GIWAXS Investigation of the Crystallinity of Titania Thin Films

J. Perlich, C. M. Papadakis, E. Metwalli, A. M. Sommer, C. Deiter, W. Drube, M. Memesa, J. S. Gutmann, and P. Müller-Buschbaum

TU München, Physikdepartment LS E13, James-Franck-Str. 1, 85747 Garching (Germany)
1 HASYLAB at DESY, Notkestr. 85, 22603 Hamburg (Germany)
2 Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz (Germany)
3 Institute for Physical Chemistry, Johannes Gutenberg University, Jakob-Welder-Weg 10, 55099 Mainz (Germany)

The creation of nanostructured titania thin films is of great interest for many applications, due to their electrical performance as a semiconductor. The performance depends strongly on the morphology of the nanocomposite films as well as the crystallinity. For the preparation of the titania thin films, we combine the amphiphilic triblock-copolymer poly(ethylene glycol methyl ether methacrylate)-block-polydimethylsiloxane-block-poly(ethylene glycol methyl ether methacrylate) ((PEO)MA-b-PDMS-b-MA(PEO)), which acts as the templating agent, with inorganic sol-gel chemistry [1, 2]. First, the triblock copolymer is fully dissolved in isopropanol and tetrahydrofuran, which is a good solvent for both blocks. Afterwards, hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP) are added to the polymer solution as the source for the sol-gel process. Because HCl and TTIP are poor solvents for the hydrophobic block, a so-called good-poor-solvent pair induced phase separation leads to the formation of nanostructures by film preparation via spin-coating. The different morphologies are controlled by the solvent concentration. In order to obtain crystalline titania thin films in the final step, calcination is conducted at higher temperature in air. Preliminary investigations of the crystallinity with conventional X-ray diffraction have shown a significant dependence of the obtained crystalline phase (anatase, rutile or brookite) on the calcination temperature [1]. Because of the different lattice structures of the respective crystallographic phases, different electronic band structures are realized, and hence different band gaps result after calcination. Besides the absolute value of the calcination temperature, it is important whether the temperature is reached in a ramp-up or whether the sample is exposed to the maximum value at once.

For the investigation of the crystallinity of the sol-gel templated titania thin films, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) at beamline BW2, HASYLAB [3, 4]. With the experimental geometry of the GIWAXS-setup a highly efficient probing of the thin film is realized, because the small incident angle of the beam enables a long effective path inside the film, and hence a maximization of scattering events. The plane of the thin film surface was oriented vertically, and the sample was mounted inside a He-purged cylinder with a transparent Kapton cover. The sample-to-detector distance was approximately 0.7 m. These measurements were performed at an X-ray wavelength of 1.24 Å. The incident angle of the beam was fixed to 0.25°. At a beam size of (5000 × 300) µm² (hor. × vert.) at the sample position, this results in a footprint of the beam on the sample surface of approximately 115 mm. In-plane diffraction patterns were collected as a function of the scattering vector $q_{||}$.

In detail, we have investigated the influence of the temperature ramp-up used for the calcination of the spin-coated polymer-nanocomposite films. We started with identical polymer-nanocomposite films on glass substrates prepared from identical solutions, which resulted in a distinct titania morphology after calcination. Figure 1 shows the measured in-plane diffraction patterns of the titania thin films after calcination at a temperature of 450 °C for 4 h after ramping up slowly or rapidly. The black (lower) curve in the main diagram represents the titania thin film calcined with a ramp-up of 6.25 K/min, which is the standard condition employed for preparation [2]. The curve exhibits three distinct diffraction peaks, as shown in the magnification, comprising two single peaks at 2.223 Å⁻¹ and 2.642 Å⁻¹ as well as a double peak centred around 3.145 Å⁻¹. Additionally, in the range of 1.0 Å⁻¹ ≤ $q_{||}$ ≤ 2.6 Å⁻¹, a broad bump in intensity is observed, which indicates the presence of amorphous material in the sample system, namely the amorphous glass substrate. The red (upper) curve is from the sample with a ramp-up of 13.3 K/min. The curve does not reveal any significant
in-plane diffractions, only a strong amorphous bump, which results also from the glass substrate. We conclude that the titania thin film does not exhibit crystallinity after the calcination. For manufacturing, it would have been desirable to obtain crystalline titania even with a fast ramp-up because this would have reduced the overall time needed for preparation.

Figure 1: In-plane GIWAXS intensity profile of the nanostructured titania films after calcination at 450 °C for 4 h after temperature ramp-ups at 6.25 K/min and 13.3 K/min, respectively. The high-resolution scans of the respective diffraction peaks are shown on the right side.

In summary, the successful GIWAXS investigation of titania thin films reveals the crystallinity and illustrates exemplarily the influence of the selected calcination conditions onto the actual obtained crystallinity. A further and more detailed investigation of the calcination conditions is necessary to develop a complete picture of the behaviour as a function of the ramp-up conditions. In addition, it would be of huge interest to explore the influence of the calcination temperature itself onto the thin film crystallinity.

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References