Combinatorial investigation of nanostructures formed in a
titanium dioxide based nanocomposite film on top of
fluor-doped tin oxide layers

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In the past decade, there is a growing interest in the field of polymer-based photovoltaic (PV) technologies and conversion concepts. Typically, PV devices are built in a sandwich structure on indium tin oxide (ITO) or fluor-doped tin oxide (FTO) coated glass substrates. Both, ITO and FTO, are transparent metal oxides, and thus ideal as transparent electrodes. Because ITO/FTO has a variable workfunction, it is rarely used as the lone bottom electrode. Either PEDOT-PSS or TiO₂ is used for the transparent material deposited on top of the ITO/FTO substrate, resulting in opposite polarity devices due to differential workfunction steps. TiO₂ is a promising candidate as an electron acceptor and transport material, as confirmed by its use in dye-sensitized cells and hybrid polymer/TiO₂ cells. When light is incident on TiO₂, it becomes relatively conducting so that the quasi Fermi-level of the photodoped TiO₂ appears to play an important role in determining the open circuit voltage. Both TiO₂ and PEDOT-PSS have been shown to improve device performance over bare ITO/FTO. The morphology of the TiO₂ layer greatly influences the efficiency of the devices and interface structure between ITO/FTO and the TiO₂ barrier layer is of special interest. One very promising way to fabricate nanostructured TiO₂ layers on top of ITO/FTO is a solution-based sol-gel process [1]. An amphiphilic block copolymer, poly(styrene)-block-poly(ethyleneoxide), denoted P(S-b-EO), is used as a template to obtain nanocomposite films, followed by calcination at 450° C for 4 hours to obtain crystalline TiO₂ nanostructures.

Within the present investigation we apply a combinatorial approach to focus on P(S-b-EO)-titania nanocomposite structures on the FTO film. Thus we address the first important step in creating the anode of a PV device. Instead of a simple homogenous FTO layer on the glass substrate a thickness gradient between the homogeneous FTO layer and the bare glass surface is investigated (see fig. 1b). Part of the 654 nm thick FTO layer (Solaronix SA) on boroalumino silicate glass (TCO10-10) was removed by etching resulting in the wedge-shaped gradient between the intact FTO layer and the bare glass surface. The composite film P(S-b-EO) is prepared by spin-coating. The TiO₂ nanostructures have a nanowire-like shape due to the chosen conditions [2].

The structural investigation is based on a combination of the surface sensitive scattering technique, grazing incidence small angle X-ray scattering (GISAXS), and a moderate micro-focussed X-ray beam (size (H*V) 60*30 µm²) [3]. The scattering experiment was performed at the beamline BW4 at HASYLAB (Hamburg) at wavelength of 0.138 nm, a sample-detector distance of 1.97 m and at an incident angle of 0.72°. The FTO-gradient was aligned perpendicular to the X-ray beam. Position sensitivity was achieved by scanning the FTO-gradient. A region of 1 mm was scanned in steps of 50 µm. Thus the change in FTO thickness from 654 nm to the bare glass surface was probed completely. Fig. 1a shows the corresponding two dimensional (2d) GISAXS patterns [4]. Already the 2d GISAXS patterns show a clear change along the gradient due to the change in the morphology. For analysis line cuts in out-of plane direction from the 2d GISAXS pattern [3] are performed. To emphasize on the structure of the FTO layer the cuts were performed at the critical angle of FTO and in addition to probe the structure of the nanocomposite film cuts were performed at the critical angle of PS. Characteristic lateral distances ξ of the FTO and the nanocomposite film were modelled with a structure factor. A Lorenzian-type distribution of ξ was assumed to account for statistical deviations from this nearest neighbour distance. In the fit the experimentally determined resolution function was taken into account. Major result is the characteristic lateral length ξ for both layers. In Fig. 1c these information are plotted as a function of the position along the FTO-gradient.
The FTO film exhibits a dominant length of 18 nm, which is unchanged as a function of the position. The absence of FTO is correlated with the vanishing of this lateral length. The shape of the gradient is extracted from the intensity of the related structure factor peak normalized by the primary intensity $I_{\text{FTO}}/I_o$. As visible in Fig. 1c in the beginning the gradient is quite steep due to the applied etching [4]. Again the vanishing of this intensity marks the end of the part covered with FTO. FESEM is not suited to display the gradient properly, due to the angular parallax and atomic force microscopy fails due to its extremely localized sampling area.

The nanowire-shaped TiO₂ parts of the nanocomposite film give rise to a lateral length of 200 nm, corresponding to the distance between adjacent nanowires, on top of the thick FTO film. Along the gradient this structure changes. It decreases down to 90 nm on the pure glass surface. Between both limiting values the decrease is due to the FTO-gradient (see Fig. 1c). This dependence on the substrate surface shows that the applied sol-gel process is not only sensitive to parameters of the solution which define the position in the ternary phase diagram [2] and the applied preparation conditions in terms of humidity and temperature. The resulting structures of the nanocomposite film strongly depend on flow field installed during the spin coating and on the acting interface potential. The flow field on the rough FTO layer differs from the one on top of the smooth glass surface. FTO and glass as well as both blocks PS and PEO differ in polarity and surface energy. Consequently, different morphologies of the P(S-b-EO) matrix, which acts as a template during the sol-gel process, can be formed, depending on the FTO layer thickness [4].

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References