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Intrinsic properties of anodic TiO_2 nanotube layers: in-situ XRD annealing of TiO_2 nanotube layers

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Abstract

In this work, in-situ annealing of TiO_2 nanotube (TNT) layers in an XRD chamber was carried out to investigate the crystallization process of the TNT layers in details. TNT layers of different thicknesses, i.e. 1, 5 and 20 µm, and of different morphology, i.e. double wall vs. single wall, were annealed in the temperature range from room temperature to 500 °C with two distinctly different annealing rates. Additionally, three different annealing atmospheres were explored, namely air as an oxidative, N_2 as an inert, and $5\%H_2/95\%N_2$ as a reductive atmosphere. XRD patterns were measured every 15 °C of the heating ramp and the crystallite sizes of anatase phase were calculated from the anatase peak using Scherer equation at each data point. The differences in crystallization behavior for the different TNT layers as well as the effect of the annealing atmosphere for 5 µm thick TNT layers are described and discussed.

Keywords: TiO_2 nanotube layers, in-situ XRD, annealing, crystallization

1. Introduction

Since the first reports [1,2], anodic TiO_2 nanotube (TNT) layers have gained significant scientific as well as technological attention. An advantage of anodic TNT layers compared to e.g. hydrothermal TNTs is the direct fabrication on Ti substrates, resulting in a conductive back contact on the backside of the TNT layers. This results in a plethora of different applications of the TNT layers, e.g. in solar energy devices, photocatalysis, Li-ion batteries or sensors [3,4].

Anodic TNT layers can be produced in electrolytes of different chemical nature, i.e. aqueous acidic [5] and neutral [6,7], or organic electrolytes [8–11], all having the presence of fluoride ions in common, most typically in the form of NH_4F. While the etching rate of TiO_2 is relatively high in aqueous electrolytes, resulting in comparably short TNT layers, it is advantageously slowed down in electrolytes based on organic solvents. Thus, comparably thick TNT layers with thicknesses between ~1 µm and several hundreds of µm can be produced in organic electrolytes. The most commonly used organic solvents for the TNT layer production are glycerol and ethylene glycol [3,4].

TNT layers produced in electrolytes based on glycerol and ethylene glycol show two distinct different TNT morphologies: while single-wall (SW) TNTs are produced in glycerol-based electrolytes, a double-wall (DW) morphology can be observed in ethylene glycol-based electrolytes [12]. Detailed studies showed that the DW morphology consists of an outer wall made of almost pure TiO_2 while the inner wall is made of less pure TiO_2 containing fluoride and carbon species stemming from the electrolyte, i.e. from the decomposition of ethylene glycol in the high electric field [13–17]. The inner (contaminated) wall of the TNTs can be removed by selective etching procedures in piranha solution at elevated temperatures resulting in SW TNT layers consisting of almost pure TiO_2 [18–20]. Compared to their non-etched (as-prepared DW) counterparts, these SW TNT layers revealed superior performance for the use in dye sensitized solar cells (DSSC) [17,18] and photocatalysis [20–22], and showed higher conductivity [17,23], and increased photoelectrochemical performance [23,24].

The as-prepared amorphous TNT layers possess an intrinsically low conductivity [25]. Furthermore, they possess an unfavorable high amount of recombination centers which hinder efficient charge transport [26,27]. Thus, the TNT layers are usually annealed before further use for most applications. In the past years, many different annealing possibilities have been exploited, such as water [28–30], microwave [31,32] or laser annealing [33–35]. However, most commonly the annealing is carried out thermally in a muffle oven [36,37] or in a rapid thermal annealer [12] at temperatures between 400 °C and 500 °C for one to three hours. Thermal annealing of TNT layers at such temperatures results in the formation of anatase structure, which is the most favorable TiO_2 phase for (photo-)electrochemical and (photo-)catalytic applications as it reveals the highest electron mobility [38,39]. Rutile phase, which has a lower electron mobility, is usually formed at higher annealing temperatures [23,40,41].

Meanwhile, many studies report on the influence of the annealing temperature and atmosphere on the crystallinity and subsequent performance of TNT layers in various different applications [37,42–48]. Generally, in these studies it was found that lower annealing temperatures result in higher performances of the TNT layers due to a lower resistance of the layers, as no rutile phase was formed. However, the thermal annealing leads to the formation of a thermal oxide layer on the interface between the TNTs and the underlying Ti substrate, which increases the resistance of the TNT layers [41]. The thickness of this thermal oxide layer is increasing with higher annealing temperatures [23,41].

The first annealing study on short TNT layers prepared in HF based electrolyte was carried out by Varghese et al. in 2003 in oxygen and dry and humid argon atmosphere [40]. The authors annealed the TNT layers at 230 and 280 °C and in the range between 430 and 880 °C in 50 °C steps using a heating rate of 4 °C/min and a heating time of 3 h. They found that the crystallization of the TNT layers to anatase phase starts at 280 °C, independently of the annealing atmosphere. Anatase crystallite sizes increased for annealing temperatures up to 480 °C and decreased upon annealing at higher temperatures as rutile phase appeared. However, crystallite sizes for annealing temperatures between 280 and 430 °C were not evaluated and discussed [40]. Acevedo-Peña et al. [43] observed a crystallization of TNT layers produced in ethylene glycol-based electrolyte at a temperature of 325 °C after 0.5 h of soaking at this temperature (heating rate: 10 °C/min). Other studies on TNT layers and TiO_2 nanofibers [42,44,49] did not use any intermediate annealing temperatures between room temperature or 200 °C (a temperature at which the TNT layers do not crystallize yet) and 400 °C, at which an anatase peak can be seen. Except the study of Varghese et al. [40], also other studies [44,49] investigated the anatase crystallite sizes and found an increase with higher annealing temperature. However, it must be pointed out that in none of these studies (except in the discussed study of Varghese et al. [40]) anatase crystallite sizes at annealing temperatures lower than 400 °C were shown and that these are not in-situ annealing studies, as the current work. Moreover, the TNT layers and TiO_2 nanofibers were annealed at the final annealing temperature for at least 0.5 h.

An in-situ X-ray diffraction (XRD) investigation during the annealing process was first shown by Oh et al. [50] in a temperature range from 30 to 550 °C for ~15 µm thick TNT membranes (i.e. TNT layers separated from the underlying Ti substrate). The study showed that the amorphous to anatase transformation starts at ~327 °C for a heating rate of 0.25 °C/min, while higher heating rates shifted the anatase formation towards higher temperatures. No rutile phase formation was found upon annealing up to 550 °C. However, the fact that the in-situ XRD was carried out on TNT membranes might drastically change the resulting structure, compared to TNT layers on Ti substrates as no thermal oxide layer can be formed underneath the TNTs. This thermal oxide layer is of particular interest, as it is known for TNT layers on Ti substrates, that the rutile phase growth starts from it [40,41]. Furthermore, the TNT layers are in most applications used attached to the underlying Ti substrate, using the Ti substrate as electrical back contact.

Verissimo et al. [51] carried out in-situ XRD investigation of TNT layers with a thickness of ~200 nm on commercially pure (CP) Ti in comparison with TNT layers on Ti-Nb (~820 nm thick) and Ti-Nb-Sn (~970 nm thick) alloys and observed a temperature increase in the amorphous-to-anatase and anatase-to-rutile phase transformation for the alloys. Additionally, two publications report on the crystallization of TNTs by in-situ heating transmission electron microscopy (TEM) [52,53]. However, in these cases the annealing was carried out on single TNTs or TNT bundles at pressures $<10^{-5}$ Pa, which is far from conditions used usually (i.e. atmospheric pressure).

In this work, for the first time an extensive in-situ XRD study is presented showing the annealing of TNT layers of different thickness (1, 5, and 20 µm) on their Ti substrates in a temperature range from room temperature (RT) to 500 °C. Differences on the on-set crystallization temperature for anatase formation are shown for the different TNT layers using two distinctly different heating rates (2.1°C and 21 °C) and different annealing atmospheres (air, N_2 and H_2). This study will in future facilitate the choice of annealing conditions to receive the most favorable TNT layers for the different applications. Furthermore, it will make the annealing process more economically and environmentally friendly, as unnecessary high annealing temperatures and times can be avoided.

2. Experimental

TNT layers of a size of 1 cm^2 with different nanotube dimensions were employed in this study (see also **Table 1**). TNT layers with a thickness of ~1 µm and an inner diameter of ~80 nm were produced in glycerol-based electrolyte containing 50 vol% H_2O and 270 mM NH_4F at 20 V for

100 min [54]. TNT layers with a thickness of ~5 µm and an inner diameter of ~250 nm were produced in ethylene glycol-based electrolyte containing 10 vol% H_2O and 150 nm NH_4F at 100 V for 4 h [54,55]. TNT layers with a thickness of ~20 µm and an inner diameter of ~130 nm were produced in ethylene glycol-based electrolyte containing 1.5 vol% H_2O and 176 mM NH_4F at 60 V for 4 h [56]. More detailed descriptions of the TNT layer production and their morphologies can be found in the given references.

5 µm thick SW TNT layers were produced by etching in piranha solution [24]. Firstly, the as-prepared TNT layers were pre-annealed at 135 °C for 1 h in air using a heating rate of 15 °C/min. Afterwards, they were etched in hot (70 °C) piranha solution (3:1, H_2SO_4: H_2O_2) for 12 min, rinsed with water and soaked in isopropanol for 24 h. Afterwards the SW TNT layers were dried at room temperature.

Scanning electron microscopy was carried out using a field-emission scanning electron microscope (FE-SEM JEOL JSM7500F). Dimensions of the TNTs were measured using proprietary Nanomeasure software on at least five SEM images for each dimension.

X-ray diffraction was measured at 3kW diffractometer Smartlab from Rigaku. The diffractometer was set up in Bragg-Brentano geometry using Cu Kα radiation (λ = 1.54 Å) equipped by 1D-detector Dtex-Ultra. The Cu lamp operated at current 30 mA and voltage 40 kV.

For in-situ measurements, the heating chamber HTK 16N from Anton Paar was used. The TNT layers were placed inside the chamber on a heated platinum strip. The annealing experiment itself consisted of multiple heating steps with 15 °C increments, achieved with heating rates of 2.1 and 21 °C/min, accompanied by measuring of the X-Ray pattern at each step temperature. When 500

°C was reached, the XRD pattern was measured, then the temperature was hold for one hour and the XRD pattern was measured again.

For measurements in hydrogen (Hydrostar H5N (95%N, 5%H), SIAD) and nitrogen (Linde, purity 99.99999%) atmosphere the chamber was evacuated first and then the required gas was introduced. During the annealing experiment a continuous gas flow through the chamber was ensured.

The crystallite sizes were calculated from the measured diffraction patterns using software HighScore Plus.

3. Results and Discussion

TNT layers with three different thicknesses, 1 μm, 5 μm, and 20 μm, were employed in this study as shown in **Figure 1**. Exact dimensions of the TNT layers are given in **Table 1**. As one can see, all TNT layers consist of well-defined TNTs. Except the TNT diameter and TNT layer thickness, also the wall thickness is varying for the different TNT layers, with the thinnest walls of ~8 nm observed for the 1 μm thick TNT layers and the thickest walls of ~24 nm for the 5 μm thick TNT layers on the top of the layers. Obviously, the wall thicknesses at the bottoms of the TNT layers are in all cases thicker than at the top the TNT layers (**Table 1**). This phenomenon can be explained by an etching effect of the fluoride ions in the electrolyte solution during anodization which is very strong at the nanotube tops resulting in a V-shape of the nanotubes. The third and fourth columns of **Figure 1** show the nanotube bottoms in a direct and in a cross-section view after annealing of the nanotube layers. A thin thermal oxide layer formed during annealing underneath the TNT layers can clearly be seen.

Additionally, it must be noted that the TNT layers prepared in ethylene glycol-based electrolytes (herein the 5 µm and 20 µm thick TNT layers) reveal a double-wall (DW) morphology, as can be seen for the 5 µm thick TNT layer in **Figure 1H**. This stems from the decomposition of ethylene glycol under the high electrical field [12–14,24]. The inner wall is not visible on the top-view SEM images of the TNT layers, but only in the deeper parts as the fluoride anions in the anodization electrolytes etch the inner wall on the top of the TNT layers. Due to the DW morphology the ratio between the wall thickness on the bottom and the top of the TNT layers is higher for the 5 µm and 20 µm thick TNT layers than for the 1 µm thick TNT layer which reveals a single-wall (SW) morphology.

Figure 2 shows the in-situ XRD patterns for the TNT layers of different thicknesses annealed in air with heating rates of 2.1 and 21 °C/min up to 500 °C. The XRD patterns were recorded between $2\theta = 23°$ and $2\theta = 30°$, as in this range the (101) diffraction peak for TiO_2 anatase phase ($2\theta = 25.3°$, ICSD: 154603, [57]) and the (110) diffraction peak for TiO_2 rutile phase ($2\theta = 27.4°$, ICSD: 168138, [58]) appear. XRD pattern measurements in longer 2θ ranges were avoided to decrease the measurement time and not to disturb the heating of the XRD chamber and consequently the annealing of the TNT layers. The heating rate of 2.1 °C/min was chosen as typical heating rate during annealing (i.e. heating from room temperature (20 °C) to 400 °C within 3 hours), and 21 °C/min as the 10 times faster heating rate.

As one can see in **Figure 2**, in case of the 1 µm thick TNT layers the appearance of the anatase diffraction peak (further denoted as on-set crystallization temperature) was firstly noticed at temperatures of ~315 °C and ~330 °C, while for the 20 μm thick TNT layers, the anatase diffraction peak appeared at temperatures of ~315 °C and ~345 °C for heating rates of 2.1 °C/min and 21 °C/min, respectively. In case of the 5 μm thick TNT layers, the anatase diffraction peak was only visible at higher temperatures of ~360 °C and ~375 °C for heating rates of 2.1 °C/min and 21 °C/min, respectively. Diffraction peaks of rutile phase are not visible for any of the TNT layers, however, the nominal position of rutile dominant (110) diffraction peak is indicated in the patterns to clearly demonstrate that there is no rutile present. The higher on-set crystallization temperature compared to Varghese et al. [40], who observed an on-set crystallization temperature of 280 °C, can be explained by the fact that they kept the TNT layers for 3 h at the temperature of 280 °C and thus gave the TNT layers longer time to crystallize. Herein, however, the temperature was increased continuously from room temperature to the final temperature of 500 °C, where it was kept only for 1 h.

Interestingly, for the 5 μm thick TNT layers, higher temperatures were needed to start the crystallization of the amorphous layers compared to the 1 μm and 20 μm thick TNT layers. Thus, there is no clear trend of the on-set crystallization temperature on the TNT layer thickness. No direct literature on this topic can be found as this is the first study dealing with in-situ annealing of TNT layers with different thickness. However, a recent study on the crystallization of very thin sputtered TiO_2 films revealed that TiO_2 films in the range between 64 nm and 200 nm have similar crystallization temperatures between 250 and 300 °C [59]. Therefore, it is expected that the enhanced on-set crystallization temperature of the 5 μm thick layer is related to other causes than the TNT layer thickness, as e.g. the TNT wall thickness or impurities within the inner TNT walls, as discussed below in more details.

The temperature needed for the amorphous-to-anatase transformation was for all TNT layers dependent on the heating ramp and increased for higher ramps. This can be explained by a shorter annealing time in case of a heating ramp of 21 °C/min compared to a heating ramp of 2.1 °C/min. As a result of the shorter annealing time, the transformation took place at higher temperatures [50]. Additionally, for all TNT layers, independently of the heating ramp, a small shift in the position of the anatase peak towards smaller 2θ was observed, which was approximately equal for all TNT layers of different thickness (~0.15-0.2 degree) and is probably due to a deformation of the heating strip caused by the thermal expansion during heating.

Average anatase crystallite sizes were calculated from the measured anatase peak for all TNT layers annealed in air at all temperatures using Scherer equation. The results are given in **Table 2**. It must be noted here that the crystallite sizes are giving average sizes and that the crystallites in the TNT walls have partly a round and partly an elongated shape. **Figure 3** shows the TEM image of a DW 5 µm thick TNT annealed at 400 °C for 1 h (typically used annealing conditions in many publications) for visualization of the crystallite shape. This image provides a clear proof of mixed crystal shapes. Similar as observed in the literature, the anatase crystallite size overall slightly increased with the annealing temperature [37,40,41,44]. An initial decrease of the crystallite size was observed for most TNT layers, which was not observed in earlier literature on TNT layer annealing, due to a lack of crystallite size calculations at temperatures between 280 and 400 °C [40,44]. However, it might be explained by a release of stress formed during anodization. TiO_2 has a larger volume than Ti, thus during anodization a volume expansion was observed [60,61]. This results in internal tensile stress within the TiO_2 due to a lack of space. Portion of the internal tensile stress is released by the formation of TNTs instead of a compact layer. Residual tensile stress might be released during crystallization of the TNT layers, which results in a decrease of the crystallite size. After the stress is released a re-crystallization process takes place and the crystallites start to grow in size. After soaking the TNT layers for 1 h at 500 °C, the crystallite size further increased. A reason for this can be the healing of defects, i.e. oxygen vacancies, in the anatase structure by annealing at higher temperatures [62]. The 5 µm thick TNT layer annealed with a heating rate of 21 °C/min is an exception, and the crystallite size decreased during the whole crystallization time (i.e. heating and soaking for 1 h at 500 °C). The exact reason for this unexpected behavior is unknown, however, it could be explained with the relatively fast heating rate, which does not give enough time to the TNT layers to release all stress and re-crystallize.

It is known that the crystallization of anodic oxide layers is slower in the presence of impurities [63–65]. The anodic TNT layers contain some impurities stemming from the electrolyte, namely some fluorides originating from the NH_4F in the electrolytes and some carbon compounds (hydrocarbons, carbides) originating from the ethylene glycol or glycerol, which decompose in high electrical fields [13,14]. These impurities can be especially found in the inner wall of the double walled TNTs produced in ethylene glycol-based electrolytes, while the outer wall consists of almost pure TiO_2 [13,14]. The 1 µm thick TNT layers used in this study were produced in glycerol-based electrolyte at a relatively low potential of 20 V and do not show any double wall morphology, as the glycerol does not decompose at such low electrical fields. However, both, the 5 µm thick TNT layers as well as the 20 µm thick TNT layers, show a double wall morphology. Detailed investigations of the annealed DW TNT layers at their bottoms and inner wall thickness measurements on several samples and SEM images revealed a somewhat thicker inner wall for the 5 µm thick layers, i.e. 47.1 ± 14.5 nm, compared to the inner wall of the 20 µm thick DW TNT layers, i.e. 37.7 ± 6.9 nm. This gives confidence that the 5 µm thick DW TNT layers contain some higher amounts of impurities compared to the 20 µm thick DW TNT layer, resulting in a slightly increased crystallization temperature.

To verify if the impurities within the inner wall of the 5 µm thick DW TNT layers led to the higher on-set crystallization temperature, the as prepared DW TNT layers were etched to SW TNT layers. **Figure 4** shows SEM images of the DW and SW TNT layers depicted on the nanotube bottoms after annealing at 500 °C, while **Figure 5** shows a scheme of amorphous and annealed DW and SW TNTs. As one can see, for the SW TNT layer the inner wall was completely removed during the etching step, leaving just the outer wall consisting of almost pure TiO_2. The corresponding in-situ XRD patterns of the 5 µm thick SW TNT layers are shown in **Figure 6**. Indeed, for a heating rate of 2.1 °C/min the on-set crystallization temperature was decreased to ~330 °C, which is still higher than the on-set crystallization temperature for 1 µm and 20 µm thick TNT layers at the same heating rate. For a heating rate of 21 °C, however, the on-set crystallization temperature was similar to the DW TNT layer, i.e. ~375 °C. Thus, it seems that the impurities within the inner wall of the DW TNT layers increase the on-set crystallization temperature, but this is not the only reason for the increased on-set crystallization temperature. Another possible reason for the higher on-set crystallization temperature of the 5 µm thick TNT layers compared to the other TNT layers could be the overall increased wall thickness of the 5 µm thick TNT layers (i.e., ~103 nm vs. ~58 nm for the 5 µm and 20 µm DW TNT layers and ~55 nm and ~20 nm for the 5 µm and 20 µm SW TNT layers). A detailed investigation of this phenomenon should be content of a future study.

Similarly, as for the DW TNT layers, the average crystallite sizes for the SW TNT layers (**Table 3**) initially decreased and then increased with annealing temperature, which might be explained with a re-crystallization process during annealing. Overall, the average crystallite sizes of the SW

TNT layers are slightly bigger than in case of the DW TNT layers. Reasons for this could be manifold. In case of the DW TNT layers a small gap can be found between the inner and outer wall in which smaller grains could be formed during the annealing process. The growth of this crystallites is limited by the available space. Additionally, the inner wall has a different chemical composition than the outer wall as it contains impurities of carbon and fluoride species and is probably more defective than the outer wall which is composed of almost pure TiO_2 [13–17]. Thus, average crystallite sizes of the DW TNT layers reveal crystallites of the inner and outer wall, while the average crystallite sizes of the SW TNT layers take just the high purity outer TiO_2 wall into account (see also the scheme in **Figure 5** for better visualization). Furthermore, the removal of the inner wall leads to a larger diameter (more space) within the TNTs. These factors could lead to different average crystallite sizes for the DW TNT layers compared to the SW TNT layers.

It is also noteworthy that in contrary to the DW TNT layer, the average crystallite sizes of the SW TNT layer annealed using a heating rate of 21 °C/min followed the trend of an initial average crystallite decrease before the average crystallite sizes increase. This could be explained with the impurities within the thick inner walls of the 5 μm thick DW TNT layers which possibly needed longer time for the stress release compared to the outer walls, consisting of relatively pure TiO_2.

For comparison, 5 μm thick DW TNT layers were annealed in N_2 atmosphere, i.e. an inert atmosphere, and in $5\%H_2/95\%N_2$ atmosphere, i.e. a reductive atmosphere. The results are depicted in **Figure 7**. As one can see, the on-set crystallization temperature was slightly increased in both atmospheres, to ~360 °C and ~375 °C for a heating rate of 2.1 °C/min and to ~375 °C and ~390 °C for a heating rate of 21 °C/min in N_2 and H_2/N_2 atmosphere, respectively. This phenomenon of increased crystallization temperature in oxygen-free atmosphere was already observed for mesoporous TiO_2 nanoparticles annealed in N_2/H_2 and N_2 atmospheres [66] as well as for TiO_2 nanofibres annealed in Ar atmosphere [67] and was attributed to the lack of oxygen in the annealing atmosphere [67]. This is in contrast to the anatase-to-rutile transformation which appears at lower temperatures during annealing in oxygen-free atmospheres compared to annealing in air [66–68].

The average crystallite sizes were approximately constant (~ ±2 nm) during annealing at all temperatures for both heating rates in both annealing atmospheres, as shown in **Table 4**. Also, after soaking the TNT layers for 1 h at 500 °C the crystallite size did not increase any more significantly, with exception of the 5 μm thick TNT layer annealed in N_2 atmosphere with a heating rate of 21 °C/min. A rather minimal increase of the crystallite size with annealing temperature in the same two atmospheres was also observed by Robben et al. [66] for mesoporous TiO_2, but a particular reason for this phenomenon was not discussed.

4. Conclusions

In summary, the crystallization behavior of TNT layers with different thicknesses were investigated using in-situ XRD. The results show that upon annealing in air, 1 μm and 20 μm thick TNT layers started crystallizing at similar temperatures, while for 5 μm thick TNT layers an ~30 °C higher temperature was needed to see the first presence of the diffraction peak of anatase. After etching of the 5 μm thick DW TNT layers to SW TNT layers, the on-set crystallization temperature was decreased for a low heating rate of 2.1 °C/min, however, did not change for a high heating rate of 21 °C/min. Thus, the on-set crystallization temperature for the different TNT layers does not show a clear trend on the TNT layer thickness, but seems to be dependent on the concentration of impurities within the TNT layers and on the nanotube wall thickness. The anatase crystallite sizes overall increased with the annealing temperature due to the healing of defects within the crystalline structure at higher temperatures. Upon annealing in N_2 or H_2/N_2 atmosphere the on-set crystallization temperatures were slightly increased compared to annealing in air atmosphere. In contrast, the anatase crystallite sizes were approximately constant during annealing at all temperatures in these inert atmospheres.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper**.**

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Figure captions

Figure 1. SEM top views (A,E,I), cross-section (B,F,J), nanotube bottom views (C,G,K) and nanotube bottoms in cross-section view (D,H,L) of the 1 µm (A,B,C,D), 5 µm (E,F,G,K), and 20 µm (I,J,K,L) thick TNT layers. The nanotube bottom views and nanotube bottoms in cross-section view were taken after annealing at 500 °C to make the thermal oxide layer visible. All scale bars show 100 nm.

Figure 2. In-situ XRD patterns of 1 µm, 5 µm and 20 µm thick DW TNT layers recorded during annealing in air with heating rates of 2.1 and 21 °C/min. The XRD patterns were captured in 15 °C steps from 30 °C to 500 °C and after 1 hour soaking at 500 °C. The temperatures given in the graphs give the annealing temperature when the anatase peak was visible. A – anatase, R – rutile.

Figure 3. TEM image of a DW 5 µm thick TNT annealed at 400 °C for 1 hour with a heating rate of 2.1 °C/min.

Figure 4. SEM images of the 5 µm thick DW (A) and SW (B) TNT layers depicted on the nanotube bottoms.

Figure 5. Scheme of amorphous (A) and crystalline (B) DW (left) and SW (right) TNTs. The inner wall of the DW structure contains impurities of C and F species.

Figure 6. In-situ XRD patterns of 5 µm thick SW TNT layers recorded during annealing in air with heating rates of 2.1 and 21 °C/min. The XRD patterns were captured in 15 °C steps from 30 °C to 500 °C and after 1 hour soaking at 500 °C. The temperatures given in the graphs give the annealing temperature when the anatase diffraction peak was visible. A – anatase.

Figure 7. In-situ XRD patterns of 5 µm thick DW TNT layers recorded during annealing in N_2 and H_2 atmosphere with heating rates of 2.1 and 21 °C/min. The XRD patterns were captured in 15 °C steps from 30 °C to 500 °C. The temperatures given in the graphs give the annealing temperature when the anatase diffraction peak was visible. A – anatase.

Tables

Table 1. TNT layer thickness, nanotube diameter and wall thicknesses of the TNT layers used.

Name	Layer thickness / µm	TNT diameter top / nm	Wall thickness on top / nm	Wall thickness on bottom / nm
1 µm	1.3 ± 0.1	80.4 ± 12.1	7.8 ±1.8	22.2 ± 5.0
5 µm DW	6.1 ± 0.4	229.2 ± 25.5	23.5 ± 7.4	103.1 ± 20.4
20 µm DW	19.9 ± 1.1	133.3± 12.6	12.2 ± 4.3	57.8 ± 7.4

Table 2. Average anatase crystallite sizes of the TNT layers annealed in air.

Temperature / °C	Average crystallite size / Å					
	1 µm, 2.1 °C/min	1 µm, 21 °C/min	5 µm, 2.1 °C/min	5 µm, 21 °C/min	20 µm, 2.1 °C/min	20 µm, 21 °C/min
315	386	-	-	-	780	-
330	468	422	-	-	712	-
345	450	452	-	-	656	795
360	440	431	433	-	611	655
375	450	426	445	436	598	635
390	445	426	440	479	553	616
405	457	431	431	447	537	581
420	457	433	429	436	545	542
435	466	440	426	424	545	521
450	470	442	436	409	553	528
465	476	452	436	405	553	532
480	484	460	436	401	553	539
495	499	479	438	394	569	535
500*	542	518	468	333	598	569

* after 1 h soaking at 500 °C

Table 3. Average anatase crystallite sizes of the 5 μm thick SW TNT layers annealed in air.

Temperature / °C	Average crystallite size / Å	
	2.1 °C/min	21 °C/min
345	645	-
360	584	-
375	545	355
390	541	527
405	511	511
420	475	492
435	481	432
450	486	410
465	486	414
480	483	430
495	492	425
500*	478	444

* after 1 h soaking at 500 °C

Table 4. Average anatase crystallite sizes of the 5 μm thick DW TNT layers annealed in N_2 and H_2 atmosphere.

Temperature / °C	Average crystallite size / Å			
	N_2 atmosphere		H_2/N_2 atmosphere	
	2.1 °C/min	21 °C/min	2.1 °C/min	21 °C/min
360	359	-	-	-
375	450	454	459	-
390	455	451	461	321
405	452	451	439	481
420	447	456	449	444
435	455	454	444	423
450	455	459	444	421
465	460	454	444	412
480	460	456	441	421
495	471	461	454	412
500*	482	504	451	414

* after 1 h soaking at 500 °C