Gold nanoparticle deposition onto doped polyaniline thin films – an in situ investigation with a combination of µGISAXS and imaging ellipsometry

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Conducting composite materials based on polyaniline and gold have a broad range of possible applications in the fields of electronics, optics and biology. In this work the deposition of gold nanoparticles as a droplet in aqueous dispersion onto a thin film consisting of poly(styrene-*b*-ethylene oxide) and doped polyaniline is used to obtain such a composite. A dopant is necessary to transform polyaniline into an electric conducting state. The block copolymer together with polyaniline and the dopant campher sulfonic acid (CSA) is spin-coated out of chloroform solution on pre-cleaned silicon wafer. A composite with 20 nm spherical gold nanoparticles is established by solution casting of a drop of gold nanoparticle dispersion. The combination of µGISAXS (grazing incidence small angle x-ray scattering with a micro-focused x-ray beam) and imaging ellipsometry applied for this experiment has been developed at the MiNaXS (Micro- and Nanofocus X-ray Scattering) beamline P03 of PETRA III [1, 2].

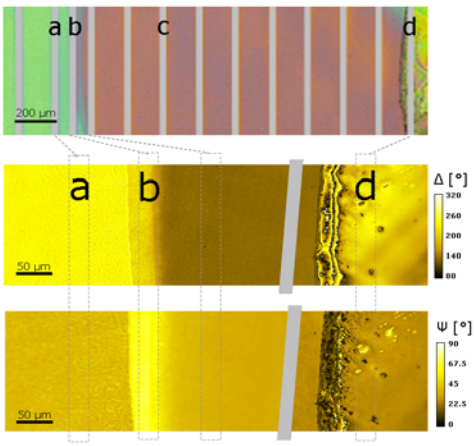

Figure 1: *Optical characterization of composite film: top row shows the real color optical microscopy image from the outside of the droplet (a) towards the center of the droplet (d). The thin film of doped polyaniline appears green, the outer range of the dried droplet of gold nanoparticles appears pink and the gray lines mark the positions where the sample is probed with the x-ray beam. Second and third row show the 2d maps of the ellipsometric values delta and psi. These maps are combined of several discrete maps recorded just before the x-ray experiment. In the images a, b, c and d refer to distinct positions on the sample where the scattering experiment has been performed.*

One of the key features of the combined instrument is that after an initial alignment the x-ray beam and the laser beam of the imaging ellipsometer cross on one spot on the sample. This allows for a scanning GISAXS experiments in a chosen region of interest. For the composite structure evolved with a drying droplet this scan starts from the inside towards the center of the droplet in 200 µm steps as shown in Fig. 1. The sample was investigated with a chosen wavelength of 0.0965 nm at an incident angle of $\alpha_i = 0.45°$. The sample to detector distance is set to 2.47 m.

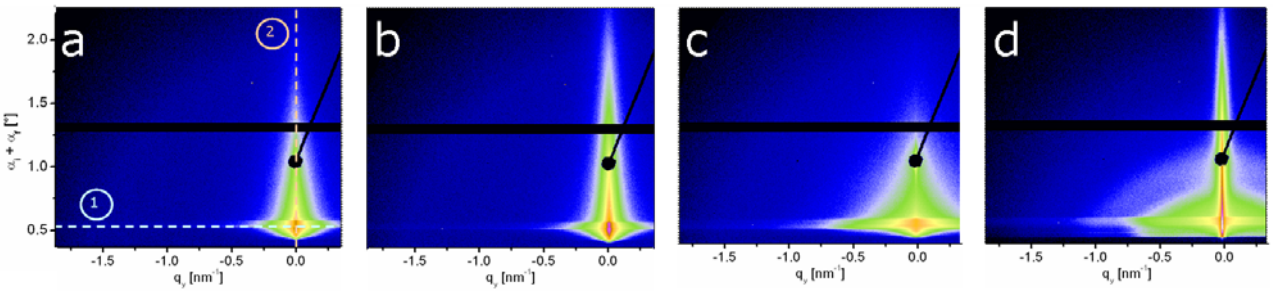

Figure 2: *2d GISAXS patterns of representative positions a, b, c and d as marked in Fig. 2.*

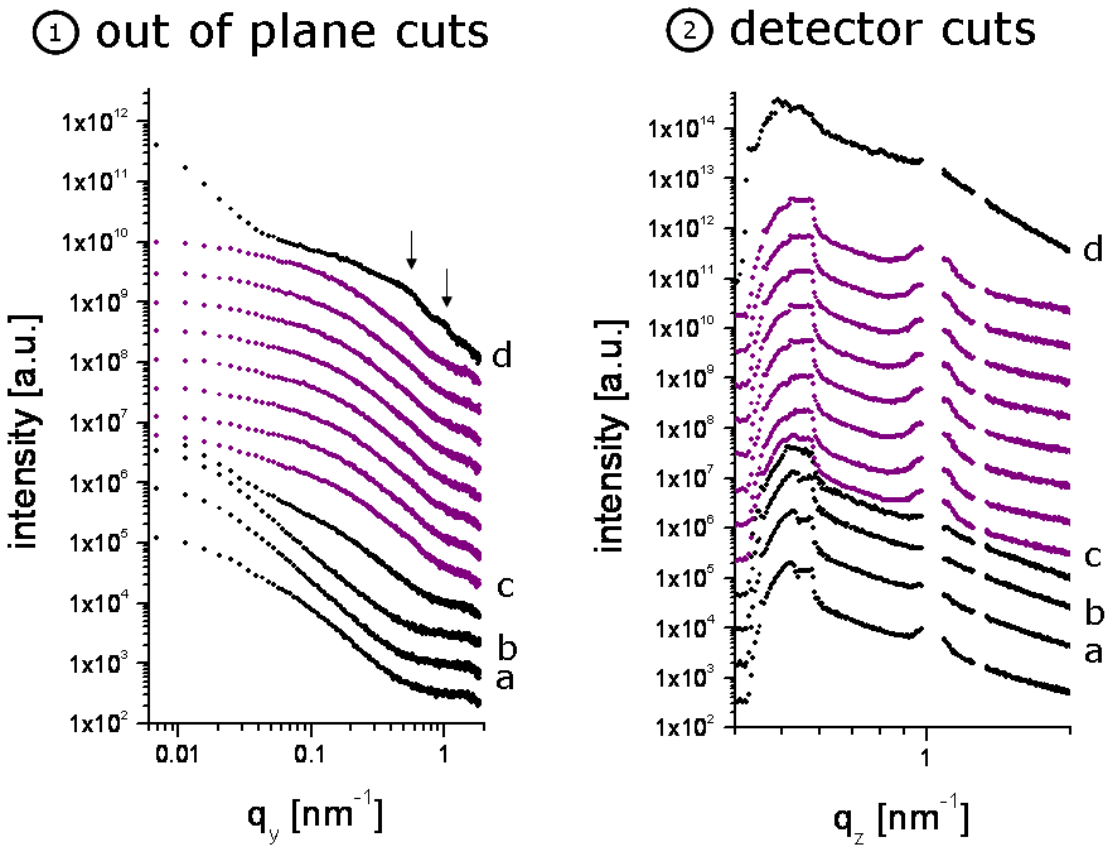

Figure 3: *Out of plane cuts and detector cuts from GISAXS pattern as marked (1) and (2) in Fig. 2. Scan from outside the droplet (bottom curve) to center of droplet (top curve). Intensity is shifted for clarity. Arrows indicate peaks originated by gold nanoparticles.*

In the region outside the droplet (position marked with "a" in figure 1) the crystallized dopant CSA is enriched at the surface as visible with the imaging ellipsometer. Next to the first boundary of the dried droplet (position b) with increased surface roughness there is a larger rather homogeneous region (position c) with minor gold nanoparticle coverage. A rough top layer of gold nanoparticles is only built up in the center of the droplet with distinctive scattering (position d).

As the combined instrument with GISAXS and imaging ellipsometry is particularly suited for the investigation of kinetic processes also the development of the composite structure during the drying process was followed. For this kinetic experiment a small droplet of nanoparticle dispersion was put on a certain chosen position on the sample and the drying was followed in-situ by recording the ellipsometric data (psi and delta) and the GISAXS data. In the initial stage after droplet application the detected intensity is low due to absorption of the water droplet. Due to the evaporation of solvent, the water drop shrinks and drying and layering of gold nanoparticles can be followed until a stable structure is built up.

References

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