Detecting the Penetrationdepth of Organic Semiconductors into Mesoporous Titaniumdioxid Films in Solar Cells by EDX

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Dye-sensitized solar cells (DSSC) seem to be a good and low-cost alternative to conventional silicon solar cells. In these devices nanostructured titaniumdioxid films are coated with a monolayer of a light-absorbing dye. The pores in the titaniumdioxid films are filled with a liquid redox electrolyte for the transport of the positive charges and regeneration of the dye. However, these electrolytes are corrosive and may easily leak out of such devices.

Replacing the liquid electrolyte by solid state organic hole conducting materials (OHC) leads to poorer efficiencies of the cells [1,2]. Some ongoing research work has pointed out pore-filling as critical parameter in such solid state dye sensitized solar cells [3,4]. Measuring the penetration of the organic semiconductor into the porous titaniumdioxid films is possible with energy dispersive x-ray spectroscopy (EDX).

In this study, the layer stack of the device is prepared on silicon-silicondioxid-substrates in order to facilitate the electron microscopy studies (Figure 1; for preparation details of solar cells see [4]). Preparation of the cross sections is done by cracking the samples and polishing them with a broad Ar-ion beam along the edge of a masking plate [5,6]. This technique is especially suitable for polishing material mixes of very different hardness. Another advantage is that the cross section preparation with Ar-ions does not cause any implantation of the beam ions into the polished material in contrast to focused ion beam sputtering (FIB). Additionally, Ar-ions cause less amorphisation in the polished area than the Ga-ions in FIB.

The cross sections in this work have been prepared in an external apparatus and then been transfered into an field emission scanning electron microscope (FE-SEM) equipped with an EDX-detector. The resulting cross sections are found to be flat and smooth (Figure 1). This is a prerequisite for the EDX analysis because protruding edges of different layers would result in artificial x-ray signals.

The EDX measurements are carried out as line scans perpendicular to the layer stack of the device (Figure 1). The acceleration voltage is decreased down to 5 kV in order to yield higher resolved line scans. EDX measurements with such low voltages can only be performed for light elements like carbon, oxygen and silicon. However, the investigated layers can be easily distinguished by correlating the amount of this light elements with the SEM images of the cross sections (Figure 1).

The line scans nicely show the different layers and the penetration of the organic material into the titaniumdioxid film (Figure 2). The resolution of the line scans is in the range of 50 to 100 nm. It is also shown that the initial carbon signal in the pure OHC layer drops down sharply at the OHC-TiO_2 interface. Then it decreases almost linearly with the decreasing amount of OHC in the TiO_2 layer. The intensity drops down to zero at the TiO_2-SiO_2 frontier. However, quantification is quite difficult due to the low acceleration voltage and the poor x-ray signals.

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In conclusion Ar-ion cross section polishing is a very appropriate tool for the preparation of cross sections of multi layer systems with very different hardnesses. The EDX-analysis of so produced smooth and flat cross sections allows the investigation of the pore filling of organic semiconductors into the nanoporous TiO_2 layer in model systems for dye sensitized solar cells.

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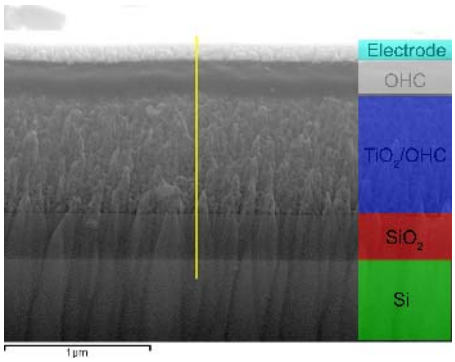

Figure 1. Ar-ion polished cross section of a measured layer stack. The different layers are labeled in the coloured sketch at the right. The yellow line in the middle indicates the position of the line scan.

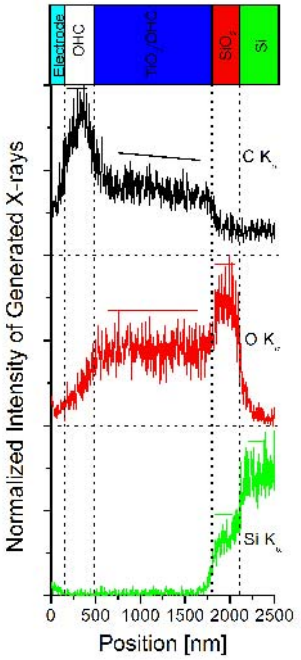

Figure 2. Example of typical line scan data. Different layers are labeled in the coloured sketch above. All layers can be recognized in x-ray signals of the light elements carbon (black), oxygen (red) and silicon (green).

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