doi:10.1017/S1431927617003397

Microsc. Microanal. 23 (Suppl 1), 2017

Characterization of Porous, TiO_2 Nanoparticle Films Using On-Axis TKD in SEM – a New Nano-Analysis Tool for a Large-Scale Application

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Dye sensitized solar cells (DSSCs) attracted great attention as a low-cost alternative to fossil energy, but also to other photovoltaic energy conversion systems. The core of a DSSC mostly consists of a porous micrometer thick film such as titanium dioxide mostly in form of nanoparticles (NP) as electron carrier, easily screen-printed at industrial scale (Figure 1a and 1b). The performance of the cell is amongst others linked to the morphology and formation of the NPs within the layer [1]. Characterization of the NP network is a challenging task, since common techniques mainly work with isolated or dispersed particles rather than particle layers. The constituent NPs in our work are bipyramidal anatase crystals manufactured via a shape-controlled routine, of 50 nm mean length and 32 nm mean width measured by Transmission (Scanning) Electron Microscopy (T(S)EM) and, respectively, 67 nm by 44 nm as measured with atomic force microscopy (AFM) (dimensions are expressed as Feret max and Feret min, respectively [2]).

The particulate layers were characterized using the new technique Transmission Kikuchi Diffraction (TKD) in a SEM [3]. In principle TKD works similar to the established Electron Backscatter Diffraction (EBSD) technique, which is a powerful method to identify grains/crystals via indexing Kikuchi pattern and determine their crystal orientation. However, on-axis TKD can reach a considerably better spatial resolution down to 2 nm and is, consequently, a technique well-suited for the investigation of nano-crystalline material including characterization of size and shape of NPs. This spatial improvement is gained by preparation of electron-transparent foils from the respective material leading to reduced background intensity, enhanced Kikuchi contrast and reduced beam broadening in comparison to conventional EBSD [4].

Thus, TKD samples were prepared as thin as possible using conventional Focused Ion Beam technique (FIB) avoiding excessive amorphisation or Gallium ion implantation into the sample surface by thinning down with falling acceleration voltage beginning with 30 kV and finishing with 2 kV. To remove the very rest of amorphous skin and possible contamination from electron beam scanning, the FIB lamella was showered with low-kV Argon ions using the Fischione 1040 NanoMill® at Fischione instruments facility (Export, PA, USA). The on-axis TKD measurements were performed with the Bruker *e*-Flash^{FS} retrofitted with the OPTIMUS® detector head (Bruker Nano GmbH, Berlin).

Figure 1d shows a raw inverse pole figure map presenting the crystal orientation of a TiO_2 NP layer obtained by on-axis TKD from which parameters like grain size and grain shape can be deduced. Some beam instabilities can be recognized in the acquired TKD orientation map caused by charging of the non-conductive, light and porous material. The drift areas were neglected (see black areas in Figure 1e) to avoid miscalculating the distributions of grain size in Figure 1f and aspect ratio in Figure 1g. For better statistics, incomplete grains at the frame edge as well as grains smaller than 4 pixels were excluded. The average grain size of 52 nm, that means the arithmetic mean of the equivalent circular diameters (ecd) of the as-before fitted ellipses, agrees well to the measured sizes by TEM/TSEM (ecd = 40±7 nm) and AFM (ecd = 52±3 nm) on the starting TiO_2 NP material. Likewise, the aspect ratio for the NPs of 0.62 from TKD is in good agreement with 0.64 for TSEM and 0.66 for AFM measurements. The latter techniques are challenging with respect to sample preparation and automatic analysis, since they require isolated particles on substrates, while TKD is suitable for both isolated particles and stacked particles (maximum 3 layers in transmission axis).

By rapidly scanning densely packed nanocrystals, a huge number of particles can be identified within just one measurement: for instance, the measurement in Figure 1d contains more than one millions of points and 2334 of grains/NPs identified and was acquired in 1h10min only. Moreover, non-beam sensitive samples remain available after TKD analysis, e.g. for further in-detail studies by TEM. In conclusion, on-axis TKD is a promising alternative for time-saving determination of NP parameters such as size and shape, with statistical relevance, and as they are assembled in the respective material [5].

References:

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[5] This work was supported by the SETNanoMetro Seventh Framework Programme project (project number 604577; call identifier FP7-NMP-2013_LARGE-7). Thanks to Pawel Nowakowski from E. A. Fischione Instruments, Inc. for careful polishing of our samples.

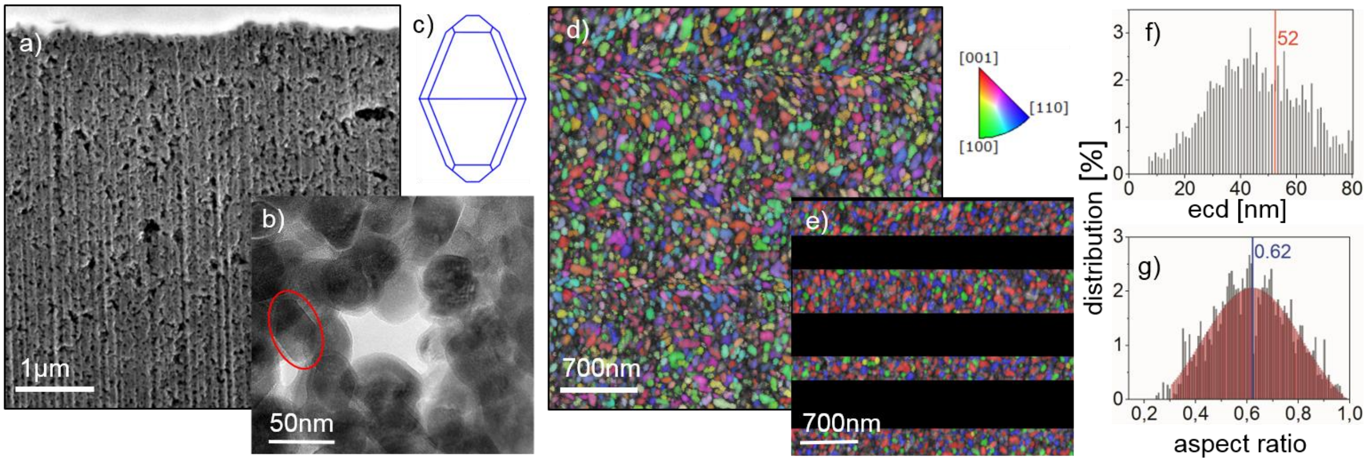

Figure 1. a) FIB cross-section of a screen printed TiO_2 nano-particulate layer; b) TEM image of FIB prepared thin lamella of same layer, red ellipse marks the side view onto a single particle as schematically shown in c), d) part of a grain raw orientation distribution map using Inverse Pole Figure coloring (IPF") along the X-axis by TKD, e) grain distribution map, here with drift areas disregarded for calculation of f) equivalent circular diameter (ecd) distribution, and g) aspect ratio distribution calculated from minor and major axes ratio of fitted ellipses.