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

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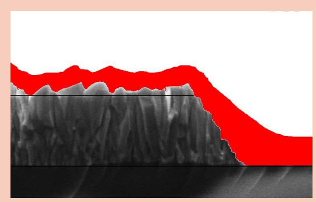
Nanostructures formed in a titanium dioxide (TiO_2) - poly(styrene)-block-poly(ethyleneoxide) nanocomposite film on top of fluor-doped tin oxide (FTO) layers are investigated. The combinatorial approach is based on probing a wedge-shaped FTO-gradient with grazing incidence small angle x-ray scattering (GISAXS) in combination with a moderate micro-focus x-ray beam. The characteristic lateral length is given by adjacent nanowire-shaped TiO_2 regions. It decreases from 200 nm on the thick FTO layer to 90 nm on the bare glass surface.



Sketch of the FTO gradient coated with a nanocomposite layer probed in the combinatorial approach.

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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 TiO_2 is used for the transparent material deposited on top of the ITO/FTO substrate, resulting in opposite polarity devices due to differential workfunction steps. TiO_2 is a promising candidate as an electron acceptor and transport material, as confirmed by its use in dye-sensitized cells [1, 2] and hybrid polymer/TiO_2 cells [3–5]. When light is incident on TiO_2, it becomes relatively conducting so that the quasi Fermi-level of the photodoped TiO_2 appears to play an important role in determining the open circuit voltage. Both TiO_2 and PEDOT-PSS have been shown to improve device performance over bare ITO/FTO [6, 7]. The morphology of the TiO_2 layer greatly influences the efficiency of the devices and interface structure between ITO/FTO and the TiO_2 barrier layer is of special interest [8]. One very promising way to fabricate nanostructured TiO_2 layers on top of ITO/FTO is a solution-based sol-gel process [9]. 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^o C for 4 hours to obtain crystalline TiO_2 nanostructures.

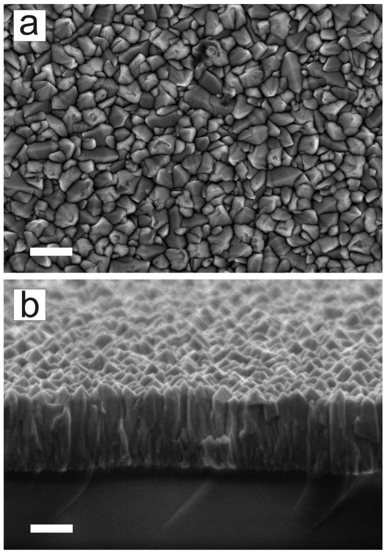

Figure 1 FESEM images picturing the typical FTO layer morphology in a) top view and b) side view.

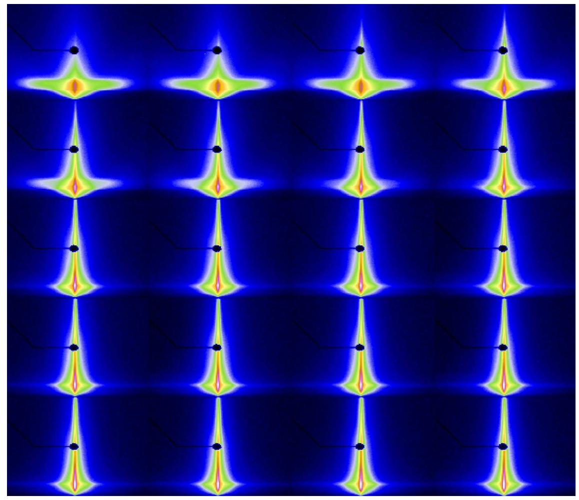

Figure 2 Composite image comprising the 2d scattering patterns from 20 positions along the FTO-gradient (left to right and top to bottom). The top left scattering pattern was measured at the largest FTO thickness and the bottom right one at the bare glass substrate. Each 2d image shows an angular range of $\pm$ 1.05^o in horizontal (out of plane) and 1.86^o in vertical direction. The specular peak is blocked with a small beamstop.

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. 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. Scanning electron microscopy (FE-SEM) images were obtained on field emission SEM (LEO 1530 "Gemini") operated at an accelerating voltage of 3 kV. FTO shows the characteristic columnar morphology of tin oxide crystals (see Fig. 1).

For preparation of the composite film P(S-b-EO) (Polymer Source Inc.) with number molecular weight M_n(PS)= 19000 g/mol and M_n(PEO)= 6400 g/mol and a small molecular weight distribution D= 1.05 was used. The sample solution used for spin coating the PS-b-PEO-titania composite film was prepared out of 4.0 g 1,4-dioxane, 0.0636 g HCl and 0.0462 g titanium tetraisopropoxide (TTIP) all added together to 40.5 mg P(S-b-EO) on a balance, immediately. After complete addition the common solution was stirred for about 1 hour. After spin coating (relative humidity 30 %, temperature 22^o C, 0.3 ml solution, 2000 rpm, 60 s) the P(S-b-EO)-titania nanocomposite film results on top of the FTO gradient. The TiO_2 nanostructures have a nanowire-like shape due to the chosen conditions [10].

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 μm^2) [11]. 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 α_i= 0.72^o. 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. 2 shows the corresponding two dimensional (2d) GISAXS patterns. 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 [11] are displayed in Fig. 3. To emphasize on the structure of the FTO layer the cuts were performed at the critical angle of FTO (Fig. 3a) and in addition to probe the structure of the nanocomposite film cuts were performed at the critical angle of PS (Fig. 3b). 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 neighbor distance. In the fit the experimentally determined resolution function was taken into account [12]. Major result is the characteristic lateral length ξ for both layers.

In Fig. 4 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

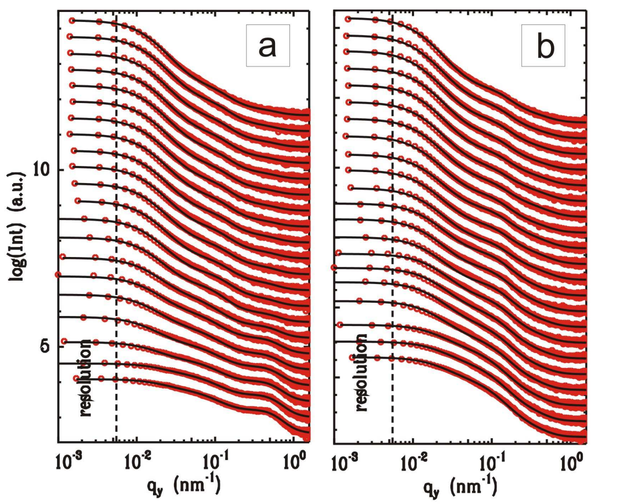

Figure 3 Line cuts from the 2d GISAXS intensity at the critical angle of a) FTO and b) PS. The curves are shifted along the y-axis for clarity (bottom - FTO and top - glass part of gradient). The solid lines are fits to the data. The dashed lines indicate the resolution limit.

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_{FTO}/I_o. As visible in Fig. 4 in the beginning the gradient is quite steep due to the applied etching. Again the vanishing of this intensity marks the end of the part covered with FTO. FE-SEM 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.

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The nanowire-shaped TiO_2 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. 4). 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 [10] 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.

In summary, the applied combinatorial approach allows for an investigation of one gradient sample which represents a full set of samples (given by the number of scanned positions along the gradient). The FTO-thickness gradient replaces many individual samples with different FTO layer thickness. Because prepared during one single preparation step, the combinatorial approach enables to overcome all problems related to sensitivity on many coupled parameters in complicated sample preparations such as the sol-gel process. Thus the FTO layer thickness modifies by itself the distance between adjacent nanowires, which are present inside the P(S-b-EO)-titania nanocomposite film. Because the preparation of the P(S-b-EO)-titania nanocomposite film on top of FTO typically marks the first step in the build-up of a PV device, our results emphasize the importance of identical conditions regarding the FTO layer. Moreover, it demonstrates that the FTO layer thickness can be used to tailor the structural parameters of the nanocomposite film. In addition, the presented combinatorial approach based on gradients, is a powerful tool in structure optimization. Instead of a full bunch of individual samples, desired conditions to obtain structures of a well defined size can be worked out within one simple experiment. However, due to the necessity of having access to GISAXS with a moderate micro-focused X-ray beam, this approach is limited to large scale facility research.

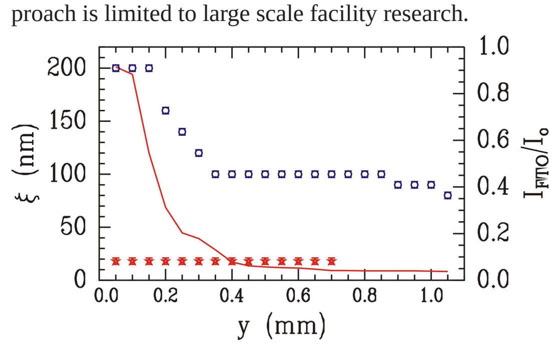

Figure 4 Detected characteristic lateral length ξ of the FTO layer (solid symbols) and of the nanocomposite film (open symbols) plotted as a function of the position in gradient direction y. For comparison the relative change in the FTO signal I_{FTO}/I_o (solid line) is superimposed to show the gradient position.