Controlling the Spatial Direction of Hydrothermally Grown Rutile TiO_2 Nanocrystals by the Orientation of Seed Crystals

Julian Kalb,[1,*] James A. Dorman,[2] Stephan Siroky,[3] and Lukas Schmidt-Mende[1,*]

[1] Department of Physics, University of Konstanz, Universitätsstraße 10, 78457 Konstanz and Germany
[2] Cain Department of Chemical Engineering, 3307 Patrick Taylor Hall, Louisiana State University, Baton Rouge, LA 70803, United States
[3] Department of Chemistry, University of Konstanz, Universitätsstraße 10, 78457 Konstanz, Germany
* Corresponding author: Julian Kalb and Lukas Schmidt-Mende. Email: julian.kalb@uni-konstanz.de; lukas.schmidt-mende@uni-konstanz.de

Supporting Information

We provide additional information about the structure in different hydrothermally grown rutile TiO_2 nanostructures and further 1D defects.

Morphology of hydrothermally grown layers on rutile single crystals

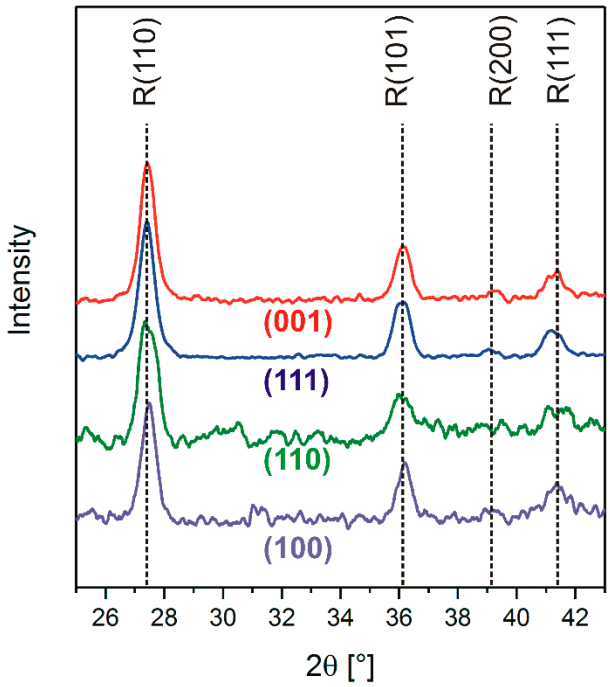

Figure 1: XRD pattern of the hydrothermally grown films on rutile (001), (111), (110), and (100) single crystals. To optimize the surface sensitivity an incident angle of 2° was used during the measurement. The diffraction pattern shows only peaks for rutile TiO_2 labelled with R(110), R(101), R(200), and R(111). Additionally, the existence of any other TiO_2 morphology is excluded. The diffraction patterns are normalized for the R(110) reflex.

Structure in rutile TiO_2 nanocrystals grown on {100} facets and other seed layers

We compare the structure observed in hydrothermally grown nanocrystalline films on macroscopic {001} facets with the structure in hydrothermally grown rutile TiO_2 nanorods on polycrystalline rutile FTO, polycrystalline sprayed anatase TiO_2, and polycrystalline sol-gel rutile TiO_2 films. The results are shown in Figure 2. The structure in all samples is very similar indicating that it originates rather from the growth conditions than from the seed properties. More important, the structure consists of tiny nanofingers that are always aligned in parallel with the growth direction.

[1] Hence, the growth direction on the macroscopic seeds that are investigated in this study can be determined from the alignment of these nanofingers.

To obtain polycrystalline anatase TiO_2 films spray pyrolysis was employed. Thereby, a solution with titanium diisopropoxide bis(acetylacetonate) ($C_{16}H_{32}O_6Ti$, 75 wt% in isopropanol, Sigma-Aldrich) and ethanol (C_2H_6O, 99.9% purity, VWR) with a ratio of 1:10 was sprayed on a polished silicon (100) wafer on a hotplate at 450 °C. This temperature was kept for 15 min, then decreased within 15 min to 120 °C, and kept for 24 h at 120 °C. The polycrystalline rutile TiO_2 films were made with a sol-gel method on the silicon wafers. The sol-gel was made from a mixture of 154 mg diethanolamine (DEA, $C_4H_{11}NO_2$, ≥98% purity, Sigma-Aldrich), 2 mL ethanol (C_2H_6O, 99.9% purity, VWR), and 510 µL titanium(IV) butoxide ($C_{16}H_{36}O_4Ti$, 97% purity, Sigma-Aldrich). Another 260 µL ethanol and 26 µL distilled water were added after stirring for 3 h. Afterwards, the solution was kept in the dark for 12 h. The sol-gel was spin coated at 2000 rpm for 60 s. Subsequently, the sample was kept on a hotplate at 120 °C for 24 h. The sprayed and sol-gel films were annealed in a rapid thermal processing (RTP) oven at 850 °C in oxygen (500 sccm) for 2 h employing a heating/cooling rate of ±1 °C/s. Commercial FTO on aluminoborosilicate glass (TCO10-10, Solaronix SA) was taken as an alternative seed layer.

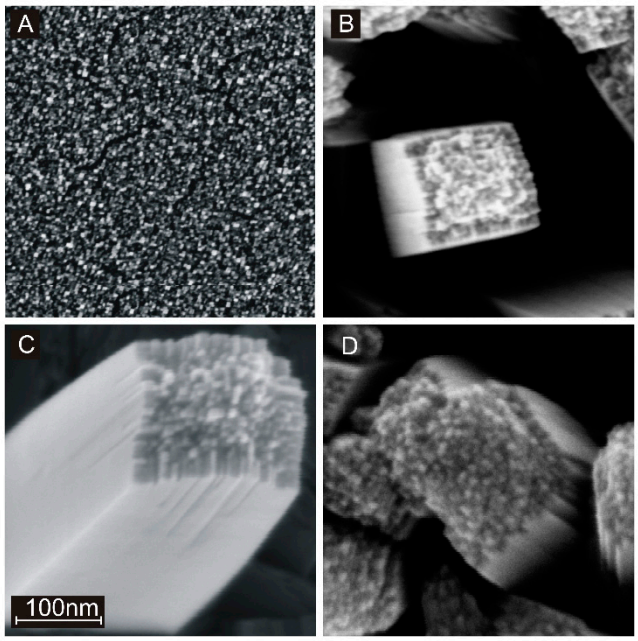

Figure 2: SEM image of rutile TiO_2 nanocrystals grown on a macroscopic {001} facet (A) (same structure as shown in Figure 1 in the main report), on polycrystalline rutile FTO film (B), on polycrystalline sprayed anatase TiO_2 film (C), and on polycrystalline sol-gel rutile TiO_2 film (D). Growth on the anatase film is most likely triggered by crystal defects or nanoparticles that support the hydrothermal growth of rutile TiO_2 nanorods. [2] The scale bar is the same for all panels.

Expanded 1D defects on {110} facets

Besides the well-aligned walls on {100} facets shown in Figure 2 of the main report, there are also more irregular and wider line defects as shown in Figure 3 below. These defects might originate from scratches caused by friction with dirt particles during substrate handling. Damaging the surface by scratching offers additional crystal facets and nanoparticles. However, these facets are disordered and thus, nanorods grow with randomly distributed angles. In order to confirm this mechanism, a seed facet was scratched manually with a scalpel achieving a similar growth activation.

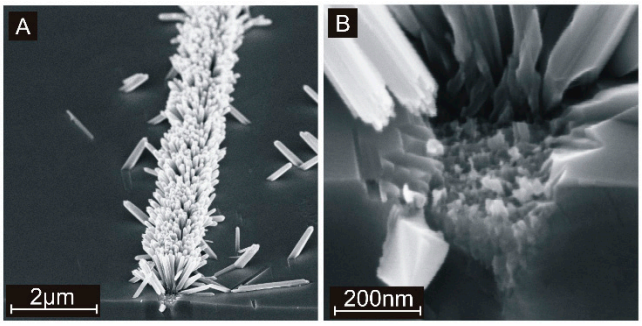

Figure 3: A) SEM cross-section image of an expanded defect on a {110} single-crystalline rutile TiO_2 substrate. B) Zoom of the cross-section in Panel A.

References

[1] A. Wisnet, S. B. Betzler, R. V. Zucker, J. A. Dorman, P. Wagatha, S. Matich, E. Okunishi, L. Schmidt-Mende and C. Scheu, "Model for Hydrothermal Growth of Rutile Wires and the Associated Development of Defect Structures," *Crystal Growth & Design*, vol. 14, pp. 4658–4663, 2014.

[2] D. Li, F. Soberanis, J. Fu, W. Hou, J. Wu and D. Kisailus, "Growth mechanism of highly branched titanium dioxide nanowires via oriented attachment," *Crystal Growth & Design*, vol. 13, pp. 422–428, 2013.