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ARTICLE TYPE

Fabrication of hierarchically structured titania thin films via combining nano imprint lithography with block copolymer assisted sol-gel templating

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Electronic Supplementary Information

Experimental

Titania Thin Film Preparation

Silicon wafers were used as substrates which were cleaned in an acid bath before use [1]. The sol-gel was prepared using the commercial diblock copolymer poly(styrene-block-ethylene oxide) (P(S-b-EO)) as obtained from the manufacturer (Polymer Source Inc., polydispersity 1.04, M(PS) = 16000 g mol^{-1}, M(PEO) = 5000 g mol^{-1}). To obtain the foam-like nanostructure a weight ratio of 1,4-dioxane, hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP) of 92:7.5:0.5 was chosen. This ratio yields an effective surface area of roughly 60 m²/g, as calculated from SEM and GISAXS measurements. First, the diblock copolymer was dissolved in 1,4-dioxane, which acts as a good solvent for both blocks. Next, HCl, as a selective solvent, and TTIP were added drop wise under constant stirring. After an aging time of one hour, the sol-gel solution was spin-coated (1600 rpm, 30 s; Delta 6 RC TT, Süss MicroTec) onto the cleaned silicon wafer. These films were then directly used for imprinting. The soft embossing was done with an Obducat NIL-2.5. The machine is equipped to provide temperatures up to 250 °C and pressures up to 70 bar. The sample is placed inside the imprinting machine with the silicon stamp placed on the titania/polymer sample. For airtight sealing several layers of aluminum foils were used to cover the sample and the stamp. After heating up the sample to 120 °C, an air pressure of 60 bar was applied for 30 minutes. The sample was allowed to cool down below 80 °C before removing the stamp. To remove the polymer matrix and to converting the titania into its anatase phase, the sample was put into a tube furnace after the imprinting step (400 °C, 4 hours, heating ramp 6.25 °C min^{-1}).

Stamp Fabrication

The stamp used for this work was made from a silicon wafer via optical lithography. For this, the silicon substrate is first cleaned with an acidic bath, and subsequently coated with a photoresist (S1805, Microposit, 3000 rpm, 30 s). Using a mask aligner (MJB 3, Karl Suss) with a custom made chromium mask, the resist is illuminated and afterwards developed (Microposit 351 Developer) [1]. A sulfur hexafluoride (SF6)/ octafluorocyclobutane (C_4F_8) plasma is applied to etch the silicon substrate (150 s, PlasmaLab 80Plus Oxford Instruments). After the lithography process, the stamp was cleaned in an acidic bath to completely remove the photoresist. Prior to the imprinting process, the stamp was coated with 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS, Alfa Aesar) which served as an anti-sticking layer.

Characterization

The scanning electron microscopy measurements were performed with a Zeiss Gemini NVision 40 field emission scanning electron microscope (5.0 kV, working distance 3.1 mm, aperture 10 µm). The images were analyzed with the software ImageJ v1.43u.

The optical microscopy images were taken with a Zeiss Axiolab A with a resolution of 610 nm and analyzed with the software ImageJ v1.43u.

The atomic force microscopy measurements were performed with an Autoprobe CP Research AFM instrument under ambient conditions. The obtained images were analyzed with the Gwyddion AFM software v2.20. To obtain height and lateral structure information, line cuts were taken perpendicular to the channel structure and averaged over 100 pixels.

The photoluminescence was studied with a fluorescence spectrometer (LS 55 fluorescence spectrometer, Perkin Elmer) using a xenon discharge lamp. The excitation wavelength was 350 nm and thus chosen below the bandgap of anatase TiO2 [2]. Additionally, a 350 nm cutoff filter was used to block the excitation source.

The X-ray diffraction measurements were carried out on a Siemens D500 XRD diffractometer equipped with a Cu cathode operated at 40 kV and 30 mA. The XRD patterns were obtained directly from the thin film. The reference peaks for anatase TiO2 were taken from The International Centre for Diffraction Data

(ICDD)

The grazing incidence small angle X-ray scattering experiments (GISAXS) were performed at the beamline BW4 at the Deutsches Elektronen Synchrotron, DESY in Hamburg, Germany (wavelength 0.138 nm, sample–detector distance 2.084 m, and incidence angle $\alpha_i = 0.35°$). A moderately micro-focused beam of 36 × 18 µm² (v × h) was used, resulting in a beam footprint on the sample surface of 3.0 mm in beam direction. The scattered signal was recorded with a MarCCD camera (2048 × 2048 pixels, pixel size 79.1 × 79.1 µm²). The specular reflected beam is shielded either with a spherical or rod like beam stop to protect the detector from beam damage. For a quantitative analysis of the lateral structures, line cuts along the q_y-direction were fitted in the framework of the distorted wave Born approximation [3]. Using the local monodisperse approximation, cylindrical form factors were placed on a 1-dimensional paracrystal.

Inner volume morphology of the nanostructured titania film

To investigate the morphology of the inner volume of the nanostructured titania films, firstly the cross section was investigated with SEM (figure S1(a)). For this, the sample was tilted to an angle of 60°. Therefore, not only the cross section but also part of the sample surface is visible on the SEM image. The black arrow acts as guide to the eye to clarify the vertical part of the film and thereby shows the film thickness. The nanoporous structure, which is observable from top view SEM image is existing throughout the film volume. To obtain more quantitative information about the nanoporous structure of the film, GISAXS measurements were performed with titania films with and without the embossing step to investigate the influence of the embossing procedure on the nanostructure. Figure S1(b) and (c) show the 2D-images which were obtained from the GISAXS experiment in a false color scale of the non-embossed and embossed film, respectively. For the case of the embossed film, an additional horizontal signal is arising around the position of the specular beam, which is highlighted by the grey dashed circular line. This feature originates from the intersection of the grid like superstructure with the Ewald sphere in reciprocal space when the channels are aligned parallel to the x-ray beam [4]. In order to get more quantitative analysis, horizontal line cuts along the q_y-direction were done at the critical angle of titania. The two resulting cuts are shown in figure S1(d), where the lower curve with the circular symbols correspond to the non-embossed film, and the upper curve with the square symbols corresponds to the titania film with applied embossing step. Both curves were fitted as described above to obtain insight about structural information. For the non-embossed film, a pronounced shoulder is visible which is attributed to nanopores inside the titania film with a diameter of 35 nm – denoted as Λ_1. The same structure is found again in the lateral cut of the embossed film, as indicated with the vertical arrow. Additionally, a strong signal at the lower q_y-region is visible in the embossed sample. This signal originates from the superstructure which was imposed on the film by the embossing procedure, reflecting the width of the elevated areas of the film with a size of 350 nm – denoted as Λ_2 – which is in good agreement with the observations from the AFM data (see figure 2(b)). It shall be noted here that the periodicity of 4 µm is not visible here in the GISAXS data as it lies above the resolution limit, which was set to emphasize on the nanostructure.

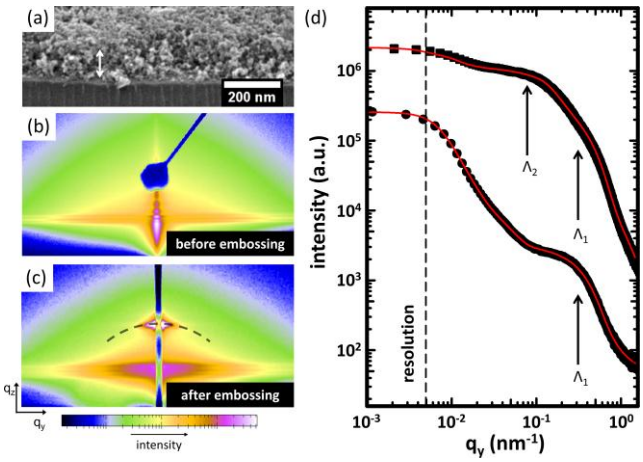

Fig. S1 (a) Cross section SEM image of a nanostructured titania film. The arrow indicates the film thickness. 2D-GISAXS data of a nanostructured titania film (b) without and (c) with the embossing step. The dashed line in (c) indicates the scattering signal originating from the intersection of the embossed channel structure with the Ewald sphere. (d) shows two lateral line cuts of the titania film without (lower curve, circles) and with (upper curve, squares) embossing step. The upper curve is shifted along the y-axis for clarity. The scattering contributions originating from the nanostructure and the superstructure are indicated via the arrows, labeled with Λ_1 and Λ_2.

Notes and references S

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