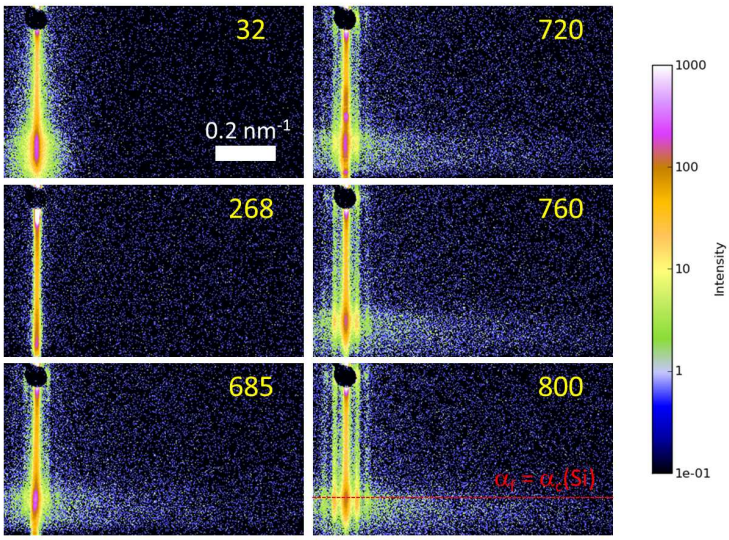

Figure 1: Selected μGISAXS data (exposure time per frame 95 ms) recorded in situ during spray deposition of PS colloids (nominal diameter 194 nm) in dispersion in ethanol (C = 10 mg/mL) on a acid-clean Si-wafer. The intensity is displayed in a logarithmic scale. The frame number is indicated in the top right corner. Start of the spray cycle (frames 268) defines t = 0 s. The horizontal red dashed line indicates the position of the out-of-plane cut corresponding to an exit angle $\alpha_f = \alpha_c(Si)$.

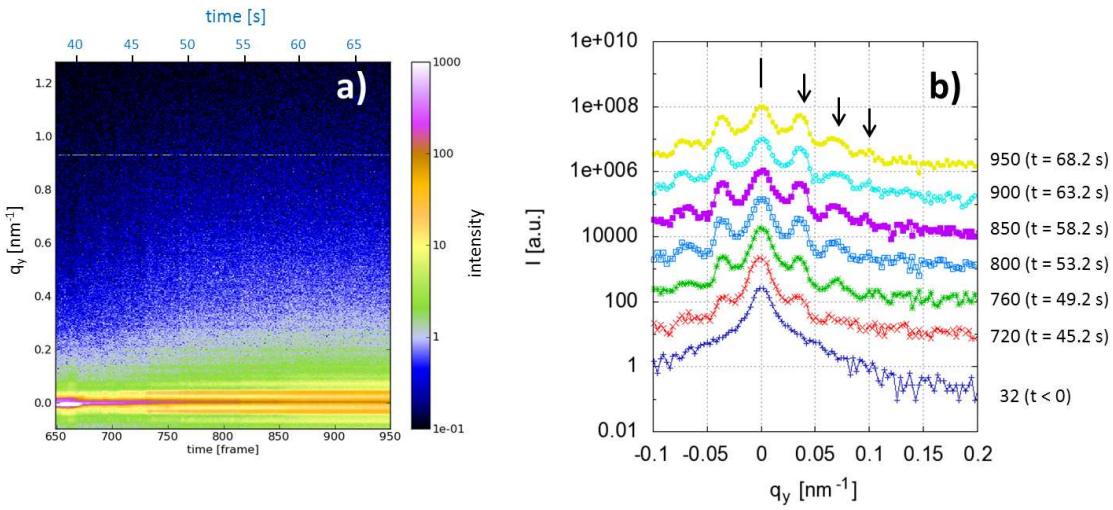

Figure 2: a) Evolution of the out-of-plane cut $\alpha_f = \alpha_c(Si)$ as indicated by the horizontal red dashed line in Fig. 1 during solvent evaporation with a time resolution of 100 ms. The intensity is displayed in a logarithmic scale. b) Selected out-of-plane cuts $\alpha_f = \alpha_c(Si)$. The curves were shifted for better visibility. The vertical arrows highlight the positions of the first three maxima at q_y = (0.032±0.001), (0.065±0.001) and (0.097±0.001) nm^{-1} resp.

Figure 1 shows the μGISAXS data recorded in situ during spray deposition of PS colloids (nominal diameter 194 nm) on a acid-clean Si-wafer. One can clearly see the emergence of side maxima while the solvent is drying. See also Figure 2a) and b). The positions of the three first side maxima at q_y = (0.032±0.001), (0.065±0.001) and (0.097±0.001) nm^{-1} reveal a typical lateral length scale of (195±5) nm which corresponds to the nominal diameter of the PS colloids. The rapid increase in the number (higher order peaks) and in the intensity of the side maxima indicates a fast lateral ordering of the colloids on the Si-substrate. In less than 60 s a laterally ordered polymer thin film is installed.

Colloidal polymer thin films were prepared by using the novel technique of spray deposition. Analysis of the GISAXS data reveals fast ordering kinetics of the polymer colloids on the Si-substrates. Quantitative analysis of the μGISAXS data is still underway.

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