The Influence of Post-Growth Heat Treatments and Etching on the Nanostructure and Properties of Rutile TiO$_2$ Nanowires

Von der Fakultät für Georessourcen und Materialtechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation vorgelegt von M.Sc.

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Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar
Nur wenige wissen,
wie viel man wissen muss,
   um zu wissen,
wie wenig man weiß.

Werner Heisenberg
Abstract

Titanium(IV) oxide is one of the most promising materials for environmental and energy applications. Although it is already in application nowadays, still fundamental questions concerning the relation between synthesis conditions, nanostructure, defects and properties remain to be solved. This knowledge is the key to develop new Titanium(IV) oxide materials with tailored properties.

This work approaches the problem by detailed investigation of hydrothermally grown rutile Titanium(IV) oxide nanowire arrays before, during and after certain post-growth treatments, namely heating and etching. The emphasis is set on the interplay between nanostructure and optical as well as electrical properties. Advanced transmission electron microscopy is used for a detailed characterization of the Titanium(IV) oxide nanowires and the properties are determined by ultra violet-visible spectroscopy and current-voltage measurements. For the post-growth heat treatment, mainly three heating conditions, which differ in temperature and environment, are conducted. Including the as-grown nanowires, which serve as a reference, four types of nanowires are investigated with respect to the influence of post-growth heat treatments: as-grown nanowires, nanowires annealed in air at 500 °C, nanowires annealed in nitrogen at 500 °C and nanowires after a heat treatment in vacuum at 1050 °C. In addition, post-growth etching of the nanowire arrays is used, in order to obtain a variety of new one-dimensional morphologies with high surface areas.

Due to the hydrothermal growth conditions, the as-grown nanowires are built by a nanofiber bundle and are full of defects, especially oxygen vacancies. Using a heat treatment at 500 °C in air leads to a transformation of the nanofiber bundle to a single-crystalline nanowire. In addition, this heat treatment is capable to condense oxygen vacancies in voids, which intersperse the nanowire. The void formation can be observed in situ by transmission electron microscopy and the resulting voids are encapsulated by a Ti$^{3+}$ rich material. As a result, the optical properties of nanowires after a heat treatment at 500 °C in oxygen improve as the band gap and defect related Urbach absorption are decreased. Furthermore, the removal of oxygen vacancies in the crystal structure converts the intrinsically n-type conducting nanowires to an insulator. Changing the heating environment to nitrogen does not affect the vacancy condensation. However, due to the slightly reducing atmosphere of nitrogen, the surface-near defects do not vanish and a core-shell nanowire, with a single-crystalline core that is full of voids and a Ti$^{3+}$ rich shell, results. Due to the core-shell structure, the properties are completely changed and the nanowire arrays appear black instead of white and posses a metal-like conductivity.
An increase of the annealing temperature to 1050 °C leads to void and defect free Titanium(IV) oxide nanowires. These nanowires show additional faceting at the tip, in order to compensate the free volume. The high temperature requires nanowire arrays grown on Silicon substrates and leads to diffusion of Silicon atoms. Consequently, this heat treatment results in the formation of a core-shell nanowire, but with an insulating, 4 nm thick Silicon(IV) oxide shell. Such a shell is promising for application as it suppresses undesired back-transfer of electrons. Thus, the last two heat treatments lead to nanowires with beneficially changed surfaces.

This work is concluded with some synthesis strategies to derive new morphologies for solvothermally grown nanowires, which possess even larger surface areas. Using a combination of solvothermal growth, etching and heat treatment, the synthesis of nanostructures ranging from highly fibrous nanowires, over nanowires with tiny channels to rectangular nanotubes, is enabled.
Zusammenfassung


Preface

This work was partially supported by the Deutsche Forschungsgemeinschaft (DFG). The financial support within the project "Identification and overcoming of loss mechanisms in nanostructured hybrid solar cells - pathways to more efficient devices" is gratefully acknowledged.

The following publications contribute to this thesis:

**Paper I**

**Role of Vacancy Condensation in the Formation of Voids in Rutile TiO$_2$ Nanowires**

Alena Folger, Petra Ebbinghaus, Andreas Erbe and Christina Scheu

*ACS Applied Materials & Interfaces* **2017**, *9*, 13471

**Paper II**

**Tuning the Electronic Conductivity in Hydrothermally Grown Rutile TiO$_2$ Nanowires: Effect of Heat Treatment in Different Environments**

Alena Folger, Julian Kalb, Lukas Schmidt-Mende and Christina Scheu

*Nanomaterials* **2017**, *7*, 289

**Paper III**

**Fabrication and Characterization of Abrupt TiO$_2$-SiO$_x$ Core-Shell Nanowires by a Simple Heat Treatment**

Alena Folger, Julian Kalb, Lukas Schmidt-Mende and Christina Scheu

*APL Materials* **2017**, *5*, 086101
**Paper I:** A. Folger did the synthesis and performed the measurements at the electron microscope and at the ultraviolet-visible spectrometer. P. Ebbinghaus measured the infrared spectra and B. Breitbach performed X-ray diffraction experiments. A. Folger analyzed the data and reconstructed the tomogram. All co-authors interpreted and discussed the data. A. Folger wrote the paper, which was edited and approved by all authors.

**Paper II:** A. Folger synthesized the material and did the electron microscopy and ultraviolet-visible measurements. J. Kalb performed the current-voltage measurements. A. Folger and J. Kalb analyzed the data of the respective experiments. Heating of the nanowire films in air and nitrogen was done by B. Breitbach. All co-authors interpreted and discussed the data. A. Folger wrote the paper with contributions from J. Kalb and all authors revised the manuscript and gave approval to the final version.

**Paper III:** J. Kalb synthesized the nanowire arrays on Silicon substrates and performed the heat treatment in vacuum. A. Folger performed (transmission) electron microscopy measurements and analyzed the data. All co-authors interpreted and discussed the data. A. Folger wrote the manuscript. All authors edited and approved the manuscript.
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## Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>0D</td>
<td>Zero-dimensional</td>
</tr>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>ABF</td>
<td>Annular bright field</td>
</tr>
<tr>
<td>ADF</td>
<td>Annular dark field</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>Back scattered electron</td>
</tr>
<tr>
<td>ButOH</td>
<td>Butanol</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline Silicon</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>DF</td>
<td>Dark field</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cell</td>
</tr>
<tr>
<td>ED</td>
<td>Electron diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>ELNES</td>
<td>Electron energy-loss near edge structure</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Water</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark field</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HR</td>
<td>High-resolution</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>IV</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>N$_2$</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>
NP  Nanoparticle
NW  Nanowire
O\textsubscript{vac}  Oxygen vacancy
PCTF  Phase contrast transfer function
PE  Primary electron
SAED  Selected area electron diffraction
SE  Secondary electron
SEM  Scanning electron microscopy
STEM  Scanning transmission electron microscopy
TEM  Transmission electron microscopy
Ti\textsubscript{int}  Titanium interstitial
TiO\textsubscript{2}  Titanium(IV) oxide
Ti(OBut)\textsubscript{4}  Titanium(IV) butoxide
Ti\textsubscript{vac}  Titanium vacancy
UV  Ultra violet
UV-vis  Ultra violet-visible
VB  Valence band
XRD  X-ray diffraction
ZLP  Zero-loss peak
List of symbols

\( \alpha_{\text{abs}} \)  
Absorption coefficient

\( \alpha_{\text{ext}} \)  
Extinction coefficient

\( \alpha \)  
Semi-convergence angle

\( A \)  
Amplitude

\( \beta \)  
Semi-collection angle

\( C_s \)  
Spherical aberration

\( \Delta_{SO} \)  
Spin-orbital splitting energy

\( \Delta f_{\text{Scherzer}} \)  
Scherzer defocus

\( \Delta f \)  
Defocus

\( d_{hkl} \)  
Lattice distance

\( E_{\text{X-ray}} \)  
Energy of the characteristic X-rays

\( E_g \)  
Band gap

\( E_U \)  
Urbach energy

\( F_{hkl} \)  
Structure factor

\( h\nu \)  
Photon energy

\( I \)  
Intensity

\( k_{AB} \)  
Cliff-Lorimer constant

\( \lambda \)  
Wavelength

\( L \)  
Crystallite size

\( n \)  
Refractive index

\( \Psi_0(\vec{r}) \)  
Exit wave function

\( q \)  
Momentum transfer

\( \rho \)  
Density

\( \theta_B \)  
Bragg angle

\( u \)  
Spatial frequency

\( \nu \)  
Frequency

\( \omega \)  
Fluorescence yield

\( Z \)  
Atomic number
Titanium(IV) oxide (TiO$_2$) lives up to its name. While the Titans in Greek mythology were the rulers of the Golden Age, TiO$_2$ has the potential to be the ruler of the Renewable Energy Age. Already today, TiO$_2$ is everywhere around us in our daily life. Its bright, white color makes it the most used pigment in the world, protects us from sunburn and is frequently used as a food additive (E171).\[^1\]

Beyond that, the valuable electronic and optoelectronic properties of TiO$_2$ facilitate its use in many more applications. In 1972, the discovery of Fujishima and Honda that TiO$_2$ splits water (H$_2$O) into oxygen and hydrogen under solar light irradiation,\[^2\] uncovered the hidden abilities of TiO$_2$. Since then, sights have been set on TiO$_2$ as a material for solar light driven applications, such as solar cells, water splitting devices and photocatalytic water purification.\[^3\] This research got an additional boost when O'Regan and Grätzel presented the dye-sensitized solar cell (DSSC).\[^4\] This solar cell consists of a mesoporous TiO$_2$ electrode that is covered with a dye and surrounded by a liquid electrolyte. It enables the production of solar cells with significantly decreased costs and shorter energy payback times compared to the most common Silicon-based solar cells.\[^5\] Admittedly, the use of a liquid electrolyte in DSSCs, e.g., LiI/I$_2$, has some drawbacks such as high recombination rates due to electron back transfer to the electrolyte and leakage problems.\[^6,7\]

Within the last years, several solar cells based on DSSCs have been invented, which use a solid electrolyte. Among these, inorganic-organic hybrid solar cells,\[^8\] all-solid-state DSSCs\[^9\] and perovskite based solar cells\[^10\] are noteworthy. In the inorganic-organic hybrid solar cell, an inorganic photoanode, mainly TiO$_2$ covered with an organic dye, is immersed in a hole conducting polymer such as Poly(3-hexylthiophen-2,5-diyl).\[^8\] For all-solid-state DSSCs usually all parts consist of inorganic materials. Here, the photoanode is a metal oxide, such as TiO$_2$, which is sensitized with quantum dots (CdSe, CuInS$_2$). For the hole conduction inorganic materials (e.g., CuI or CuSCN) are used.\[^9\] In recent years, perovskite solar cells lead to a significant increase in solar cell efficiency. A new efficiency record of 22.1 % was reported by Yang \textit{et al.} in June 2017 for a solar cell that consists of a TiO$_2$ photonanode, a Lead halide perovskite acting as the light-harvesting layer (CH(NH$_2$)$_2$PbX$_3$) and an organic hole conductor (Poly(triarylamine)).\[^11\]
Introduction

Beside these changes that take the entire solar cell device and the combination of different components into account, a lot of research is focused on the improvement of the TiO\textsubscript{2} photoanode itself. The disordered network of TiO\textsubscript{2} nanoparticles (NPs) in mesoporous films, which can be found in most solar cells, has several disadvantages. The numerous grain boundaries between the particles result in low electron transport and high recombination rates of photo-excited electrons.\cite{12,13} As both restrict the overall efficiency of the device, the morphology was modified and one-dimensional (1D) assemblies, such as TiO\textsubscript{2} nanowire (NW) arrays, were incorporated in order to accelerate charge mobility along defined transport paths.\cite{13,14} However, the increase in efficiency was low.\cite{15}

Within the last years, intensive research has been done to increase the performance of TiO\textsubscript{2} electrodes. Besides tuning the morphology, the key is the modification of the surface and defect engineering. Different changes in morphology, including ultralong NWs with high aspect ratios,\cite{16,17} branched NWs\cite{18–23} and the replacement of dense NWs by hollow nanotubes,\cite{24–27} have been used to increase the surface area. In combination with a suitable surface modification, such large surface areas can be even more effective. Surfaces can be either self-modified or changed by covering the TiO\textsubscript{2} nanostructure with a thin shell of a second material. In 2002, Palomares et al. reported that DSSCs show increased efficiencies, if the mesoporous TiO\textsubscript{2} is covered by a shell of Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}.\cite{28} Since this discovery, various, mostly insulating, materials have been used as shell material.\cite{29–31} Nevertheless, surface modifications are also possible by using reducing conditions. Here, especially black TiO\textsubscript{2}, owing a defective and highly active surface layer, is noteworthy. This defective surface is currently discussed to be the origin of the enhanced photocatalytic performance of black TiO\textsubscript{2}.\cite{32–34} The discovery of black TiO\textsubscript{2} shows that besides morphology and surface modification, a third leverage point, namely defect engineering, profoundly influences the performance of TiO\textsubscript{2} devices. Such surface and crystal defects stem from oxygen vacancies (O\textsubscript{vac}), doping with Ti\textsuperscript{3+} or disorder in the atomic arrangement and have a strong influence on the properties of TiO\textsubscript{2}.\cite{35,36}

Along with these findings, additional fields of application for TiO\textsubscript{2}, namely Li-ion batteries,\cite{37–41} memristors,\cite{42–44} and sensors\cite{45–47} showed up. Recently, a lot of work was conducted to gain a fundamental understanding of rutile TiO\textsubscript{2} NWs, which are usually grown by a wet chemical approach, the so-called hydrothermal synthesis. So far, the main focus was set on the growth of these NWs and its nanostructure in the as-grown state.\cite{19,48,49} All of these studies showed that transmission electron microscopy (TEM) is essential to understand the nanostructure of the as-grown NWs and to develop appropriate growth models. Due to these detailed TEM studies the NWs in the as-grown state are well understood nowadays. Typically, they consist of a single crystal
on the root, which splits into a bundle of nanofibers at the top due to a defect cascade.\textsuperscript{[48]} However, these as-grown NWs underperform compared to NWs, which were modified after the growth, e.g., by annealing. For example, Wisnet \textit{et al.}\textsuperscript{[50]} showed an increased efficiency for hybrid solar cells by incorporating post-growth annealed rutile TiO$_2$ NWs instead of as-grown NWs. They found that the internal nanostructure changes during the annealing process, including the formation of voids. Although a vanishing of defects was discussed as the origin of the improved efficiency, a detailed investigation of the internal changes is absence. The same applies for insulating shells that cover TiO$_2$ photoanodes and black TiO$_2$. For all of these materials increased efficiencies in application are reported.\textsuperscript{[28–34]} However, the underlying mechanism and the modified nanostructure are not well understood yet, because of a lack of detailed TEM investigation. Such TEM studies are crucial due to the small dimensions of the structural features, the important role of interfaces and the fact that many of these changes take place in the interior of TiO$_2$ and thus, are invisible for surface sensitive analysis methods. For black TiO$_2$ a more detailed investigation of the material has been conducted using TEM.\textsuperscript{[51]} First studies show promising results and highlight that besides the structural changes also the influence of a locally changed oxidation state has to be taken into account. In order to obtain this information with high spatial resolution, an in-depth investigation of the post-growth modified TiO$_2$ using electron energy-loss spectroscopy (EELS) is essential. In 2015, Tian \textit{et al.} investigated black TiO$_2$ NPs by combining TEM and EELS. They showed that besides the crystallinity at the surface also the surface near chemistry (oxidation state and composition) changes, which affects the properties significantly.\textsuperscript{[51]} Nevertheless, TiO$_2$ in general and TiO$_2$ NWs in particular still offer many mysteries, which have to be revealed. Among the wide variety of open questions, which cannot be answered at once, this thesis focuses on changes that arise upon post-growth annealing or etching of rutile TiO$_2$ NWs and thus, will shed some more light on TiO$_2$. At the end of the day only a deep understanding of the material at the nanometer scale and its influence on the properties offers a targeted application and will help to keep TiO$_2$ in its Olymp - the field of renewable energy.

\subsection*{1.1 Aim of the thesis}

The aim of this thesis is to develop suitable post-growth modifications for hydrothermally grown rutile TiO$_2$ NWs that allow to tailor the (internal) nanostructure, defect distribution and the related properties. To achieve this goal, the nanostructure and defects before, during and after certain post-growth treatments (heating and etching) are chara-
1 Introduction

1.2 Outline of the thesis

TiO$_2$ NW arrays are grown by a hydrothermal synthesis approach, which is modified from the one of Liu and Adyil\cite{52} in order to obtain NWs with optimized length and diameter for further investigations. Hydrothermally grown rutile TiO$_2$ NWs are chosen, as the synthesis method is highly reproducible and an intrinsically high density of defects, mainly stacking faults and O$_{\text{vac}}$, occurs. A variation of post-growth treatments, namely heating in different environments and hydrothermal etching are applied in order to manipulate the (internal) nanostructure as well as the defect distribution. Different TEM techniques, including imaging, diffraction and spectroscopy, are utilized to analyze the induced changes and thus, help to understand the modified TiO$_2$ NWs in detail. Special attention is devoted to identify deviations from the generic Ti$^{4+}$ valency, as this can be attributed to O$_{\text{vac}}$, which are the most prominent lattice defects in TiO$_2$. However, the scope of this work is not restricted to the investigation of theses defects. The correlation of the heat induced structural changes and the related changes in (opto)electronic properties and stability of the material are also considered.

1.2 Outline of the thesis

This thesis is sectioned in eight chapters. The introduction in Chapter 1 provides an insight in the broader context of TiO$_2$ and energy related materials. In Chapter 2, a brief summary about TiO$_2$ NWs, and the solvothermal synthesis is given. A detailed description of the experimental conditions conclude this chapter. Chapter 3 provides a theoretical background about the analytical techniques applied in this work and states the detailed experimental conditions that were used. The results of this thesis are presented in Chapter 4 to 7. In Chapter 4 the influence of a heat treatment at 500 $^\circ$C in air is studied and a vacancy condensation mechanism, which explains the observed changes, is derived. Chapter 5 demonstrates, how different heating environments (air or nitrogen (N$_2$)) influence the structure and especially the electronic properties of the NWs. While these two chapters focused on moderate annealing temperatures of 500 $^\circ$C, the fabrication of TiO$_2$-SiO$_x$ core-shell NWs, presented in Chapter 6, requires temperatures of 1050 $^\circ$C. Such a high temperature is capable to produce TiO$_2$-SiO$_x$ core-shell NWs with TiO$_2$ cores that are free of structural and lattice defects. A suitable combination of hydrothermal growth, etching and heating offers the possibility to design new NW morphologies. This topic is discussed in Chapter 7. Finally, the work is concluded in Chapter 8 and a short outlook about open questions and future work is given.
2 Nanostructured TiO$_2$: Properties and synthesis

The intention of this chapter is to provide a brief overview about the properties and synthesis of nanostructured TiO$_2$, while focusing on characteristics that are important for this work.

2.1 Titanium dioxide

TiO$_2$ is an abundant, chemically stable and bio-compatible metal oxide. Its physical, electrical and optical properties make TiO$_2$ a good candidate for many applications such as paints, paper, plastics and cosmetics.\cite{1} Since the discovery of its photocatalytic activity by Fujishima and Honda,\cite{2} emerging research on TiO$_2$ related to energy conversion and storage has started.\cite{53} Concurrently, TiO$_2$ is getting increasingly important for storage devices, due to its memristive properties.\cite{42}

2.1.1 Crystal structure and physical properties

TiO$_2$ exists in three natural polymorphs, but additional metastable modifications can be obtained synthetically by applying harsh conditions, especially high temperature and pressure. The natural polymorphs are tetragonal anatase, tetragonal rutile and orthorhombic brookite, but only rutile TiO$_2$ is thermodynamically stable, whereas brookite and anatase transform to rutile TiO$_2$ at 930 °C and 1070 °C, respectively.\cite{54}

The crystal structure of the three modifications can be described by a three-dimensional (3D) network of distorted [TiO$_6$]$^{8-}$ octahedra, which differs in terms of the distortion and alignment (edge- and/or corner-sharing) of the octahedra. Regarding the octahedron distortion, rutile and anatase are very similar. They have two long Ti-O bonds in axial direction and four short Ti-O bonds in equatorial direction, following the concept of Jahn-Teller distortion for six-fold coordinated $d$-group metals. Due to the distortion, the O-O bonds differ in length and one can distinguish between four equatorial edges and eight pyramidal edges.\cite{55} For brookite, no systematic distortion can be found and
2 Nanostructured TiO$_2$: Properties and synthesis

2.1 Titanium dioxide

the six Ti-O bonds as well as the 12 O-O bonds have different bond lengths. Consequently, no distinction between pyramidal and equatorial edges is possible.\cite{55} Figure 2.1 shows the crystal structures of the three polymorphs and highlights the different connections of the TiO$_6$ octahedra. In anatase (see Fig. 2.1a) every second pyramidal edge of a [TiO$_6$]$^{8-}$ octahedron is edge-sharing with adjacent octahedra in all three crystal directions. Thus, the anatase crystal structure is built by edge-sharing zig-zag chains of octahedra and comprises infinite channels in a and b direction.\cite{56} The shared edges have contracted O-O bond length. In rutile TiO$_2$ (see Fig. 2.1b) only two opposing edges are connected to the next octahedron and infinite chains in c direction are formed. Again, the edge-sharing O-O bonds are contracted. Adjacent chains are cross-linked, as every edge-sharing oxygen is, in addition, corner-sharing with the respective oxygen atom of the next chains in a and b direction.\cite{56} This octahedra alignment leads to channels in c direction. In the brookite crystal structure (see Fig. 2.1c), each octahedron has three shared edges. Similar to rutile, the octahedra connect to edge-sharing chains along the c direction, but the chains are linked with each other in a and b direction by both shared vertices and shared edges. Thus, in a and b direction, the brookite crystal structure compromises characteristics from the anatase and from the rutile crystal structure. In addition, similar to rutile, infinite channels are formed in c direction.\cite{57} The chemical environment of Ti and O is rather the same for all polymorphs and thus, they also show similar physical and chemical properties. They are densely packed, high refractive index ($n$) materials and posses an indirect band gap ($E_g$) of around 3 eV, which

Figure 2.1: Crystal structures of most stable TiO$_2$ modifications, showing Ti atoms (light blue) octahedrally surrounded by O atoms (red). The structures belong to a) anatase, b) rutile and c) brookite. Please note that the size of the spheres do not correspond to the atomic or ionic radii.
makes TiO$_2$ almost insulating. A closer look to the absolute values shows that the consistent order from anatase over brookite to rutile in terms of number of shared edges is also reflected in the crystal lattice parameter and physical properties (see Tab. 2.1).

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Space group</th>
<th>Lattice parameters [Å]</th>
<th>ρ [g/cm$^3$]</th>
<th>$n$</th>
<th>$E_g$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>$I4/amd$</td>
<td>a=b=3.78, c=9.51$^{[56]}$</td>
<td>3.84$^{[58]}$</td>
<td>2.49$^{[59]}$</td>
<td>3.20$^{[60]}$</td>
</tr>
<tr>
<td>Brookite</td>
<td>$Pcab$</td>
<td>a=9.18, b=5.45, c=5.15$^{[61]}$</td>
<td>4.11$^{[58]}$</td>
<td>2.58$^{[59]}$</td>
<td>3.13$^{[60]}$</td>
</tr>
<tr>
<td>Rutile</td>
<td>$P4_2/mmm$</td>
<td>a=b=4.59, c=2.96$^{[56]}$</td>
<td>4.26$^{[58]}$</td>
<td>2.61$^{[59]}$</td>
<td>3.01$^{[60]}$</td>
</tr>
</tbody>
</table>

Besides the $E_g$, the surface reactivity and the electron mobility mainly determine the performance of TiO$_2$ in photo-electrochemical application. Each polymorph has different low energy surfaces (rutile: $\{110\}$,$^{[67]}$ brookite: $\{111\}$ and $\{210\}$,$^{[55]}$ anatase: $\{101\}$.$^{[63]}$). These surfaces usually have a bigger share in natural crystal habits. However, these thermodynamically favored surfaces are not necessarily the most reactive ones (rutile: $\{111\}$,$^{[64]}$ anatase: $\{001\}$.$^{[65,66]}$). In addition, there is a spatial separation of reduction and oxidation sites for all TiO$_2$ polymorphs. For reduction, the highest activity is found on rutile $\{110\}$,$^{[67]}$ brookite $\{210\}$,$^{[68]}$ and anatase $\{101\}$,$^{[60]}$ surfaces, whereas oxidation is favored on rutile $\{111\}$,$^{[67]}$ brookite $\{212\}$,$^{[68]}$ and anatase $\{001\}$,$^{[69]}$ facets. Concurrently, the electron mobility is far less determined by the polymorph, than its degree of crystallinity and defect density. In order to improve reactivity, conductivity, and $E_g$, different approaches are used for TiO$_2$. Two of them, namely defect engineering and nanostructuring, have a significant influence on this work and thus, are discussed in more detail in the following sections.

### 2.1.2 Defects in TiO$_2$

Usually TiO$_2$ is not stoichiometric, but has a slight oxygen-deficiency and can be better described by TiO$_{2-x}$$^{[70]}$. This oxygen-deficiency can be related to different types of O$_{\text{vac}}$ or Titanium interstitials (Ti$_{\text{int}}$) and leads to n-type semiconducting properties in TiO$_2$. A full description of these point defects is possible by the so-called Kröger-Vink notation, which takes the charge and the lattice position of the defect into account. However, the exact determination of the charge and the lattice position of defects is not possible by the methods applied in this work, and thus, the defects are termed in a more general way by the use of O$_{\text{vac}}$ and Ti$_{\text{int}}$. Independent of the charge and the lattice position, point defects, such as vacancies (Ti or O) and interstitials (Ti$^{3+}$/Ti$^{4+}$ or impurities), play a major role.
in thermal stability, conductivity, light absorption and photocatalysis of TiO$_2$.\[^{[71]}\] Thus, using a suitable defect engineering, the properties of TiO$_2$ can be modified. Although O$_{\text{vac}}$ are dominating, also other defects influence the properties of TiO$_2$ and have to be taken into account.

Due to most synthesis conditions of rutile TiO$_2$ or when exposing TiO$_2$ to a reducing environment, donor type defects, namely O$_{\text{vac}}$ and Ti$_{\text{int}}$, form. O$_{\text{vac}}$ are the predominant ones, whereas Ti$_{\text{int}}$ represent a minority in rutile. On the other hand, extensive oxidation of rutile leads to Titanium vacancies (Ti$_{\text{vac}}$), which are acceptor type defects and convert the intrinsically n-type conducting rutile to a p-type semiconductor.\[^{[72]}\]

Among all these defects, O$_{\text{vac}}$ are best understood. The presence of O$_{\text{vac}}$ leads to a distortion in the crystal structure, which expands the lattice parameters of O$_{\text{vac}}$-rich rutile.\[^{[73]}\] As a consequence, the position of the $t_{2g}$ and $e_g$ energy levels changes.\[^{[74]}\] Nevertheless, these O$_{\text{vac}}$ are not static but can diffuse within the structure.\[^{[75]}\] Diffusion can occur randomly, directed from bulk to surface\[^{[76]}\] or in such way that O$_{\text{vac}}$ ordering takes place.\[^{[77,78]}\]

For high concentrations of O$_{\text{vac}}$ crystallographic shear planes can form. An ordered array of these planar defects leads to changes in the crystal structure and the so-called Magneli phases of titanium oxide are formed.\[^{[79,80]}\] They can be described by Ti$_n$O$_{2n-1}$, where $4 \leq n \leq 20$.\[^{[81]}\] For high O$_{\text{vac}}$ concentrations, these Magneli phases are thermodynamically more stable,\[^{[82,83]}\] but in nanomaterials high concentrations of O$_{\text{vac}}$ are stabilized in the TiO$_2$ crystal structures as well.\[^{[84]}\]

### 2.1.3 Nanostructured TiO$_2$

In nanostructured materials, the particle size is decreased to the nanoscale in at least one direction. Consequently, the surface-to-volume ratio is shifted towards higher surface areas, which results in higher reactivity, as more active sites are available. In addition, the properties might change due to quantum size effects.\[^{[85]}\] Nanostructured TiO$_2$ can be classified by its morphology and one distinguishes between zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) material, analogous to the number of dimensions that are not nanoscale.\[^{[86]}\]

For 0D materials all dimension are confined to the nanometric size regime and 0D nanostructures in TiO$_2$ are typically NPs. They are synthesized by flame hydrolysis\[^{[87]}\] or solution based synthesis methods.\[^{[88]}\] TiO$_2$ NPs can be as small as 3 nm\[^{[89]}\], might exhibit a shape with energetically unfavored surfaces,\[^{[90]}\] and are also commercially available as P25 or P123.\[^{[87]}\]

1D nanostructures are NWs, nanorods, nanobelts or nanotubes. The high aspect-ratio
of the 1D morphology offers a directionality, e.g., in terms of electron transport, and allows to minimize the amount of inactive phases, when using appropriate synthesis conditions.\textsuperscript{[91]}

The class of 2D nanostructures includes all materials that have one dimension restricted to the nanoscale. In terms of free-standing TiO\textsubscript{2} nanostructures, this definition is true for nanosheets. They are usually obtained by exfoliation of layered material,\textsuperscript{[92,93]} but also solvothermal reactions enable the synthesis of nanosheets, if suitable capping or surface directing agents are used.\textsuperscript{[94]} TiO\textsubscript{2} nanosheets are advantageous compared to other nanostructures, as they can have only active facets,\textsuperscript{[95]} but their synthesis is complex and requires harsh conditions.\textsuperscript{[92,96]}

Finally, 3D TiO\textsubscript{2} nanostructures have an extended network in all directions, but as they consist of nanoscale building units, they still offer the properties of nanomaterials.\textsuperscript{[97]} Such structures can be mesoporous (inverse opal) films, which are obtained by sintering of NPs on a flat substrate or around ordered polymer particles.\textsuperscript{[98]} Apart from this 3D network, which is obtained on detours, 3D TiO\textsubscript{2} networks can also be obtained straight away.\textsuperscript{[99]}

Among all these morphologies, 1D nanostructures are the most promising ones, as they offer evident advantages in terms of properties and feasible synthesis. Due to the large aspect ratio, 1D structures provide large (active) surface areas and a direct charge transport from the interface, where the charges are generated, to the back electrode of the device.\textsuperscript{[13,14]} These properties make them suitable for many applications that are related to photo-electrochemical processes.\textsuperscript{[3]} In principle, 1D materials can be divided in hollow (tubes) and solid (rods, wires, belts) nanostructures. Hollow materials posses larger surface areas, but a small tube diameter might not be accessible for relevant processes or materials. For example, studies on hybrid solar cells showed that pores of several tens of nanometers and TiO\textsubscript{2} nanotubes cannot be completely filled with a polymer material.\textsuperscript{[100,101]} The synthesis of nanotubes was for a long time restricted to template-based fabrication methods,\textsuperscript{[102]} but within the last years, new strategies have been developed for the synthesis of nanotubes.\textsuperscript{[25,26,103]} For NWs, there are various synthesis approaches, but the ones yielding NW arrays on a substrate are most relevant for application. Besides template-based fabrication methods,\textsuperscript{[104]} oxidation of Ti foils\textsuperscript{[105,106]} and solvothermal growth methods\textsuperscript{[20,52]} are the most pertinent ones. The latter is noteworthy, as it offers the possibility to synthesize quasi single-crystalline rutile TiO\textsubscript{2} NW arrays,\textsuperscript{[48]} whereas the others usually lead to amorphous or mesocrystalline materials.
2.2 Solvothermal synthesis

Solvothermal synthesis is a solution based synthesis strategy that is also used for nanostructured TiO$_2$. Compared to other classical synthesis strategies, such as solid-state and sol-gel reactions, it offers direct access to crystalline material in various morphologies at comparably low temperatures.$^{[107]}$

Every solution-based, chemical reaction taking place in a sealed reaction vessel, e.g., an autoclave, at a temperature that is higher than the boiling point of the solvent is defined as solvothermal reaction. Under these conditions, pressure is built up inside the vessel and changes the properties of the solvent. The pressure increases disproportionally with temperature, but is also affected by additional experimental conditions, such as filling of the vessel, dissolved salts and pH value. Depending on the selected reaction temperature and the respective pressure, the reactions take place in the sub- or supercritical regime of the solvent. Usually, solvothermal reactions are heterogeneous reactions, which can be divided in dissolution, nucleation and crystallization. All of these steps are influenced by the chemical and thermodynamical parameters of the reaction system.

The most commonly used and best studied solvent is H$_2$O. The respective solvothermal reactions are termed hydrothermal reactions. The influence of increasing temperature and pressure on the fundamental properties of H$_2$O is well understood.$^{[108]}$ The viscosity of water decreases with increasing temperature and thus the mobility of dissolved ions is increased.$^{[109]}$ Concurrently, the dielectric constant and the ion product of water change while crossing the critical point. Thus, H$_2$O is a good solvent for ionic and polar species in the subcritical regime, whereas nonpolar species can be dissolved by H$_2$O in the supercritical regime.$^{[110]}$ as supercritical H$_2$O has a very small dielectric constant. In addition, the ion product and thus, the dissociation of H$_2$O to H$_3$O$^+$ and OH$^-$ is highest under subcritical conditions, which accelerates the hydrolysis.$^{[111]}$ Consequently, the increase of temperature and pressure changes the properties of water compared to ambient conditions in such a way that it behaves like a completely new solvent.$^{[112]}$ Therefore, it facilitates the solvothermal synthesis of material or morphologies, which cannot be accessed by other methods.
2.3 Experimental details

In the following sections, the experimental conditions for solvothermal growth of rutile TiO$_2$ NWs utilized in this work, as well as the used post-growth treatments are described.

2.3.1 Solvothermal reactions

TiO$_2$ NWs were synthesized according to a solvothermal synthesis method described by Liu and Aydil.\cite{52} For all reactions, the chemicals were used without further purification.

Solvothermal TiO$_2$ NW growth on fluorine-doped tin oxide (FTO)

Typically, a reaction solution was prepared by adding drop-wise 150-250 µL of Titanium(IV) butoxide (Ti(OBut)$_4$) [Ti(OC$_4$H$_9$)$_4$, purum, Sigma-Aldrich] to a mixture of 5 mL of solvent and 5 mL of concentrated hydrochloric acid (HCl) [37 wt%, analytical grade; Sigma-Aldrich] under vigorous stirring. Usually, the solvent was deionized H$_2$O, but some reactions were also carried out with butanol (ButOH) [C$_4$H$_9$OH, Sigma-Aldrich].

FTO substrates were cleaned in an ultrasonic bath using isopropyl alcohol, acetone, and ethanol. Afterwards two of them were placed vertically in a Teflon liner with the glass side facing each other. The reaction solution was transferred to the Teflon liner that was placed inside a steel autoclave. The solvothermal reaction was performed at a defined temperature between 150-180 °C for different reaction times, ranging from 3 h to 6 h. The exact conditions used for the studies in Chapter 4, 5 and 7 are summarized in Table 2.2. Afterwards, the autoclave was cooled down to room temperature. The FTO substrates, covered with TiO$_2$ NW arrays, were rinsed with deionized water and dried with compressed air.

<table>
<thead>
<tr>
<th>Sample used in</th>
<th>Solvent</th>
<th>Volume (Ti(OBut)$_4$)</th>
<th>Temperature</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 4 (XRD)</td>
<td>H$_2$O</td>
<td>250 µL</td>
<td>150 °C</td>
<td>6 h</td>
</tr>
<tr>
<td>Chapter 4 (SEM, TEM)</td>
<td>H$_2$O</td>
<td>200 µL</td>
<td>150 °C</td>
<td>6 h</td>
</tr>
<tr>
<td>Chapter 4 (Stability tests)</td>
<td>H$_2$O</td>
<td>150 µL</td>
<td>150 °C</td>
<td>3 h</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>H$_2$O</td>
<td>250 µL</td>
<td>150 °C</td>
<td>4.5 h</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>H$_2$O</td>
<td>200 µL</td>
<td>150 °C</td>
<td>3 h</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>ButOH</td>
<td>200 µL</td>
<td>150 °C</td>
<td>3 h</td>
</tr>
</tbody>
</table>
Hydrothermal TiO$_2$ NW growth on c-Si wafer

Polished, boron-doped, p-type (100) crystalline Si (c-Si) (sheet resistance: 25 $\Omega$/cm$^2$) covered with a 2 nm thick native oxide layer was used as substrate. TiO$_2$ seed films for the hydrothermal growth of TiO$_2$ NWs were obtained by sputtering 40 nm Ti. Direct current sputter deposition was done at room temperature (chamber pressure: 6.67 $\times$ 10$^{-3}$ mbar, Ar flow: 20 sccm) and a sputter target (99.995 % Ti, Testbourne Ltd, Basingstoke, England) was used. The deposition rate was 1.67 Å/s at a sputter power of 300 W. Subsequently, the Ti films were oxidized in a rapid thermal processing oven with oxygen atmosphere (O$_2$ flow: 500 sccm). Heating up to 850 °C was performed with a heating rate of ±1°C/s and the temperature was hold for 2 h. The obtained polycrystalline rutile TiO$_2$ films on c-Si were placed in a Teflon liner, filled with an aqueous growth solution. The solution consisted of 12 mL deionized H$_2$O, 8 mL HCl [37 wt%, analytical grade, Sigma-Aldrich] and 350 µl Ti(OBut)$_4$ [Ti(OC$_4$H$_9$)$_4$, purum, Sigma-Aldrich]. Subsequently, the Teflon liner was sealed and the autoclave reactor was heated in an oven at 180 °C for 3 h. Afterwards, the autoclave was cooled down to room temperature within 10 min using water. The TiO$_2$ NW arrays, grown on c-Si were rinsed with deionized water and dried with compressed air.

Hydrothermal etching of TiO$_2$ NWs on fluorine-doped tin oxide

TiO$_2$ NWs were etched during a hydrothermal reaction. 10 mL of etching solution were prepared by mixing 5, 6, 6.5 or 7 mL of deionized H$_2$O with concentrated HCl [37 wt%, analytical grade, Sigma-Aldrich]. Two FTO substrates, covered with TiO$_2$ NW arrays, were put vertically in a Teflon liner that was placed inside of a steel autoclave. The 3.7-6.1 M HCl solution was transferred to the Teflon liner. The hydrothermal reaction was performed at 150 °C for 1-3 h. Afterwards, the autoclave was cooled down to room temperature. The FTO substrates, covered with etched TiO$_2$ NW arrays, were rinsed with deionized water and dried with compressed air.

2.3.2 Heat treatments

Some of the TiO$_2$ NW arrays were further subjected to different heat treatments in order to evaluate changes in the nanostructure during thermal load in different environments. The respective experimental conditions are summarized in the following.
2.3 Experimental details 2 Nanostructured TiO$_2$: Properties and synthesis

**Heat treatment in air**

In the first set of experiments, the heat treatment of TiO$_2$ NW arrays grown on FTO substrate was performed on a hot plate at 500 °C for 4 h in air. The temperature was manually raised every minute by 50 °C up to 500 °C.

**Heat treatment in N$_2$**

In another experiment, the TiO$_2$ NW arrays grown on FTO were annealed at 500 °C for 4 h under N$_2$ atmosphere. A 50 °C/min ramp up to 500 °C was performed on an Anton Paar DHS 1100 heating stage, which was covered with a graphite dome to obtain a constant N$_2$ atmosphere of 1.35 bar.

**Heat treatment in vacuum**

The NW arrays grown on c-Si wafers were annealed at 1050 °C in an evacuated rapid thermal processing oven for 2 h. The heating rate was set to 60 °C/min and the chamber pressure was roughly 1.6 mbar.

**2.3.3 Ultrasonic treatment**

The NW covered FTO substrate was put in a small vessel. The vessel was filled with deionized H$_2$O and placed in the ultrasonic device, which was also filled with water. The water level was kept below the height of the vessel. Ultrasonic treatment was performed for 15 min at an ultrasonic frequency of 35 kHz. After the treatment, the FTO substrate with the partially delaminated NW array was dried with compressed air.
3 Characterization

The following chapter summarizes the basic concepts of the characterization techniques applied in this thesis. A brief introduction about each technique will be provided but detailed explanations will be restricted to phenomena that are of importance for this work. In addition, details about the applied, experimental conditions will be given in the end of this chapter.

3.1 Electron based imaging and diffraction

In electron microscopy, primary electrons (PEs) of the electron beam interact with the sample, which can be a bulk material or a thin, electron transparent specimen. Such an electron bombardment causes elastically and inelastically forwarded as well as elastically back scattered electrons. Moreover, as a result of the energy transfer during the inelastic scattering processes, the emission of X-rays, cathodoluminescence, secondary and Auger electrons may occur. The energy of the PE depends on the acceleration voltage and is preserved in elastic scattering, during which the PE interacts with the atomic nucleus. In contrast, electrons that scatter inelastically can lose up to some keV of their initial energy within one scattering event due to interactions with electrons in the sample. Depending on the imaging or diffraction method applied, parts of these electrons are detected and used for morphological and structural characterization. The following sections briefly describe the electron based imaging and diffraction techniques that were utilized in this work.

3.1.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique to image the surface and morphology of materials. A convergent electron beam of PEs ($E_0 < 20$ keV) is generated with either a thermal emitter or a field emission gun. The beam scans over the specimen and parts of the electrons that are ejected from the surface after the interaction of the PEs with the specimen, are detected for each point. The resulting signal is amplified and a topographic or atomic number ($Z$) contrast image is obtained. The information stored in the image
differs according to the used detector, which either detects only secondary electrons (SEs) or back scattered electrons (BSEs) or both signals. On one hand, SEs are emitted after an inelastic collision of PE with the material. In this process, the PE transfers part of its energy to valence electrons, which are ejected from the solid. These SEs have kinetic energies lower than 50 eV and thus their escape depth is only several tens of nanometers. Consequently, these electrons are suitable to image the specimen topology with high resolution. Especially at corners, SEs from both sides can escape the material, which leads to a high signal at corners and gives rise to the 3D impression of the SE image. In SEM mainly two detectors are used for SEs, the Everhart-Thornley detector and the in-lens detector. The Everhart-Thornley detector has a positive potential applied on a grid to attract the SEs and is mounted diagonal above the specimen, which leads to an additional shadowing effect and a stronger 3D impression. In contrast, the in-lens detector is mounted in the electron column above the specimen. This position offers a rotational symmetry around the optical axis and a sophisticated magnetic field from the pole piece. Consequently, the SEs are collected without shadowing effects but with high signal, which enables imaging at low acceleration voltages and facilitates high lateral resolution. In-lens SE images reveal thin surface films, which are invisible for the Everhart-Thornley detector\cite{113} and differences in the work function can be detected.\cite{114}

On the other hand, BSEs are primary electrons that exit the specimen on the surface after several quasi-elastic scattering events. Their energy is slightly smaller than the energy of the PEs and the escape depth is on the order of $\mu$m, leading to limited lateral resolution. The probability of back-scattering increases with increasing $Z$ and thus BSE images have a strong $Z$ contrast.

### 3.1.2 Transmission electron microscopy

In TEM, information about the nano- and crystal structure of sufficiently thin samples ($<100$ nm) can be obtained with much higher spatial resolution compared to SEM, because the energy of the electrons is higher (100-300 keV) and the interaction volume is much smaller. The imaging is comparable to that of an optical microscope in transmission mode, as in TEM, the specimen is illuminated by a parallel electron beam and the resulting signal of the (in)elastically scattered and transmitted electrons is detected on a fluorescence screen. Figure 3.1 shows the construction of a conventional TEM. The electron beam is generated by an energy source, such as a thermionic emitter, a cold field emission gun or a Schottky emitter. The condenser lens system controls the size and the current of the beam penetrating through the specimen. The electrons interact with the
atoms of the specimen and lead to two different types of contrast, namely mass-thickness contrast and diffraction contrast. Mass-thickness contrast is affected by electron scattering, which occurs due to the $Z$, the density of the material and the specimen thickness and arises in both crystalline and amorphous material. Diffraction contrast, on the other hand, only originates from crystalline materials and is related to Bragg diffraction. After the electron-specimen interaction the electrons pass the objective and projector lens and are displayed on the screen. For TEM, different detection modes can be used to obtain the desired information about the specimen. In this work, selected area electron diffraction (SAED), bright field (BF), dark field (DF) and high-resolution (HR) TEM imaging are used. The underlying concepts of these techniques are briefly described in the following.

3.1 Electron based imaging and diffraction

Electron diffraction

When the electrons pass through the specimen, they can be elastically scattered by the Coulomb potentials of the atoms. If the material is crystalline, and thus, the atoms are ordered, the potential distribution, which determines the scattering function for elec-
trons, shows a specific periodicity. As a result, the scattered electrons have defined path differences for each scattering direction. For path differences that are an integer multiple number of the wavelength (\(\lambda\)), constructive interference occurs. The conditions for constructive interference for a certain lattice distance (\(d_{hkl}\)) are described by the Bragg equation (3.1).

\[
2 \cdot d_{hkl} \cdot \sin(\theta_{\text{Bragg}}) = \lambda
\]  

(3.1)

The Bragg angle (\(\theta_B\)) is the scattering angle between the interfering electrons and is on the order of 10 mrad because of the short \(\lambda\) of high energy electrons. Due to the small scattering angles, the diffraction pattern represents roughly a planar section of the reciprocal lattice.

When single-crystalline materials are oriented in a specific zone-axis, the Bragg law is fulfilled for several \(d_{hkl}\), due to the large size of the Ewald sphere, which cuts the rel-rods of the thin sample. In the back focal plane, all electrons with the same \(\theta_B\) and a defined direction are focused to one point and a periodic pattern of reflections forms (see Fig. 3.1c). This diffraction pattern is projected to the screen and the position of the reflections relative to each other in the pattern is used to determine the phase and the orientation of the analyzed material. In contrast, the interpretation of the reflection intensities is not straightforward, as for electron diffraction (ED) on specimens thicker than 10 nm, dynamical diffraction effects have to be taken into account. As a result, forbidden reflections can be detected in the ED. In addition, ED patterns are influenced by confined specimen volumes perpendicular to the electron beam, which results in streaking of the reflections.[115]

A selected area aperture can be used to limit the specimen area that contributes to the ED pattern and enables a detailed crystallographic analysis of the specimen with several hundreds of nm resolution. This aperture is inserted into the first image plane of the objective lens (see Fig. 3.1b).

**BF and DF imaging**

BF and DF TEM utilizes the distribution of the electrons with respect to the scattering angles and directions in the back focal plane. An objective aperture is inserted in the back focal plane of the objective lens (see Fig. 3.1a), which selects the reflections in the reciprocal space, from which electrons are used for the image formation. The resulting image is dominated by diffraction contrast.

In the BF mode, an aperture is centered around the central, non-scattered beam. Consequently, low scattering regions appear bright, whereas strong scattering (high \(Z\)) and
differing areas are dark in the BF image (see Fig. 3.1d).

For DF imaging, the aperture is centered around a Bragg diffracted beam and all electrons, except the ones of the corresponding \( d_{hkl} \) in a defined orientation, are blocked. As a result, most of the specimen appears dark and only crystalline areas in the specific orientation, contributing to this reflection, appear bright (see Fig. 3.1e). To avoid large aberrations, which increase with increasing \( \theta_B \) for off-axis DF, it is preferable to tilt the incident beam until the Bragg diffracted beam is parallel to the optical axis (on-axis DF).

**HR imaging**

In HR TEM, the specimen is illuminated parallel but no objective aperture is used. Consequently, all electrons passing the specimen are used for the image formation. The contrast in the image results from the interference between these coherent electron waves and contains all information up to high spatial frequencies.

When the electron beam passes through the specimen, the electrons interact with the Coulomb potential of the atomic nuclei and the phase of the incoming plane wave is shifted depending on the Coulomb potential of the nuclei and the number of electron-nuclei interactions (thickness). Thus, each electron wave that leaves the specimen, the so-called exit wave, has its unique phase \( \varphi \). The exit wave function \( \Psi_0(\vec{r}) \) contains all information about the specimen as a function of the position vector \( \vec{r} \). Assuming a thin specimen, which fulfills the requirements of a weak phase object, the amplitude \( A \) of the electron wave is constant and the \( \Psi_0(\vec{r}) \) can be described by Equation 3.2.

\[
\Psi_0(\vec{r}) = A(\vec{r}) \cdot e^{i\varphi(\vec{r})} \quad (3.2)
\]

The exit wave propagates through the microscope, which leads to an additional modulation of the electron wave. Due to the spherical aberration \( C_s \) and the defocus \( \Delta f \), not all spatial frequencies \( u \) are transferred with the same phase. The phase contrast transfer function (PCTF) in Equation 3.3 describes this oscillation of the contrast, due to the objective lens system.\cite{116,117}

\[
PCTF = \sin(\pi \Delta f \lambda u^2 + \frac{\pi}{2} C_s \lambda^3 u^4) \quad (3.3)
\]

The final image wave forming the HR image is a convolution of the exit wave with the PCTF and limits the intuitive interpretation of HR images, which is even more complicated as not the wave, but only the square of the wave amplitude can be detected. For this reason, image simulation is required to determine the atom positions. However, for a limited range of (small) \( u \), the PCTF is negative and almost constant. A reasonable
selection of the $\Delta f$ shifts the first zero-crossing to higher $u$. Within this range, a direct image interpretation (black atoms on bright background) is possible. The optimum $\Delta f$ is defined by the Scherzer defocus ($\Delta f_{\text{Scherzer}}$) (see Eq. 3.4)\cite{118} and the first zero-crossing of the PCTF at $\Delta f_{\text{Scherzer}}$ defines the maximum spatial resolution of the microscope.

$$\Delta f_{\text{Scherzer}} = -1.2\sqrt{C_s \cdot \lambda} \quad (3.4)$$

In addition, the resolution of the microscope is affected by the limited coherence of the electron beam and instabilities of the specimen and the detector. As a result, damping of the PCTF occurs, which decreases the resolution further to the point resolution. The damping can also be tuned by $\Delta f$. However, the best $\Delta f$ for slow damping, the so-called Lichte defocus, is far away from $\Delta f_{\text{Scherzer}}$.\cite{119} Nevertheless, lattice periodicity in the analyzed material remains unchanged by the PCTF and is independent of $\Delta f$ and damping. Thus, information about $d_{hkl}$ and the angle between respective planes can be extracted. This information allows to determine the crystal structure on a local scale.

### 3.1.3 Scanning transmission electron microscopy

Similar to SEM, in scanning transmission electron microscopy (STEM), a convergent electron beam scans over the specimen, but the electrons that are detected for each scanning point are transmitted electrons with defined scattering angles. Depending on the interaction, the angles range from some mrad to angles larger than 50 mrad. Comparable to conventional BF and DF TEM, the image is formed by selecting direct or scattered beams. Instead of an aperture in the back focal plane, different detectors with specific collection angles are used to define, which electrons contribute to the total intensity of each scanning point (see Fig. 3.2a). Although only the intensity integrated over the entire area of the detector is used for the STEM image, a meaningful interpretation of the contrast is only possible, if the potential overlap of diffraction discs on the detector is considered.

In principle, two contrast mechanisms contribute to the contrast in a STEM image, namely mass-thickness contrast and diffraction contrast. Mass-thickness contrast arises from incoherent, elastic scattering (Rutherford scattering), which is an elastic scattering at the Coulomb field of the nucleus. Its cross-section depends on the strength of the Coulomb field, which scales with $Z^2$, while the scattering probability depends on the scattering angle and peaks in forward direction. However, at angles below 50 mrad mass-thickness contrast has to compete with diffraction contrast, which originates from Bragg diffraction (coherent, elastic scattering). Due to the convergent beam of the probe, a convergent diffraction pattern is formed and the diffraction discs may overlap with each
Figure 3.2: a) Schematic drawing of a STEM with the different scattering angles and respective detectors. The resulting STEM images are shown in b)-d): b) BF, c) ADF and d) HAADF STEM image.

other and the direct beam. In the overlapping areas, interference occurs and this interference leads to image contrast.

Although all types of contrast contribute to the detected intensity, the use of different detectors and an appropriate camera length allows to select conditions, in which one type of contrast tends to dominate. According to the dominating effects, the detectors and the resulting images are assigned to BF, annular dark field (ADF) and high-angle annular dark field (HAADF). BF STEM offers contrast equal to the one of BF TEM, if the transmitted beam completely covers the BF detector, while the diffraction discs lie outside this detector. In this condition, mainly the direct beam and inelastically scattered electrons are detected. In BF images, vacuum appears bright. Within the specimen amorphous areas are brighter than crystalline material of the same composition and thus, BF STEM can be used for the analysis of crystal defects.\textsuperscript{120} The ADF STEM detector sums the intensity over the overlapping convergent diffraction discs that arise from Bragg diffraction. Contrary to DF TEM, where only one diffraction spot is considered for image formation, in ADF STEM the contrast arises from many diffraction discs that fall on the detector. In addition, also Rutherford scattered electrons are detected and contribute to the signal. In these images, vacuum is dark and crystalline material with large Z appears
3 Characterization

3.2 Electron energy-loss spectroscopy

Electron microscopy allows to achieve more information about the investigated material than one can obtain by imaging or diffraction. Especially by using thin specimens in TEM, no matter if in parallel illumination or in STEM mode, the transmitted, inelastically scattered electrons contain valuable information, which can be used for a detailed characterization of the specimen. When an electron beam passes the specimen, an interaction between the atoms in the specimen and the PEs takes place. Depending on this interaction, the electrons lose no, some or several hundreds of eV from their initial energy. EELS monitors this energy loss by dispersing electrons according to their energy in a magnetic prism. Thus, on an energy-dispersive plane, electrons with the same energy loss are focused to the same point and form a spectrum. The resulting EEL spectrum, exemplarily shown in Figure 3.3, can be divided into three main regions: the zero-loss peak (ZLP), the low-loss region and the core-loss region.

The ZLP is the most intense feature in an EEL spectrum, as the majority of the electrons pass through the thin specimen without losing energy. Its shape is mainly defined by the instrumental parameters and can be tuned by the use of a monochromator, which decreases the width and tails of this peak significantly. The width of the ZLP influences the information gained by EELS, as it determines the energy-resolution (with...
monochromator below 0.1 eV\(^{[122,123]}\). Electrons that lose some energy (up to 50 eV) due to plasmonic excitations and inter- or intraband transitions show up in the low-loss region.\(^{[124]}\) In contrast to the ZLP, which is a microscope and spectrometer dependent feature, the low-loss spectrum discloses some sample properties, such as sample thickness,\(^{[125]}\) optical properties and the band gap.\(^{[126]}\) The highest information content and the lowest intensity are found in the core-loss region, which has element specific ionization edges. These edges arise from an energy-transfer of the transmitting electron to an inner-shell electron, which is in turn exited to an unoccupied state. The energy-loss of the transmitting electron is equal to this excitation energy, which is unique for each element and corresponds to the inner-shell binding energy. The resulting element-specific edge with characteristic features emulates the unoccupied states of the investigated material and contains information about the oxidation states and bonding behavior of the respective element. In general, sharp peaks in the spectrum correspond to transitions between narrow bands. Here, the electrons are confined in states with higher density of states (DOS). In contrast, broad peaks result from transitions to a wide band. The following sections give further details on the analysis of band gaps and the near-edge fine structure, as these methods have a significant share in this work.
3.2.1 Band gap measurements

In a semiconductor, such as the studied TiO$_2$, the transition from the valence band (VB) to the conduction band (CB) is the one with the lowest excitation energy. Consequently, the onset of the first peak in the low-loss spectrum corresponds to the band gap. Thus, EELS can be used to determine the band gap of the material on a local scale. As the ZLP is still very intense at an energy loss of 1-5 eV, a careful removal of the ZLP is required.\cite{127} Afterwards, the band gap can be derived from the intersection of the zero-level with a linear regression, which is fitted along the linear region of the first peak.\cite{128} For metal oxides with a high refractive index, e.g., TiO$_2$ (see Sec. 2.1.1), the determination of the band gap is more challenging, as the peak of the VB to CB transition might be overlaid with energy losses that are related to the Čerenkov radiation.\cite{129} This radiation is emitted whenever charged particles pass a dielectric medium faster than the speed of light in this medium. To minimize high intensities for Čerenkov losses, it is mandatory to have a sufficiently thin specimen and a large semi-collection angle ($\beta$).\cite{130}

3.2.2 Chemical shifts and near-edge fine structure

The element specific ionization edges in the core-loss EEL spectra are superimposed on a background, which is caused by the tails of the ZLP and the preceding lower energy loss edges. This background can be removed by an appropriate fitting using a power-law fit.\cite{131} The edge onset of the remaining edge is characteristic for each element and represents the ionization threshold. Depending on the valency of the analyzed element, this ionization threshold shows slight variations (up to 5 eV), as different oxidation states have different binding energies and vary in the shielding of the core-hole. Depending on the screening, the edge-onset might be shifted to higher or lower energies.\cite{132} After the edge-onset, the edge shows variations in intensity that are correlated to the number of states above the Fermi level within a certain energy interval.\cite{132} The shape of the edge in the first 50 eV is called the electron energy-loss near edge structure (ELNES). It is a projection of the dipole-allowed part of the unoccupied DOS and contains information about the valency, coordination, bonding and site-geometry of the analyzed atom. As this information cannot be derived straightforward the ELNES of the edges discussed in this work (Ti–L$_{2,3}$, O–K and Si–L$_{2,3}$) are explained in the following paragraphs in more detail. For phase analysis, a deep understanding of the ELNES is not mandatory and the so-called fingerprint method, comparing the shape of the ELNES from unknown material with known references, is sufficient.\cite{133}
Ti-L\textsubscript{2,3} edge

The Ti–L\textsubscript{2,3} edge (450-470 eV), which arises from transitions of the Ti 2\textit{p} electrons to empty states in the 3\textit{d} band, consists of two white lines, independent of the valence state of Ti and its chemical environment (see Fig. 3.4).

These white lines result from the spin-orbital splitting of the filled 2\textit{p} orbitals in 2\textit{p}\textsubscript{1/2} (L\textsubscript{2}) and 2\textit{p}\textsubscript{3/2} (L\textsubscript{3}) states, which are separated by around 6 eV.

In intensity [a.u.] Energy loss [eV] 455 460 465 470

<table>
<thead>
<tr>
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<th>Intensity [a.u.]</th>
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<tr>
<td>metallic Ti</td>
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<tr>
<td>anatase TiO\textsubscript{2}</td>
<td></td>
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<tr>
<td>rutile TiO\textsubscript{2}</td>
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**Figure 3.4:** Comparison of the Ti–L\textsubscript{2,3} ELNES: a) metallic Ti\textsuperscript{[136]} b) anatase TiO\textsubscript{2}\textsuperscript{[137]} and c) rutile TiO\textsubscript{2}.

The differences between metallic Ti and Titanium oxides are reflected by changes in the position of the Ti–L\textsubscript{2,3} edge and its ELNES (see Fig. 3.4). Focusing on the threshold energy for the absorption, a shift of the edge onset to higher energies for higher oxidation states can be detected. The lower the oxidation state of the compound is, the easier it is for the other electrons to screen the core hole by relaxation and the lower is the threshold energy. In metallic Ti, for example, the screening is high and thus, it has the lowest energy onset. Concurrently, the ELNES changes. In titanium oxides, the Ti ions are surrounded by a distorted octahedron of O\textsuperscript{2–}-ions. In such a [TiO\textsubscript{6}]\textsuperscript{8–} octahedron, the overlap between the Ti 3\textit{d} and the O 2\textit{p} orbitals differs in axial and equatorial directions (see Sec. 2.1.1). The resulting molecular orbitals are split into filled, bonding 2\textit{e}\textsubscript{g} and 1\textit{t}\textsubscript{2g} states and (partially) empty anti-bonding 2\textit{t}\textsubscript{2g} and 3\textit{e}\textsubscript{g} states according to the crystal field splitting of the octahedrally coordinated transition metals. The Ti – L\textsubscript{2,3} edge probes the transition of an electron from the filled 2\textit{p}\textsubscript{1/2} and 2\textit{p}\textsubscript{3/2} levels to the 2\textit{t}\textsubscript{2g} and 3\textit{e}\textsubscript{g} levels. As different oxides vary in the occupancy of the 2\textit{t}\textsubscript{2g} levels (empty for TiO\textsubscript{2}, half filled for Ti\textsubscript{2}O\textsubscript{3} and filled for TiO), the probability of electron excitation to these states differs. Thus, changes in the relative intensity between the \textit{t}\textsubscript{2g} and \textit{e}\textsubscript{g} peaks in the ELNES, depending on the oxidation state (high \textit{t}\textsubscript{2g} peaks for TiO\textsubscript{2}, no \textit{t}\textsubscript{2g} peaks for TiO), can be detected. A method of Stoyanov et al. uses these differences in combination with the chemical shift, to calculate the valency of Ti for unknown titanium oxides.

Furthermore, the Ti–L\textsubscript{2,3} ELNES contains information about the modification of the
3 Characterization 3.2 Electron energy-loss spectroscopy

chemical compound. In titanium oxides, the $[\text{TiO}_6]^{8-}$ octahedra are slightly distorted (trigonally for $\text{Ti}_2\text{O}_3$, orthorhombic-like for $\text{Ti}_4\text{O}_7$ and tetragonally for rutile $\text{TiO}_2$), and thus, an additional splitting of the $2t_{2g}$ and $3e_g$ levels occurs. As this splitting is very small, the peaks show shoulders but no splitting into more peaks can be detected by most of the available instruments. The effect of even small changes in distortion can be seen in Figure 3.4b,c at the small shoulder of the $L_3-e_g$ peak. This peak has a shoulder towards the higher energy loss for anatase, exhibiting a $D_{2d}$ symmetry, whereas the shoulder is on the lower energy loss side for rutile, which has a $D_{2h}$ symmetry (Sec. 2.1.1).[139]

**O-K edge**

The energy losses (530-580 eV), which represent the O-K edge, are related to $1s \rightarrow 2p$ transitions. There is no spin-orbital splitting for the $1s$ orbital and thus all features probed in this edge are related to the unoccupied states. As discussed for the Ti–$L_{2,3}$ edge, these states are influenced by the surrounding atoms and for this reason, the ELNES of the O-K edge is strongly related to the composition and crystal structure of the analyzed oxide.

For oxygen in $\text{TiO}_2$, the edge starts with an intense double peak at 530 eV (see Fig. 3.5a). The distance between the peaks is similar to the $t_{2g}-e_g$ splitting of the Ti–$L_{2,3}$ edge and results from the hybridization of unoccupied O $2p$ states with empty Ti $3d$ states. As the Ti $3d$ level is split into $t_{2g}$ and $e_g$ states, the hybridization also results in two empty $\sigma$ hybrid orbitals with different energies. The O $1s$ electrons are excited to these $\sigma$ hybrid orbitals and a double peak, which is characteristic for transition metal oxides with octahedral coordination, shows up in the EEL spectrum. At higher energy losses (537-546 eV), the O-K edge of $\text{TiO}_2$ shows three more peaks, which correspond to an

![Figure 3.5: Comparison of the O-K ELNES: a) Rutile TiO₂ and b) amorphous SiO₂.](image)
excitation into hybridized orbitals of O 2p orbitals with Ti 4s and 4p orbitals. Due to imperfections in the crystal structure of TiO₂, a low signal of the O-K edge or a limited energy resolution, this triplet is often recorded as one broad peak (see Fig. 3.5a).

In comparison, the ELNES of the SiO₂ O-K edge (see Fig. 3.5b) is almost featureless and consists only of one intense peak starting at 535 eV. As Si has no empty d states that could hybridize with the O 2p states, the double peak at the beginning of the O-K edge is absent.\[^{140}\]

**Si-L edge**

The Si–L₂,₃ edge (100-150 eV) is related to dipole-allowed transitions of electrons from occupied 2p orbitals to unoccupied 3s and 3d states and reflects in addition the p → p-like transitions, which are usually dipole-forbidden. For Si these transitions are dipole-allowed due to the hybridization of s and p to sp³ orbitals. In this case, it is possible to excite electrons from the 2p state to the s-like part of the sp³ hybrid that is still p dominated. These p → p-like transitions make the interpretation of the Si–L₂,₃ ELNES difficult.\[^{141}\]

For c-Si, the ELNES starts with a sharp peak at 99 eV as shown in Figure 3.6a. This peak corresponds to 2p → 3s transitions and can be asymmetric due to the spin-orbital splitting of the 2p states to 2p₁/₂ and 2p₃/₂ states ($\Delta_{SO}=50$ meV\[^{142}\]), which is below the energy resolution. It is followed by a broad peak, comprising the 2p → 3d transitions. Most calculations fail to simulate this part of the edge, as contributions from dipole allowed p → p-like transitions are usually not taken into account for calculations.\[^{143}\]

\[\text{Figure 3.6: Comparison of the Si-L ELNES: a) Si,}^{144}\text{ and b) amorphous SiO₂.}^{145}\]

The ELNES of the Si–L₂,₃ edge in SiO₂ shows three distinct peaks (see Fig. 3.6b). The first peak arises from a 2p → 3s transition and the second peak from a 2p → 3d transition (again the spin-orbital splitting cannot be resolved). The third peak at
higher energy losses is a delayed maximum. This broad intense feature results from inner well resonances, which are characteristic for the ELNES of materials, where strong electronegative ligands are coordinated tetrahedrally around Si.\cite{146,147}

### 3.2.3 Sensitivity of the ELNES to orientation and beam damage

Although the ELNES in general is suitable to characterize a material in detail, there are two experimental challenges that might result in misleading interpretation of the data: orientation dependency of the ELNES and beam damage.

On one hand, EELS is probing the unoccupied electronic states and these states show a directionality if the analyzed material is not isotropic (e.g., amorphous or cubic). Consequently, the transition to these states depends on the momentum transfer ($q$) of the inelastically scattered electron, which might change quickly from parallel to perpendicular with respect to the direction of the incident electron beam. Thus, orientation dependency of the ELNES plays a major role for crystalline materials like rutile TiO$_2$. However, studies of Heiliger et al. showed that for rutile TiO$_2$, the orientation dependency only influences the O–K ELNES significantly, whereas the ELNES of the Ti–L$_{2,3}$ edge is almost independent of the measuring direction ($<001>$ or $<100>$).\cite{148} The orientation dependency can be decreased by performing EELS in STEM mode, which leads to a loss of the momentum resolution. In addition, the magnitude of $q_{\parallel}$ can be increased with increasing $\beta$ until it equalizes with the $q_{\perp}$.\cite{149} Although, these experimental conditions suppress the orientation dependency, EELS in zone-axis should be avoided due to channeling effects.

On the other hand, beam damage is an issue for EELS as measurements with long acquisition times and high beam currents are necessary to obtain signals with sufficient signal-to-noise ratio. These conditions might lead to radiation damage of the sample, including changes of the interatomic distances and the coordination as well as phase transformations and crystallization/amorphization. For TiO$_2$ radiation damage is an important issue, as the stability under the electron beam is quite low. Different works show that beam damage reduces TiO$_2$, which in turn has an influence on the Ti–L$_{2,3}$ and the O–K edge.\cite{150,151} To avoid these negative effects, carefully chosen measurement parameters during the EELS experiment are mandatory.

### 3.3 Photon based diffraction and spectroscopy

Besides electrons, photons can also provide information about the analyzed material. In the following sections different methods are explained, which can be used to characterize
a material by means of emitted or diffracted X-rays and by the absorption of photons with specific wavelengths.

### 3.3.1 Energy dispersive X-ray spectroscopy

Besides EELS, energy dispersive X-ray spectroscopy (EDS) can be used to obtain qualitative and quantitative information on the chemical composition of the sample. After the excitation of an inner-shell electron the remaining core-hole is filled by an outer-shell electron. The excessive energy is set free by the emission of an Auger electron or by the generation of characteristic X-rays. These processes are competitive, but the probability of X-ray emission increases with increasing $Z$ and with lower shell transitions, as defined by the fluorescence yield ($\omega$).\(^{[152]}\)

Besides the characteristic X-rays, bremsstrahlung is emitted. This radiation is generated due to retardation of the primary electrons in the Coulomb field of the nucleus and leads to a background in the spectrum, which needs to be subtracted prior to the quantitative analysis.\(^{[153]}\) In the background subtracted spectrum, the peak position is specific for the element, as the energy of the characteristic X-rays ($E_{\text{X-ray}}$) is proportional to $Z^2$ and a factor that accounts for the involved shells, while its intensity ($I$) corresponds to the concentration of the respective element. The relative peak intensities enable the quantitative analysis of the sample composition $\frac{c_A}{c_B}$ using a method developed by Cliff and Lorimer (Eq. 3.5).\(^{[154]}\) The so-called Cliff-Lorimer constant ($k_{AB}$) is a correction factor and accounts for the influence of different scattering cross-sections, the $\omega$, the acceleration voltage of the primary electrons, the sample thickness and the used detector on the measured peak intensities. The $k_{AB}$ value can be calculated from first principles or experimentally determined using samples with known composition.\(^{[155]}\) The Cliff-Lorimer equation is:

$$\frac{c_A}{c_B} = k_{AB} \cdot \frac{I_A}{I_B} \quad (3.5)$$

Quantitative analysis of light elements using EDS is limited due to the low $\omega$ and the enhanced absorption of low-energy X-rays along the X-ray emission path to reach the detector and in the detector.\(^{[156]}\)

### 3.3.2 X-ray diffraction

Similar to electrons, which are elastically scattered at the nuclei, X-rays can be elastically scattered by the electron clouds of the different atoms. The interaction between the scattered X-rays results in a diffraction pattern in the case of crystalline materials, whereas amorphous materials without ordered atomic arrangement show only diffuse
scattering. As it was described for elastic electron scattering, constructive interference of the scattered X-rays results in a detectable signal at defined $\theta_B$ according to the Bragg equation (see Eq. 3.1). Thus, every $d_{hkl}$ causes a reflection under a defined angle $\theta_B$ and can be identified by means of this relationship and correct indexing. The intensities of these reflections are determined by the structure factor ($F_{hkl}$), which is the sum of all atomic form factors ($f$) of the atoms in the unit cell, taking their coordinates $xyz$ and Miller indices $hkl$ into account. $F_{hkl}$ determines the $I$ of the respective $hkl$ according to $I \propto |F_{hkl}|^2$.

For crystals and grains in the nm range, the shape of the reflection is affected by the confined area of periodicity, which causes reflection broadening. The full width at half maximum (FWHM) of the broadened reflection ($\Delta(2\theta_B)$) at $\theta_B$ can be used to determine the crystallite size ($L$) via the Scherrer equation (see Eq. 3.6). This formula is wavelength ($\lambda$) dependent and $K$ accounts for the shape of the crystal ($K=1$ for a sphere). The Scherrer equation is:

$$\Delta(2\theta) = \frac{K \cdot \lambda}{L \cdot \cos \theta_B}$$

(3.6)

Depending on the texture of the material, the relative intensities of the analyzed material can differ from those of a powder sample. These differences in the relative intensities can be used to identify preferential orientations of a material.$^{[157]}$

X-ray diffraction (XRD) measurements of thin films on a crystalline substrate are challenging due to the large penetration depth of X-rays. As a consequence, the intensity of the substrate peaks is much higher than the peak intensity of the analyzed thin film. To overcome this limitation, grazing incidence XRD (GIXRD) can be used.$^{[158]}$ This technique utilizes total external reflection, which arises in X-rays for small incident angles, due to the slightly lower refractive index for X-ray radiation of solids compared to air. Hence, only the evanescent wave, which decays quickly in space, penetrates the material and is scattered. Consequently, the relative intensity of the film peaks increases in GIXRD.

### 3.3.3 Ultra violet-visible and infrared spectroscopy

The photon energy dependent attenuation of a light beam, when passing a material, provides information about electronic transitions and vibrational modes that can be excited in a material. Depending on the energy of the light used for the analysis, different information can be obtained.

In ultra violet-visible (UV-vis) spectroscopy, light with energies of 1.2 to 5 eV is used, and
the absorption is measured. The Lambert-Beer law (see Eq. 3.7) describes the relation between the incoming light intensity $I_0$ and the light intensity $I$ after passing through the material. $I$ is affected by the sample thickness $x$ and the extinction coefficient ($\alpha_{ext}$), which is wavelength dependent, and unique for every kind of molecule or material.

$$I = I_0 \cdot e^{-\alpha x}$$  \hspace{1cm} (3.7)

In semiconductors, strong light absorption starts when the photon energy ($\hbar \nu$) exceeds the $E_g$. A formula to model the variation of the absorption coefficient in dependence of the $\hbar \nu$ and the so-called tailing parameter $B$, which accounts for the width of the VB and CB, was devised by Tauc (see Eq. 3.8).[159] The exponent $r$ denotes the nature of allowed ($r=1/2$, $r=2$) and forbidden ($r=3/2$, $r=3$) transitions, which can be either direct ($r=1/2$, $r=3/2$) or indirect ($r=2$, $r=3$).

$$\alpha \hbar \nu = B (\hbar \nu - E_g)^r$$  \hspace{1cm} (3.8)

By plotting $(\alpha \hbar \nu)^{1/r}$ versus $\hbar \nu$ a linear dependence occurs, if the chosen transition exists in the material, and the $E_g$ can be estimated by an extrapolation of this linear region to the base line.

For materials with high structural disorder and many defects, the DOS of the VB and CB exhibit tails that extend into the band gap region. For this region, the photon energy dependent $\alpha_{ext}$ is described by the Urbach equation (Eq. 3.9). The relation is:

$$\alpha_{ext} = \alpha_0 \cdot e^{\frac{\hbar \nu - E_g}{E_U}}$$  \hspace{1cm} (3.9)

The Urbach energy ($E_U$) is a measure of disorder in the material and can be calculated from the slope of $\ln(\alpha_{ext}) - \hbar \nu$. For disordered materials, $E_U$ is in the range of several hundred meV.

In infrared (IR) spectroscopy the photons have much lower energy (0.075-0.5 eV) and the absorption is related to the activation of vibrational and rotational modes in the analyzed material. To excite the IR-active vibrations, the dipole moment has to change. IR radiation with a frequency ($\nu$) equal to a certain dipole frequency of the material is absorbed and an absorption band occurs in the IR spectrum. The intensity of the band corresponds to the change in the dipole moment and the angle between the dipole and the incoming light. Usually, an IR spectrum is a rotation-vibration spectrum. However, rotations are suppressed in solids, and the measured absorption bands with their specific energy can be only related to vibrations.

Attenuated total reflection (ATR)-IR measurements can be used for surface sensitive
IR measurements. This method uses the total internal reflection of IR radiation that arises at the interface between the sample and a Ge crystal, which is usually used for these measurements. Consequently, only the quickly decaying evanescent wave can excite vibrations in the material and thus, only vibrations close to the surface are detected by this method.\[160\]

3.4 Experimental details

3.4.1 Sample preparation

SEM samples were prepared in top-view and cross-section by breaking the FTO substrate, covered with the TiO$_2$ NWs, into small pieces. For cross-sectional samples the fracture surface was used for imaging, and the glass side was covered with conducting Silver paste to avoid charging.

For TEM measurements, scratched and cross-sectional samples were prepared. Scratched TEM samples were obtained by scraping the TiO$_2$ NWs off the FTO substrate with a scalpel. The resulting powder was dispersed on a copper grid with a holey carbon film. For in situ heating in the TEM, the powder was dispersed in ethanol using an ultrasonic bath and the solution was drop-cast on Si$_3$N$_4$ heating chips.

TEM cross-sections were prepared according to a preparation method reported by Strecker et al.\[161\] The preparation steps are shown in Figure 3.7. Two FTO substrates, covered with TiO$_2$ NW arrays were glued together using a 10:1 mixture of GATAN G1 epoxy and

![Figure 3.7](image-url)
hardener. A thin slice of the sandwich was glued in a brass tube, which was cut into discs of approximately 200 \( \mu \text{m} \) in thickness. These discs were thinned down to a thickness of about 60 \( \mu \text{m} \) using a hand grinder. A dimple grinder was used for further thinning by grinding two centered dimples in the sample until a thickness 5-15 \( \mu \text{m} \) is reached in the center. Finally, a Gatan Precise Ion Polishing System (PIPS II, Model 695) was used to mill a wedge shaped hole along the area of interest into the sample. For this, argon ions with an energy of 4 keV were bombarded onto the sample in an angle of 4\(^\circ\). Final polishing was performed at low voltages (0.3-0.1 kV).

### 3.4.2 Analytical techniques

**SEM**

For SEM images, a Zeiss Auriga Modular CrossBeam workstation equipped with an in-lens detector was used. All images were acquired at 4 kV acceleration voltage, with an aperture of 30 \( \mu \text{m} \) and at a working-distance below 5 mm. The beam current was chosen between 20 and 250 pA.

**Conventional and HR TEM**

A Philips CM20 and a Jeol JEM-2200FS field emission gun instrument, both operated at 200 kV, were used for SAED, conventional BF and HR TEM analysis. The Jeol JEM-2200FS is equipped with a Gatan charge-coupled device camera, which has an image size of \( 2 \times 2 \text{k} \) pixels and the CM20 has a Emsis Veleta camera with an image size of \( 1024 \times 1024 \) pixels. All SAED patterns shown in this thesis were recorded at the CM20 using a camera length of 880 mm and the selected area aperture 3, which corresponds to an analyzed area of around 6.5 \( \mu \text{m}^2 \). Thus, this aperture is suitable to capture a SAED pattern of an entire NW.

**STEM**

\( C_s \)-corrected STEM images were acquired at 300 kV using a FEI Titan Themis 60-300 microscope, equipped with a high-brightness field emission (XFEG) source and an aberration corrector for the probe-forming lens system. A semi-convergence angle (\( \alpha \)) of 23.8 mrad and a beam current of around 75 pA at spot size 6 were used. For annular bright field (ABF), ADF and HAADF STEM electrons scattered at angles of 8-16 mrad, 17-72 mrad and 73-352 mrad, respectively, were collected. In addition, the microscope is equipped with a Bruker EDS SUPER X detector and a high-resolution electron energy
loss spectrometer (GATAN HIGH-RESOLUTION QUANTUM ERS energy filter) for chemical analysis.

**EELS**

EELS measurements were performed in STEM mode on the FEI Titan Themis 60-300 microscope at 300 kV with a beam current of around 120 pA and $\alpha$ of 23.8 mrad. Using an aperture of 2.5 mm at the entrance of the GATAN HIGH-RESOLUTION QUANTUM ERS energy filter, a $\beta$ of 35 mrad was obtained. EELS data were recorded using dual-channel acquisition, and all spectra were corrected for channel-to-channel gain variations and dark current. Usually, core-loss spectra were recorded with a dispersion of 0.1 eV per channel and the background was removed via a standard power law fit. $E_g$ determinations and high-resolution spectra of the Ti–L$_{2,3}$ edge were acquired in the monochromatic STEM mode with a dispersion of 0.01 eV per channel. A minimum energy resolution of 0.3 eV was obtained, as determined by the FWHM of the ZLP. For $E_g$ measurements, the zero-loss tail in the low-loss spectrum was removed by a power law fit and the band gap was extracted using the linear fit method reported by Park et al.

**EDS**

Spatially resolved EDS measurements were performed at 300 kV in STEM mode with a beam current of around 120 pA and $\alpha$ of 23.8 mrad. The EDS spectra were recorded with a Super X EDS detector from Bruker and standard-free quantification using the Cliff-Lorimer equation was performed with the Bruker software Esprit 1.9.4.3348. The obtained EDS elemental maps were correlated to the HAADF STEM images.

**In situ heating in the TEM**

In situ heating experiments in the TEM were performed on the JEOL JEM-2200FS instrument in HAADF STEM mode. A DENSsolutions double-tilt heating holder and Si$_3$N$_4$ chips were used for heating the as-grown NWs. The sample was heated from 250 °C to 600 °C with a heating rate of 3.3 °C/min and the temperature was held at 600 °C for 30 min.

**TEM tomography**

Tilt series used for the 3D reconstruction were acquired using the JEOL JEM-2200FS TEM at 200 keV in HAADF STEM mode. Tilting at a tilt range of $\pm 70^\circ$ was per-
formed with a variable tilt increment according to the scheme proposed by Saxton et al.\textsuperscript{[163]} Prior to the reconstruction, the tilt series was aligned using the TomoJ\textsuperscript{[164]} add-on in ImageJ.\textsuperscript{[165]} A discrete algebraic reconstruction technique step\textsuperscript{[166]} was used for the reconstruction.

**XRD**

XRD measurements were carried out using a Seifert Type ID3003 $\theta/2\theta$-diffractometer (GE INSPECTION TECHNOLOGIES) equipped with a Meteor OD detector, using a Co-K$_\alpha$ radiation in GIXRD mode ($\alpha=2^\circ$) to reduce the FTO signal. The XRD patterns were recorded in the ($\theta/2\theta$) mode, with a $2\theta$ scan range of 10$^\circ$-120$^\circ$.

**UV-vis spectroscopy**

UV-vis data were acquired with a Perkin Elmer Lambda 800 spectrometer in transmission mode. The absorption spectra were detected in a $\lambda$ range of 300-950 nm, with a step size of 1 nm. The obtained absorption spectra were used to determine the direct and indirect $E_g$ using Tauc plots\textsuperscript{[159]} as well as the Urbach energy.\textsuperscript{[160]}

**IR spectroscopy**

ATR Fourier transform IR measurements were performed in ambient atmosphere using a Bruker VERTEX 70v spectrometer equipped with a Bruker Hyperion 3000 microscope with a $20\times$ ATR objective. For the IR analysis, the NW array was in contact with the tip of a Ge crystal (100 $\mu$m in diameter). Each spectrum, ranging from 700 to 4500 cm$^{-1}$, was averaged over 256 scans, and the spectral resolution was 2 cm$^{-1}$.

**Scratch test**

In order to investigate the mechanical stability, scratch tests were performed using a Keysight G200 nanoindenter with a round tip (diameter: 5 $\mu$m). A scratch length of 200 $\mu$m was chosen and the load applied during the scratching was increased by a ramp up to a maximum force of 20 mN or 300 mN. The scratch speed was 0.1 $\mu$m/s, which resulted in a maximum lateral force of 0.2 mN and 0.3 mN, respectively. Each sample was scratched three times with the same conditions to exclude artifacts from sample inhomogeneities.
Current-voltage measurements

The electronic properties of the TiO$_2$ NWs were determined by current-voltage (IV) measurements. A Platinum-Iridium (PtIr) (4:1) tip was used as a top electrode, because typical deposition techniques used for flat metal electrodes would infiltrate the free space between the NWs and cause short circuits. The tip was placed gently on the NW array and pushed by its own weight (0.1 g) on a bunch of NWs. A NW free part of the FTO substrate was connected with a thin Copper wire by a drop of Silver paste to obtain the bottom contact. The IV characteristics of the transient current through the PtIr/TiO$_2$/FTO sandwich were measured in N$_2$ atmosphere. Therefore, a voltage was applied with a Keithley 2401, which was also used to record the current. In these measurements, a positive electric field was pointing from the PtIr tip towards the FTO. The IV curves were obtained by changing the field from negative to positive values.
4 Role of vacancy condensation in the formation of voids in rutile TiO$_2$ nanowires

Hydrothermally grown rutile TiO$_2$ NWs have a high density of defects, such as stacking faults, dislocations, and O$_{\text{vac}}$. In this chapter, a post-growth thermal annealing procedure in air is presented, which is capable to remove these lattice defects. Based on the analytical results, a two-step mechanism is developed. First, surface-bound -OH groups dehydrate at temperatures above 250 °C, which converts the as-grown, mesocrystalline NWs to single crystals. This process is followed by condensation of O$_{\text{vac}}$ at temperatures above 500 °C and NWs with internal voids are formed. The following, detailed description of heat treatment controlled defect engineering is mostly based on a research article that was published in *ACS Applied Materials and Interfaces*.\(^\text{[167]}\)

4.1 Introduction

Titanium dioxide is one of the most versatile metal oxides and has been suggested for many different applications, for example, in the fields of photocatalytic pollutant degradation, photocatalysis, solar cells, energy storage and conversion, novel biomaterials, and so on.\(^\text{[3]}\) There has been a great deal of efforts in the development of high-performance TiO$_2$ materials with high surface areas and low recombination rates; especially nanostructures and hollow materials have attracted considerable attention. In the past few years, many different TiO$_2$ nanostructures such as mesoporous layers,\(^\text{[168–170]}\) cubes,\(^\text{[171,172]}\) tubes,\(^\text{[173,174]}\) and wires\(^\text{[20,175]}\) have been synthesized and investigated. Among these, 1D nanostructures are noteworthy because of their superior properties, for example, a large surface area and a directed electron path.\(^\text{[176,177]}\) Since Feng *et al.*\(^\text{[178]}\) developed a simple solvothermal fabrication route for the fabrication of rutile NW arrays on conducting glass, these nanostructures have been intensively studied. However, devices incorporating these hydrothermally grown TiO$_2$ NW arrays are not as good as it was predicted for highly crystalline 1D materials.\(^\text{[50,179]}\) One reason for the low efficiency of, for example,
Vacancy condensation in TiO$_2$ nanowires

4.2 Results

Hybrid solar cells is the high recombination rate of charge carriers due to the intrinsic point defects (e.g., oxygen vacancies and Ti interstitials) and lattice defects (e.g., edge dislocation and stacking faults). There are several strategies to overcome these limitations, such as doping or limiting the diffusion of carriers in one direction, for example, by the incorporation of voids into these nanostructures.\textsuperscript{179–181} First studies on voids in rutile TiO$_2$ nanoparticles were performed by Turner \textit{et al.}\textsuperscript{182} and showed that these voids are faceted.\textsuperscript{183} Since then, many strategies have been developed to introduce voids into TiO$_2$ nanostructures and various hollow TiO$_2$ nanostructures have been synthesized and analyzed. Several microwave-assisted synthesis strategies have been developed to obtain hollow anatase TiO$_2$ nanocrystals that show a much higher photocatalytic activity compared with their dense counterparts.\textsuperscript{180,181} Another approach is the calcination of precipitated precursor particles or mesocrystals, which leads to the formation of foam-like single crystals.\textsuperscript{184,185} Although most of the hollow nanostructures investigated so far are nanoparticles, there are several reports about highly efficient devices incorporating NWs with internal voids. Apart from these reports, where the voids inside of the NWs are an uncurious side effect, there are targeted methods for incorporating those voids intentionally. Wisnet \textit{et al.} used a combination of TiCl$_4$ treatment and annealing of NW arrays to reduce the recombination in hybrid solar cells.\textsuperscript{50} Recently, Liu \textit{et al.} have proposed a combination of helium ion implantation and subsequent annealing to introduce voids inside of rutile TiO$_2$ NWs, thereby enhancing photoelectrochemical water splitting.\textsuperscript{179} Another approach is the thermal treatment of H$_2$Ti$_3$O$_7$ NWs, which results in voids inside of the TiO$_2$ NWs.\textsuperscript{186} However, the resultant NWs are not rutile but possess the anatase crystal structure, and the voids arise during phase transformation due to volume differences.

Although TiO$_2$ NW arrays with voids have been incorporated in many well-performing devices such as solar cells, photoelectrodes, and others,\textsuperscript{50,179,187–189} so far, no detailed study on the formation mechanism of these voids has been reported. In the present study, we demonstrate how internal voids can be introduced into hydrothermally grown TiO$_2$ NWs through a thermal annealing process and propose a possible mechanism that explains the formation of internal voids and the related property changes of the NWs.

4.2 Results

The crystal structure of the as-grown and annealed TiO$_2$ NW arrays on the FTO substrate are investigated using glazing incidence XRD (see Fig. 4.1). All peaks either correspond to the FTO substrate (marked with filled circles) or to rutile TiO$_2$ for both the as-grown...
and the annealed TiO$_2$ NW arrays. The FWHM of the $\{101\}$ and $\{111\}$ peaks decrease, and the peaks are shifted to higher $2\theta$ values for the annealed TiO$_2$ NWs (see Fig. 4.1b,c). The peaks are used to calculate the lattice parameters $a$ and $c$. The change in the peak position, FWHM, lattice parameters $a$ and $c$, and the axial ratio $c/a$ are summarized in Table 4.1. The as-grown NWs have slightly larger lattice parameters than the annealed NWs. Only the FWHM is considerably reduced.

![Figure 4.1](image)

**Figure 4.1:** a) XRD pattern of as-grown and annealed TiO$_2$ NW arrays on FTO substrate. The peaks marked with a filled dot arise from the FTO substrate. Zoom in of b) $\{101\}$ and c) $\{111\}$ reflection of rutile TiO$_2$.

<table>
<thead>
<tr>
<th>sample</th>
<th>peak position $2\theta$ (deg)</th>
<th>lattice parameter $a$ (Å)</th>
<th>lattice parameter $c$ (Å)</th>
<th>FWHM ${101}$ (deg)</th>
<th>FWHM ${111}$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-grown</td>
<td>42.18</td>
<td>4.597</td>
<td>2.965</td>
<td>0.6429</td>
<td>0.6138</td>
</tr>
<tr>
<td>4 h @ 500 °C</td>
<td>42.22</td>
<td>4.589</td>
<td>2.953</td>
<td>0.6434</td>
<td>0.5542</td>
</tr>
</tbody>
</table>

The ATR-IR spectra of the as-grown and annealed TiO$_2$ NWs are presented in Figure 4.2. Both spectra show interference fringes.$^{[190–192]}$ Interference fringes are expected for the IR-transparent layers of several micrometers of thickness in direct contact with the ATR crystal. These fringes are neglected in the following discussion. Both samples have a strong absorption below 1000 cm$^{-1}$. This absorption is due to the Ti-O stretching modes.$^{[193,194]}$ The absorption peak in the IR-spectral region between 1000 and 1300 cm$^{-1}$ arises from the deformation vibrations of the Ti-O-H bonds.$^{[195]}$ The features below 1300 cm$^{-1}$ are not affected by the heat treatment. By contrast, the absorption in the range of 4000-2500 cm$^{-1}$ and around 1600 cm$^{-1}$ change because of the heat treatment. These peaks can be attributed to the O-H stretching and bending modes of water, bound by chemisorption and physisorption on the TiO$_2$ surface.$^{[196,197]}$
stretches modes correspond to the bridged O-H groups (around 3700 cm$^{-1}$), the terminal O-H groups (around 3670 cm$^{-1}$), and the hydrogen-bonded terminal O-H groups (around 3420 cm$^{-1}$).\[196\] The peak at around 1670 cm$^{-1}$ is an O-H bending mode of chemisorbed H$_2$O.\[197\] The sharp peak that is visible for the as-grown TiO$_2$ NWs is removed because of the heat treatment. The residual features are the above-mentioned interference fringes.

SEM investigations reveal a 1D morphology of the NWs that grow almost perpendicular to the FTO substrate (see Fig. 4.3). Neither the diameter (as-grown, 73 ± 13 nm; annealed, 70 ± 16 nm) nor the length (as-grown, 1005 ± 51 nm; annealed, 1019 ± 78 nm) of the NWs is affected by the heat treatment. However, the rough morphology at the wire top of the as-grown NWs is smoothed during the heat treatment.

TEM images of the scratched-off NWs before and after annealing (see Fig. 4.4a,e) confirm the SEM results. The as-grown TiO$_2$ NWs consist of a single-crystalline shell and a core with a high defect density building up a V-shaped defect cascade toward the wire top, as observed in earlier studies.\[48\] An edge dislocation is representatively shown in Figure 4.4c. Additionally, the NW splits into thin nanofibers (diameter: 6.1 nm), which results in a rough morphology at the wire top. The dark signal in the HAADF STEM image (see Fig. 4.4d) parallel to the growth direction of the NW indicates a lower density or an open space between the fibers. We identified it as internal surfaces between the nanofibers, which lead to a large internal free surface area of the as-grown NWs. The
4.2 Results

Figure 4.3: Top-view (a,c) and cross-sectional (b,d) SEM micrographs of the as-grown (a,b) and annealed (c,d) TiO$_2$ NWs on FTO. The insets in a) and c) show a zoomed-in view of a single NW with changed morphology at the wire top. The scale bar of the inset images is 40 nm.

Overall surface area-to-volume ratio for a NW with 6.1 nm thick fibers is 0.66 nm$^2$/nm$^3$, with the \{110\} facets [surface energy per unit area ($E_{110}$) is 0.42 J/m$^2$]\textsuperscript{[139]} representing the main surface planes. By neglecting the surface at the top end of the fibers (mainly \{111\} and \{001\} facets), one can calculate the surface energy density of the as-grown NWs as $E_{\text{surface,ag}}=2.8 \times 10^8$ J/m$^3$. However, the internal surfaces are not accessible for any process related to photocatalysis or solar cells because the spacing between the nanofibers (0.50 ± 0.16 nm) is too small for water or dye molecules to diffuse inside. The corresponding SAED pattern of the as-grown TiO$_2$ NW (see Fig. 4.4b) shows a highly oriented rutile TiO$_2$ crystal structure, differentiating from a SAED pattern of a single crystal in the [110] zone axis only by the streaking of the diffraction spots along the [110] direction. Thus, the nanofibers are highly oriented with a [001] growth direction.

For NWs heated at 500 °C for 4 h, no lattice defects are detectable, and the fibers are grown together, as there is no dark signal in the HAADF STEM image parallel to the
Figure 4.4: TEM micrographs of an as-grown (a-d) and annealed (e-h) NW. BFTEM images (a,e) and the corresponding SAED patterns (b,f) indicate a rutile crystal modification for both NWs. The HR TEM image shows an edge dislocation for the as-grown NW (c). HR HAADF STEM image of a faceted void for the annealed NW (g). HAADF STEM images indicate that the as-grown NW is built by a bundle of nanofibers (d) and the annealed NW comprises voids (h). Both images are taken from the representative areas located in the center of the NW.
4.2 Results

Vacancy condensation in TiO$_2$ nanowires growth direction (see Fig. 4.4h). Only at the NW top, a fiberlike morphology is visible. These residuals of the nanofibers are also grown together resulting in thicker nanofibers (diameter, 8.8 nm) and a much smoother morphology at the wire top. Merging of the nanofibers is a slow process, which starts already at comparably low temperatures of around 250 °C (see Movie S1$^1$). The corresponding SAED pattern of the annealed TiO$_2$ NW (see Fig. 4.4f) resembles a single-crystalline rutile TiO$_2$ crystal structure without any streaking, as both the lattice defects and the nanofibers are removed during the heat treatment. Instead of the defect-rich nanofiber bundles, the HAADF STEM image shows features that appear dark and with an elongated bipyramidal shape. According to TEM tomography reconstructions, these features can be attributed to the voids inside of the NW (see Movie S2$^2$). Using in situ TEM heating experiments (see Movie S1$^1$), we could show that within one NW, all voids form almost simultaneously as soon as a critical temperature (around 500 °C) is reached. The voids are immediately formed in their final shape and show no change in shape or size during further annealing at 600 °C for 30 min. Because of the voids, annealed NWs also exhibit an internal free surface area. The surface area-to-volume ratio for an annealed NW (originating from a NW with 6.1 nm thick nanofibers in the as-grown state) is 0.1316 nm$^2$/nm$^3$. HR STEM images prove that these voids are close to the inverse Wulff shape of rutile TiO$_2$ with main contributions of the \{001\} ($E_{001} \approx 1.15$ J/m$^2$), [$^{198}$] \{110\} ($E_{110} \approx 0.42$ J/m$^2$), [$^{198}$]$^{[198]}$ and \{111\} ($E_{111} \approx 1.3$ J/m$^2$)[$^{198}$] planes. For Wulff-shape-like voids, the average surface energy per unit surface thus can be calculated to be $E_{Wulff} \approx 0.75$ J/m$^2$, resulting in a surface energy density of $E_{surface,HT} = 9.9 \times 10^7$ J/m$^3$ for annealed NWs. However, as these voids are internal voids, these surfaces are not accessible for any chemical reactions. Cross-sectional TEM samples allow an analysis of the structure of these voids in more detail. Figure 4.4g shows that the crystalline area adjacent to the void is not distorted and that the voids are not entirely hollow, but the void surface is covered with an amorphous titanium oxide phase.

To probe the electronic structure of the NWs, we performed an EELS analysis of the as-grown and annealed TiO$_2$ NWs. The ELNES of the Ti-L$_{2,3}$ edge and the O-K edge are shown in Figure 4.5. Both spectra are recorded over a large area, representing the averaged bonding behavior and the oxidation state of the atomic species of each type of NW. The Ti-L$_{2,3}$ edge consists mainly of two doublets, representing the t$_{2g}$ and e$_g$ peaks of the Ti-L$_3$ edge at lower energy losses and the Ti-L$_2$ edge at higher energy losses. The edge onset (457.5 eV) and the peaks are not shifted with respect to each other and are close to the literature values for bulk rutile TiO$_2$.$^{[139,199]}$ The $I(L_2)/I(L_3)$ intensity ratio

$^1$The movie is available free of charge at: http://pubs.acs.org/doi/suppl/10.1021/acsami.7b01160
4 Vacancy condensation in TiO$_2$ nanowires

4.2 Results

Figure 4.5: (a) Core-loss EELS spectra of an as-grown and an annealed TiO$_2$ NW showing the Ti-L$_{2,3}$ and O-K edges. (b) Ti-L$_{2,3}$ ELNES with t$_{2g}$-e$_g$ splitting caused by the distorted oxygen octahedral surrounding of Ti atoms and (c) O-K ELNES.

is calculated as changes in this ratio are related to the Ti valance state. The analysis was done according to the procedure described by Stoyanov et al. using the following equation:

$$\frac{T_{i}^{4+}}{\Sigma Ti} = 0.21767 \cdot \left( \ln \left( \frac{I(L_2)}{I(L_3)} \right) - 0.87953 \right)$$ (4.1)

For both, Ti$^{4+}$/ΣTi (with ΣTi=Ti$^{4+}$+Ti$^{3+}$) is around 80%. Thus, the average electronic structure of the NW does not change during heat treatment, and no oxidation of incorporated Ti$^{3+}$ to Ti$^{4+}$ takes place within the detection limit. This result is emphasized by the O-K edge, which changes neither in shape nor in intensity, indicating that the heat treatment in air does not result in any oxygen uptake into the NW. Although the average electronic structure of the heat-treated NWs does not differ from that of the as-grown NWs, one can detect local changes in the electronic structure. Figure 4.6a-c shows an EELS map and the corresponding EEL spectra of an annealed NW, which was thinned for TEM observation until the top and bottom surfaces of the void were removed. This enables the analysis of the amorphous material covering the void surface, without any contribution of the crystalline rutile TiO$_2$ that surrounds the void. The EELS map is color-coded according to the onset of the Ti-L$_{2,3}$ edge, where red represents an edge onset below 457 eV and blue represents an edge onset above 457 eV. The Ti-L$_{2,3}$ edge of the amorphous TiO$_x$ material covering the void surface is shifted by 1 eV to lower energies. The amount of Ti$^{4+}$ is calculated by the $I(L_2)/I(L_3)$ intensity ratio and is around 70% for the rutile TiO$_2$, in which the void is embedded and is around 35% for the amorphous part on the void surface. Figure 4.6d shows the variation in the Ti$^{4+}$ concentration in the area of such a void, where only the crystalline matrix was removed and the amor-
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Vacancy condensation in TiO$_2$ nanowires

Figure 4.6: (a) HAADF-STEM image of an annealed TiO$_2$ NW after Ar$^+$ ion milling. The marked area was used for STEM-EELS measurements. Note that the amorphous layer in the right part is viewed edge on, whereas the part in the left is inclined and appears much more extended due to projection. (b) Corresponding EELS map is color-coded according to the edge onset of the Ti-L$_{2,3}$ edge (red, edge onset below 457 eV; blue, edge onset above 457 eV). (c) Corresponding EEL spectra for the crystalline (solid line) and amorphous (dashed line) area. (d) Ti$^{3+}$/Ti$^{4+}$ ratio in the area of a void.
phous material remained. Both the shift of the edge onset and the lower amount of Ti$^{4+}$ indicate that the amorphous material on the void surface consists of reduced TiO$_2$-x.

To investigate the influence of the changes in the crystal and electronic structure with respect to the optical properties, the band gaps of the as-grown and annealed TiO$_2$ NWs were investigated. The band gap averaged over an entire NW array is determined by UV-vis data-based Tauc plots for a direct semiconductor (see Fig. 4.7a). This Tauc plot shows an optical band gap of 2.88±0.09 eV for the as-grown NWs and a band gap of 2.56±0.03 eV for the annealed NW array. Although the measurements show that both materials weakly absorb blue light, the NW arrays appear white, which might be related to a strong light reflection caused by the NW array. The signal at energies below the optical band gap arises from the tails of the valence and conduction bands. The width of this Urbach tail, the Urbach energy, is 0.62±0.01 eV for the as-grown NWs and 0.49±0.01 eV for the annealed NWs. In addition, the band gap of a single NW for each, the as-grown and the annealed state, is determined by TEM-based EELS measurements. The corresponding, zero-loss subtracted, low-loss EEL spectra for the as-grown and the annealed NW are shown in Figure 4.7b. These measurements show a reduction in the optical band gap because of heat treatment from 2.8±0.1 to 2.4±0.1 eV. Results from EELS and the Tauc plot agree within double standard deviation.

![Figure 4.7](image_url)

**Figure 4.7:** Optoelectronic properties of the as-grown (filled squares) and annealed (open circles) NWs. (a) UV-vis-based Tauc plots of NW arrays and (b) low-loss EEL spectra of single NWs after removing the zero-loss peak.
4.3 Discussion

In the following, we present a detailed description of the as-grown and annealed NWs, using the obtained morphological, crystallographic, and spectroscopic results and propose a possible mechanism to explain the formation of the voids.

HR STEM, electron diffraction, and XRD reveal that the as-grown NWs consist of single-crystalline-like rutile TiO$_2$ nanofibers, which bundle. The nanofibers grow along the [001] direction and are highly oriented with respect to each other, resulting in a mesocrystalline material. These findings are in good agreement with previous studies on hydrothermally grown NWs.[48,49,200] According to our IR measurements, we have a high amount of hydrogen-bonded OH groups on the surfaces of these NWs. Jordan et al. found that such hydrogenbonded OH groups are present on the surface of the thin fibers and hydrogen bonds are formed between two of these fibers.[49] The distribution of distances between the nanofibers and the consequent differences in the hydrogen bond length may contribute to the broadening of the IR absorption peaks. The broadened peaks in XRD and the streaking of the electron diffraction spots originate not only from the thin fibers but also from the lattice defects inside of the NW. The main defects detected in HR TEM are edge dislocations, as shown before.[48] The amount of dislocations is difficult to determine, but the narrowing of the X-ray diffraction peaks by around 10 % during annealing and the strong contrast of the V-shaped dislocation cascade (Figure 4.4a) indicate that the overall concentration of dislocations must be quiet high in the as-grown NW. In addition, the spectroscopic analysis revealed a high Ti$^{3+}$ concentration of approximately 20 % within the entire NW; however, both XRD and electron diffraction experiments prove the rutile crystal structure and exclude the existence of any Magneli phases such as Ti$_4$O$_7$, Ti$_6$O$_{11}$, or Ti$_7$O$_{13}$.[79,80] Instead, the shift of the Ti-L$_{2,3}$ edge of Ti is caused by an incorporation of oxygen vacancies (O$_{vac}$) in the crystal structure, leading to the expanded rutile TiO$_2$ unit cell of the as-grown NWs compared with bulk TiO$_2$.[73] As the axial ratio is the same as reported for bulk rutile TiO$_2$, there is no evidence for ordering of the O$_{vac}$ along special lattice planes.

After the heat treatment, the NW morphology and the rutile crystal structure are preserved; thus, we can exclude any phase transformation taking place during the heat treatment. This result is in good agreement with previous studies, which showed that rutile TiO$_2$ is the thermodynamically most stable TiO$_2$ phase.[201] Consequently, oxygen deficiency does not influence the thermodynamics of rutile TiO$_2$. Although the NW morphology in general does not change, there is a significant change in the internal structure. The hydrogen bridged O-H groups that are on the surface of the fibers in the as-grown
NWs are removed, as the IR absorption peak around 3400 cm$^{-1}$ disappears. The physically adsorbed water evaporates as well. The nanofiber bundle transforms into a single crystal incorporating voids. These voids are anticrystals with the Wulff shape of rutile TiO$_2$ and intercalate perfectly in the lattice without causing significant stresses in the crystal structure. Based on a rough estimation, the volume fraction of the voids with respect to the entire NW volume is around 25%, which results from the rearrangement of the free space between the nanofibers (13%) and the volume covered by O$_{\text{vac}}$ (5-11%). The calculated volume fractions are in good accordance, but it is noteworthy that the errors are high, especially because the charge of the O$_{\text{vac}}$ is unknown, and thus deriving the number of O$_{\text{vac}}$ (10-20% of O in TiO$_2$) from the amount of Ti$^{3+}$ is prone to error. Similar voids are also formed in rutile TiO$_2$ nanoparticles.[182,183] Along with the nanofibers, the lattice defects are also removed, and thus the XRD shows sharper peaks, and the streaking of the electron diffraction peaks is not present anymore. Although the NWs are heated in air, there is no change in the Ti-L$_{2,3}$ edge averaged over an entire NW. Thus, on a global scale, no oxidation takes place. The stability against oxidation might be related to the perfect single-crystalline surface of the NW even in the as-grown state, which inhibits the penetration of oxygen atoms. Consequently, the oxygen content in the atmosphere is not a decisive factor for the processes taking place inside of the NW upon annealing. However, locally, the electronic structure of the NW does change significantly because of the heat treatment. HR STEM images show that there is no sharp rutile-vacuum interface for the voids, but the voids are covered with an amorphous TiO$_x$ phase. According to the EELS data, this phase has a significantly higher amount of Ti$^{3+}$, which is up to 80% of Ti$^{3+}$ in the amorphous material. However, one has to take into account that these samples are Ar$^+$ ion-milled. Ar$^+$ ion milling can produce oxygen-deficient samples because of the different sputter rates of Ti and O.$^{[202,203]}$ The Ti$^{3+}$ concentration of these samples is slightly overestimated because of Ar$^+$ sputtering. As this effect is homogeneous over the entire TEM sample, the concentration variations are not an artifact and we can state that a vacancy condensation takes place. Coincident with the accumulation of the Ti$^{3+}$ at the inner void surface, the unit cell is contracted, compared with the as-grown state, indicating a lower oxygen vacancy concentration in the rutile lattice.$^{[73]}$ All of these findings lead to the following two-step mechanism, which explains the transformation taking place inside of a hydrothermally grown rutile TiO$_2$ NW upon annealing. We postulate a two-step mechanism because there are two different phenomena: the mesocrystal merging to a single crystal and the condensation of the O$_{\text{vac}}$ to form voids. In a first step, a condensation reaction at the hydrogenbonded OH-groups takes place. The dehydratization is accompanied by the formation of a new Ti-O-Ti bond, which con-
nects two thin nanofibers. These fibers are present only in the as-grown state. It starts at the beginning of the fiber splitting close to the center part of the NW, as the distance between the two fibers is closest there. This process is repeated multiple times, and thus the nanofibers merge together in a zipperlike condensation process. This condensation starts already at quiet low temperatures of around 250 °C and is a rather slow process (see Movie S1‡). The produced water molecules leave the NW as they are gaseous at the annealing temperature. As all Ti-O-H bonds are replaced by Ti-O-Ti bonds, there is neither a global nor a local change in the oxidation state of Ti during this process, and the Ti⁴⁺/Ti³⁺ ratio remains the same as in the as-grown state.

In a second step, an agglomeration of O vac takes place. Because of the low temperature during the hydrothermal growth, there is a high concentration of defects, especially O vac in the rutile crystal structure. As the nanofibers merge together, the O vac can diffuse within the NW. Upon reaching a critical temperature (around 500 °C), O vac condense rapidly, and the voids with inverse Wulff shape are formed. Using in situ TEM heating experiments (see Movie S1‡) we could show that within one NW, all voids form almost simultaneously. The voids are immediately formed in their final shape and show no change in shape or size during further annealing at 600 °C. Such a vacancy condensation is well-known for metals,[204,205] however, it has not been observed for metal oxides so far. Our findings show that the oxygen vacancy concentration within the rutile crystal structure is significantly decreased due to the vacancy condensation upon annealing. This finding is key to understand the change in properties. According to calculations, the band gap is directly linked to the concentration of O vac.[206] Thus, the as-grown NWs with high O vac concentration inside of the rutile crystal structure exhibit a larger band gap, and the annealed NWs with less O vac in the rutile crystal structure have a smaller band gap. This change in the band gap corresponds to the band gap energies measured using UV-vis and low-loss EELS. Concurrently, the Urbach energy is decreased after the heat treatment, which indicates a lower degree of lattice disorder and less charged impurities such as O vac in the crystal structure.[207] Consequently, deep trap states in the band gap must have been reduced,[208–210] and the recombination rate of electron-hole pairs created during illumination for the annealed NWs should significantly decrease. Furthermore, the oxygen-deficient amorphous material on the void surface has a good hole conduction, and thus some of the h⁺ can be injected into the oxygen-deficient amorphous material.[211] The trapped h⁺ cannot recombine with free e⁻, and the amount of free charges is increased.

‡The movie is available free of charge at: http://pubs.acs.org/doi/suppl/10.1021/acsami.7b01160
4.4 Conclusion

We have proposed a two-step mechanism that explains the changes taking place inside of a hydrothermally grown TiO\textsubscript{2} NW upon annealing at 500 °C in air. Rutile TiO\textsubscript{2} NW arrays were synthesized on FTO glass substrates. These NWs were investigated in the as-grown state and after a 4 h heat treatment at 500 °C in air. TEM, XRD, and EELS investigations revealed highly defective, mesocrystalline NWs for the as-grown state with a high amount of lattice defects (edge dislocations and O\textsubscript{vac}). Upon annealing, the lattice defects are removed and the mesocrystal merges to a single crystal. Concurrently, the O\textsubscript{vac} condense in Wulff-shaped voids that are covered with amorphous TiO\textsubscript{x}. As the defects in the rutile crystal structure are removed, the properties of the material change. The band gap is narrowed, and mid-band gap states must have been reduced as a consequence of the vacancy condensation. One is, thus, expecting reduced carrier recombination, as the amount of O\textsubscript{vac} in the rutile crystal structure is decreased significantly.

4.5 Stability of as-grown and annealed TiO\textsubscript{2} NW arrays

The heat treatment of TiO\textsubscript{2} NWs in air does not only affect the structure and the optical properties of the NWs, but also changes other material related properties. In terms of application, especially the chemical and mechanical stability are of interest. During device fabrication, the NW arrays must withstand harsh conditions and mechanical stresses. In the following sections, the influence of the heat treatment on the chemical stability in acidic solution and resistance to scratch damage are discussed.

4.5.1 Chemical stability against acids

TiO\textsubscript{2} has an amphoteric character and thus, it is soluble in acidic and alkaline solutions. According to the Pourbaix diagram of TiO\textsubscript{2} at zero voltage, it is stable for pH values between 2.5 and 12.\textsuperscript{[212]} Thus, strongly acidic conditions are suitable to etch TiO\textsubscript{2}. In the past, TiO\textsubscript{2} was successfully etched using hot H\textsubscript{2}SO\textsubscript{4},\textsuperscript{[213]} HF-HCl\textsuperscript{[214]} or H\textsubscript{3}PO\textsubscript{4}-H\textsubscript{2}O\textsubscript{2}\textsuperscript{[215]} mixtures. Ryzhenko et al.\textsuperscript{[212]} studied the solubility of rutile TiO\textsubscript{2} aqueous solutions of HCl, HF, H\textsubscript{2}SO\textsubscript{4}, NaOH, and NaF under hydrothermal conditions of 500 °C and 1000 bar, but due to the low concentration of etching agent, the pH was close to 7.\textsuperscript{[216]}

In this work, the chemical stability was investigated by etching of the NW arrays under hydrothermal conditions using a 4.3 M HCl solution, which has a pH close to 0. According to the Pourbaix diagram,\textsuperscript{[212]} these conditions should be suitable to dissolve TiO\textsubscript{2} without applying a voltage. The as-grown and annealed TiO\textsubscript{2} NW arrays after etching are shown
4.5 Stability of TiO$_2$ nanowires

Vacancy condensation in TiO$_2$ nanowires

Figure 4.8: SEM images of a) as-grown and b) annealed TiO$_2$ NW arrays after etching in HCl.

in Figure 4.8. Independent of the pre-treatment (as-grown or annealed in air), the NWs still attach to the FTO substrate. However, significant differences between the as-grown and the annealed NWs can be seen. The as-grown NWs changed their morphology from a wire to a tube, whereas the NWs annealed at 500 °C in air for 4 h still have a wire-like morphology after the etching. Consequently, the resistance against acidic solutions is much higher for the NWs that are annealed at 500 °C.

These results are in good agreement with the mechanisms derived for the heat treatment in air. The core of the as-grown NW is built by a bundle of nanofibers and thus, has many free surfaces, which are covered with Ti-OH groups. These surfaces can be attacked by H$^+$ and accordingly, the etching of this part of the as-grown NW is fast. In contrast, the wall, which is already single-crystalline in the as-grown state, has a higher stability and withstands the acidic conditions. These different etching rates within the as-grown NW result in hollow NWs. The NWs annealed at 500 °C in air consist mostly of a dense material with voids in the interior and has much less reactive Ti-OH groups. As a result, they are almost not etched by the acidic solution under hydrothermal conditions. However, Figure 4.8b shows that also annealed NWs can be etched at the rough surface of the NW tip or if the surface is damaged. These results lead to the conclusion that the etching behavior mainly depends on the amount of active, Ti-OH rich surfaces, which are present in a large fraction at the as-grown NWs.

4.5.2 Mechanical stability

In addition to a harsh chemical environment, the NW arrays might be affected by mechanical stresses. For bulk TiO$_2$ the mechanical properties are known (Young’s modulus: 283 GPa, hardness: 7-11 GPa), but nanosized and porous materials usually show a different mechanical behavior. For TiO$_2$ nanotube arrays nanoindentation was
used to study the mechanical properties. Such arrays show a decreased Young’s modulus and hardness\cite{220–222} compared to the bulk properties. Although both, nanotubes and nanowires build an array of several μm long 1D nanostructures, the results from the nanotubes cannot be directly transferred to NWs, because the geometry and crystallinity (amorphous or anatase TiO$_2$) of nanotubes differs from the one of the rutile TiO$_2$ NWs. In this work, scratch tests were performed to analyze the resistance to scratch damage of the TiO$_2$ NW arrays. The SEM images in Figure 4.9 show the NW arrays after scratching.

For both samples, the NWs cannot be detached from the FTO substrate. This results are in good agreement with the results obtained by etching experiments and show that there is a strong adhesion between the FTO substrate and the NWs, if the mechanical stress is confined in a small area. Thus, both NW arrays show a certain resistance against scratch damage. In contrast, mechanical stress on the entire NW array, as obtained by an ultrasonic treatment, is suitable to detach large areas of the NW array. Such detached areas are shown in Figure 4.10 in side-view and from the bottom that was in contact with the FTO substrate prior to the ultrasonic treatment. These images indicate that during the initial state of growth a thin seed layer of TiO$_2$ forms, which mimics the structure of the FTO substrate. On top of this layer the NWs start to grow. Due to this compact seed layer, which connects the NWs with each other, the NW array withstands high chemical and locally limited mechanical stresses, such as scratches.
4.5 Stability of TiO$_2$ nanowires

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Figure 4.10: SEM image of a detached NW array in the as-grown state achieved by ultrasonic treatment. a) is a side-view and b) shows the bottom of the array, which was attached to the FTO substrate before.

Although the force during scratching is not high enough to detach the NWs, the scratching is sufficient to change the NW tip of the as-grown NWs. While the entire nanofiber bundle maintains its structural integrity, a deformed contact layer at the NW tip forms. The tips are highly deformed in scratching direction (see Fig. 4.9c). During the scratching, the nanofiber bundle has to sustain combined bending and compression load. As the fibrous structure is built by a bundle of 6.1 nm thick and around 2 $\mu$m long nanofibers that are only connected by weak hydrogen bonds with each other, they exhibit a large aspect ratio. Thus, the compression can be neglected and the plastic deformation at the NW tips is dominated by a bending of the nanofibers during scratching. Similar deformation mechanism are found for carbon-nanotube bundles.$^{[223–225]}$ In contrast, the NWs annealed in air show only a weak response to the lateral force of the scratch and almost no deformation can be seen (see Fig 4.9f). These NWs are a single-crystalline material that is interspersed with voids. Thus, the entire NW is interconnected by strong Ti-O-Ti bonds, and no weak hydrogen bonds are present. Due to the higher bond strength, deformation is hindered for the NWs annealed in air.

More significant differences can be seen for samples, scratched with much higher forces of up to 300 mN (see Fig. 4.11). On one hand, for the as-grown NWs the same effects as for the lower force can be observed, but due to the higher force they are more pronounced. In Figure 4.11a the force was 200 mN and the NWs are so strongly deformed that they almost form a closed layer. The nanofibers are still visible and only a minority of these fibers broke due to the higher force. On the other hand, the annealed NWs cannot withstand the forces of $\geq$200 mN and break (see Fig. 4.11b). For most NWs a smooth $\{100\}$ surface results after the fracture. Similar fracture behavior is observed after indentation.
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Figure 4.11: SEM images of a) as-grown and b) annealed NW after scratching (from left to right) with a load of around 200 mN.

Thus, the heat treatment makes the NWs harder, but more brittle. For application, both, a dense deformation layer on top of the NW array as well as broken NWs are not favored. The dense layer prevents the filling of the free space between the NWs with active material (polymer, dye, electrolyte, water). Loose NW fragments are not connected to the conducting substrate anymore, which might in best case only lead to a loss in efficiency, but can also result in worst case in short circuits within the device.
5 Tuning the electronic conductivity in hydrothermally grown rutile TiO$_2$ nanowires: Effect of heat treatment in different environments

In this chapter, the influence of heat treatments on hydrothermally grown rutile TiO$_2$ NWs is extended to different annealing environments, namely oxygen and nitrogen. This treatments allow to control the distribution of defects inside the NW and thus, give a direct access to tune the nanostructure as well as the optical and electrical properties of rutile TiO$_2$ NWs. The highly defective as-grown NW arrays have a white appearance and are n-type semiconductors, due to the high amount of O$_{\text{vac}}$. Heat treatment in O$_2$ induces a vacancy condensation and results in NWs, which possess insulating properties, whereas heat treatment in N$_2$ leads to NW arrays that appear black and have almost metal like conductivity. The following chapter is a modified version of a paper published in Nanomaterials$^{[226]}$ and shows how heat treatments in different environments can be used for defect engineering and simultaneously modify the properties.

5.1 Introduction

Nanostructured TiO$_2$ is a promising material in the field of energy conversion and storage.$^{[53]}$ In most TiO$_2$ applications, the efficiency of the device is determined by three consecutive processes: light absorption, charge separation, and electron transport. Although TiO$_2$ is widely used for energy applications, the efficiency of bare TiO$_2$ is limited by a wide band gap of around 3 eV$^{[227]}$ and a relatively low electron conductivity.$^{[228,229]}$ To overcome these limitations, defect engineering can be used to optimize the optical band gap and the electrical properties. In combination with an optimized geometry, which can be derived from theoretical calculations,$^{[230]}$ defect engineering enables the fabrication of highly active devices.

Defects can be introduced in TiO$_2$ by metal$^{[231]}$ and nonmetal$^{[232,233]}$ impurities or
dopants. However, this approach has the drawback that the dopants, especially d-block transition metals, also act as recombination centers for the generated electron hole-pairs,\textsuperscript{[234]} which in turn lowers the efficiency of the device. Other approaches to produce defective TiO$_2$ without doping are mediated by the incorporation of Ti$^{3+}$ and O$_{\text{vac}}$ via reduction,\textsuperscript{[235–237]} which might introduce surface disorder in addition.\textsuperscript{[32,238,239]} Most approaches use hydrogen environment and elevated temperatures\textsuperscript{[32,240,241]} or a hydrogen plasma\textsuperscript{[242,243]} to produce defective TiO$_2$. Similar types of defective TiO$_2$ can be obtained, if active metals, such as Zn,\textsuperscript{[235,244]} Al,\textsuperscript{[245]} or Mg,\textsuperscript{[246]} are used as a reductant. However, these harsh reductive conditions are not mandatory to obtain defective TiO$_2$. Instead, black TiO$_2$ nanoparticles with surface disorder can be obtained by annealing amorphous nanoparticles in Ar gas.\textsuperscript{[238]} Concededly, there are no reports which show that crystalline TiO$_2$, e.g., rutile TiO$_2$ NWs, can be reduced in an oxygen-deficient atmosphere, such as vacuum, Ar or N$_2$.

The effect of defect engineering on the optical band gap and the apparent color, which can be tuned from yellow over blue to black, has been studied extensively.\textsuperscript{[240,247,248]} Apart from that, reports about how structural changes, such as the introduction of O$_{\text{vac}}$ or surface disorder, influence the electrical properties are rare. So far, Nowotny and co-workers studied the influence of defect disorder on the semiconducting properties of rutile TiO$_2$ and found a strong effect on the electrical properties.\textsuperscript{[35,249,250]} Especially, a high amount of O$_{\text{vac}}$, which is intrinsically found in rutile TiO$_2$, leads to strong n-type characteristics. In addition, the influence of O$_{\text{vac}}$ on the conducting properties of TiO$_2$ NWs was evaluated by intensity-modulated photocurrent spectroscopy. For oxygen-deficient NWs, two electron-transport modes, a trap-free mode in the core and a trap-limited mode near the surface, were detected.\textsuperscript{[251]} Recently, Lü et al.\textsuperscript{[252]} investigated the effect of the surface disorder on the electrical properties. On a 40 nm thick bilayer structure of crystalline anatase ($\approx$20 nm) and amorphous TiO$_2$ (20 nm), which serves as a model system, they found a metallic conductivity at the interface between the crystalline and the amorphous part. These results give a first hint on the electrical properties of the defective, black TiO$_2$. Admittedly, in this model system the amorphous layer does not represent the surface disorder found in black TiO$_2$ adequately. It is much thicker and does not show any ordering phenomena.\textsuperscript{[252]}

In this work, we present how the electrical properties of TiO$_2$ NW arrays, incorporating rutile TiO$_2$ NWs with different defect states, can be changed. A detailed analysis of the nanostructure and the local chemical environment of three differently treated NW arrays, in combination with our results from UV-vis and IV measurements, leads to a better understanding of the underlying mechanism that are responsible for the electronic
properties of defective TiO$_2$. The results show how TiO$_2$ NWs, which are intrinsically n-type semiconductors in the as-grown state, can be converted to almost insulating TiO$_2$ NWs or NWs with a metal-like conductivity simply by using an appropriate atmosphere for the post-growth annealing.

### 5.2 Results

SEM investigations (see Fig. 5.1) reveal that the NW arrays of the three samples consist of NWs which grow almost perpendicular to the FTO substrate and are of similar size (diameter of as-grown: 164±31 nm, annealed in air: 172±16 nm, annealed in N$_2$: 157±28 nm). The high magnification SEM images in the insets of Figure 5.1 disclose slight morphological changes at the tip of the NWs. The as-grown NWs (see Fig. 5.1a) possess a rough tip, which is built by a bundle of nanofibers, as shown before by Wisnet et al.$^{[48]}$ This structure is removed for the NWs annealed in air (see Fig. 5.1b), which have a much smoother surface. The tip of the NWs annealed in N$_2$ looks like an intermediate state between the as-grown NWs and the NWs annealed in air, although it was annealed at the same temperature for the same time. For the NWs annealed in N$_2$, the nanofiber bundle is still visible at the tip, but not as prevalent as in the as-grown NWs.

![Figure 5.1](image_url)

**Figure 5.1:** SEM images of NW arrays, which are a) as-grown, b) annealed in air and c) annealed in N$_2$. The insets show a high magnification SEM image of a single NW from the respective NW array. The scale bar of the inset is 50 nm.

The HAADF STEM images in Figure 5.2, all taken from the central part of appropriate NWs, show more significant changes inside the NWs due to the annealing. While the as-grown NW is built by a bundle of nanofibers, as indicated from the SEM image, the annealed NWs are a single-crystalline material, which is interspersed with voids.$^{[50,167]}$ Nevertheless, SEM showed that even for the annealed NWs there are still residuals of the former nanofiber bundle at the tip (see Fig. 5.1b,c). The NW annealed in air does not show any further changes besides the voids, whereas the NW annealed in N$_2$ has internal voids and in addition a distinct core-shell-like structure with an approximately
10 nm thick shell. A similar shell can be detected for as-grown NWs and NWs annealed in air but it is only 1-3 nm thick. Although the nanostructures of the three NWs differ, no changes in crystallography can be detected. The diffraction patterns in the insets of Figure 5.2 correspond to rutile TiO$_2$ acquired in the [110] zone axis and deviate only by the streaking in the diffraction peaks in [110] direction, which is visible for the as-grown NW. This streaking arises from the nanofiber bundle and the high defect density in the as-grown NWs.$^{[48]}$ Thus, neither the heat treatment in air nor in N$_2$ leads to a phase transformation.

Figure 5.2: HAADF STEM image and a corresponding SAED pattern (inset) for a) an as-grown NW, b) a NW annealed in air, and c) a NW annealed in N$_2$. All images show a representative area in the center of its respective NW and the diffraction patterns were taken from entire NWs.

Despite the changes in the nanostructure, there are also differences in the local chemical environment of the three different NWs close to the surface. Figure 5.3a-c shows EEL spectra of the Ti–L$_{2,3}$ edge with different distances to the surface. Close to the surface (yellow lines), the Ti–L$_{2,3}$ edge is shifted to lower energies by around 1 eV and the ELNES shows that the splitting of the L$_2$ and L$_3$ peaks into a doublet is not resolved. This $t_{2g}$-$e_g$ splitting is typical for rutile TiO$_2$ and results from a distorted octahedral surrounding of Ti by oxygen ions,$^{[139]}$ but cannot be detected for Ti close to the surface. Instead, the Ti–L$_{2,3}$ edge is formed by broad peaks. Depending on the heat treatment, the typical ELNES of rutile TiO$_2$ occurs closer or more far away from the surface. For the NWs annealed in air, the ELNES shows the typical shape of rutile TiO$_2$ with a pronounced $t_{2g}$-$e_g$ splitting after moving 1.8 nm towards the center (orange line in Fig. 5.3b). For the as-grown NW, the broad L$_2$ and L$_3$ peaks in the ELNES are observed in the first 2.9 nm of the surface region (red line in Fig. 5.3b). The NW annealed in N$_2$ has the largest region (up to 4.8 nm, dark red line in Fig. 5.3c), where one can find an ELNES without pronounced $t_{2g}$-$e_g$ splitting. Moving farther away from the surface, the ELNES
of the as-grown NW and the NW annealed in air does not change anymore, but for the NW annealed in N\textsubscript{2} one can see that 10.4 nm away from the surface (light cyan line in Fig. 5.3c), the ELNES changes again. Following the method described by Stroyanov \textit{et al.},\cite{138} the Ti–L\textsubscript{2,3} edge is used to calculate the amount of Ti\textsuperscript{4+} relative to the total amount of Ti, which is mainly a sum of Ti\textsuperscript{4+} and Ti\textsuperscript{3+}. Figure 5.3d-f are overlays of the resulting Ti\textsuperscript{4+} gradients with a STEM image of the analyzed NW area. The shift of the Ti–L\textsubscript{2,3} edge towards lower energies close to the surface is related to a lower amount of Ti\textsuperscript{4+} in this area. Thus, close to the surface, the NWs are not fully oxidized. Inside the NW, the as-grown NW and the NW annealed in air have a constant amount of Ti\textsuperscript{4+} of around 80 %. For the NW annealed in N\textsubscript{2}, the changes of the ELNES around 10.4 nm are also linked to a lower amount of Ti\textsuperscript{4+} and the overlay in Figure 5.3f shows that this decrease of Ti\textsuperscript{4+} is closely related to the core-shell interface. The lack of Ti\textsuperscript{4+} results in an off-stoichiometric TiO\textsubscript{2-x}. In the following, the shell material will be denoted as TiO\textsubscript{2-x} to account for the high oxygen deficiency.

Figure 5.3: a)-c) Position resolved EEL spectra of the Ti–L\textsubscript{2,3} edge, for a) an as-grown NW, b) a NW annealed in air, and c) a NW annealed in N\textsubscript{2}. The position of the spectra is marked in the STEM images of d)-f) with a specific color, which is the same for the respective Ti–L\textsubscript{2,3} edge (the color changes from the NW surface to the center (left to right) in the following order: yellow, orange, red, pink, purple, blue, cyan, green, black). In d)-f), the Ti\textsuperscript{4+} gradient is overlaid with the STEM image.
To study the core-shell structure in more detail, Figure 5.4a shows a HR TEM image of a NW annealed in N\textsubscript{2}. This NW has a comparable thick shell to facilitate the analysis. One can see that the NW consists not only of a core and a shell, but of four distinctive areas. The rutile TiO\textsubscript{2} core and the crystalline TiO\textsubscript{2-x} shell are separated by a defective interface area and the shell is covered with a disordered surface layer. Around 80 \% of the NW volume can be assigned to the core, which is rutile. The shell is also crystalline and covers around 20 \% of the NW volume. The HR ABF STEM image in Figure 5.4b shows no differences in the crystal structure of the rutile core and the shell, except a small change in the d-spacing between \{110\} planes (core: d\textsubscript{110}=3.33 Å, shell: d\textsubscript{110}=3.29 Å). Although the EELS analysis shows that the shell consists of off-stoichiometric TiO\textsubscript{2-x}, no inhomogeneity in the oxygen distribution can be detected in the annular bright field STEM image (see Fig. 5.4b). Thus, an ordering of a significant amount of O\textsubscript{vac} in this part of the NW is unlikely, as it would lead to periodic changes in the atomic columns, which should be visible in ABF STEM. However, in all imaging conditions, this shell appears in a different contrast compared to the core. In the shell area, a sample thickness of 110 nm is derived using the low-loss EEL spectrum and assuming an inelastic mean free path of 276 nm for rutile TiO\textsubscript{2}.\textsuperscript{[253]} Considering an error of around 10 \% for the thickness determination by EELS,\textsuperscript{[254]} this thickness estimation is in good agreement with the total thickness of the analyzed NW, which is also shown in Figure 5.2c (around 100 nm). Thus, the changes in contrast cannot be related to a thickness effect but might be related to a change in the density of the material. The contrast changes might also be affected by the incorporation of nitrogen, but EELS measurements in the shell area, show no incorporation of nitrogen within our detection limits of \approx 1 \text{at\%}. It is noteworthy that this observation cannot be confirmed by methods other than EELS with high lateral resolution, because the nitrogen and the titanium signal overlap in other spectroscopic techniques, such as Auger and wavelength dispersive X-ray spectroscopy. The defective area, which can be seen in the HR TEM image of Figure 5.4a between the TiO\textsubscript{2} core and the TiO\textsubscript{2-x} shell is around 1.9±0.3 nm thick. The disordered surface layer of the NW has a thickness of 2.2±0.3 nm and is not completely amorphous, but shows some periodicity perpendicular to the [001] direction. Figure 5.4c is an intensity profile of Figure 5.4a in the first 4 nm next to the vacuum and perpendicular to the NW surface. This profile shows two periodic areas, but with different periodicity. The periodicity of the TiO\textsubscript{2-x} shell corresponds to the lattice spacing of \{110\} planes in rutile TiO\textsubscript{2}. Closer to the vacuum, there is a second material, which is also periodic to a certain extent, but the related lattice distances are much bigger (\approx 5 Å). This in-plane ordering in an amorphous phase is due to the underlying substrate periodicity and has been observed for other systems.
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The changes in the internal nanostructure, which are induced by annealing in different environments, influence the optical properties of the NWs. While the NW arrays incorporating as-grown NWs or NWs annealed in air appear white, the NW arrays annealed in N$_2$ are black. This color change indicates more light absorption in the visible range for the NWs annealed in N$_2$. Figure 5.5a shows Tauc plots for direct allowed band gap transitions of the three different NW arrays. The as-grown NWs have a $E_g$ of 2.98±0.06 eV, which is in good agreement with previous measurements.\textsuperscript{[167]} The $E_g$ of NWs annealed in air is significantly reduced to 2.59±0.04 eV, but for the NWs annealed in N$_2$, the obtained direct $E_g$ is again 2.96±0.03 eV. In addition, there is an indirect transition for the NWs annealed in N$_2$ with an indirect band gap of around 2.57±0.02 eV (see inset in Fig. 5.5a). In contrast, no strong indirect transition can be detected for the as-grown NWs and the...
NWs annealed in air. Absorption spectra allow not only the determination of the band gap but are also suitable to measure the so-called Urbach energy, which is a measure of the disorder in materials and leads to additional states within the band gap.\textsuperscript{[207]} The $E_U$ of the as-grown NWs and the NWs annealed in air and in $N_2$ is $0.61 \pm 0.01$ eV, $0.55 \pm 0.01$ eV and $1.65 \pm 0.01$ eV, respectively. Since UV-vis can only probe the band gap on a large scale and as the results might be influenced by the periodicity of the NW array, and the resulting interference effects, additional band gap measurements were performed using EELS. Figure 5.5b shows the corresponding zero-loss subtracted low-loss EEL spectra of the different NWs. The band gap values derived from the EELS measurements (as-grown: $2.93 \pm 0.12$ eV, annealed in air $2.41 \pm 0.06$ eV, annealed in $N_2$ $2.66 \pm 0.14$ eV) are in good agreement with the values obtained by UV-vis, considering the indirect transition for the NW annealed in $N_2$.

**Figure 5.5:** a) Tauc plot for direct band gap and b) zero-loss subtracted low-loss EEL spectra for NWs which are as-grown (petrol squares), annealed in air (red circles), and annealed in $N_2$ (green lozenges). The inset in a) shows the Tauc plot for an indirect band gap for the NW array annealed in $N_2$.

Besides the optical properties of the NWs, the electronic properties are affected by the heat treatments. Figure 5.6a shows the IV-characteristics of the as-grown NWs, the NWs annealed in air, and the NWs annealed in $N_2$. Significant differences in the electronic properties of the three devices regarding the conduction limiting mechanisms can be observed.

The as-grown NWs block the transient current for electrical fields between 0 and 12 kV/cm (see petrol line, Fig. 5.6a). At higher electrical fields, the transient current is increasing exponentially and is hence affected by Schottky emission (see petrol line, Fig. 5.6b). For an increasing negative bias, the IV-characteristic turns quickly from an exponen-
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Figure 5.6: Transient current characteristics through as-grown NWs, NWs annealed in air or in N$_2$ that is measured between a PtIr top and an FTO bottom electrode. The different plots emphasize several conduction-limiting mechanisms: a) Linear plot showing ohmic behavior and the inset is a zoom in on the point of origin, b) Schottky-plot, c) Fowler-Nordheim-plot and d) space-charge-limited current-plot.\[256\]

Thus, the Schottky barrier at the PtIr/TiO$_2$ interface is smaller than the one at the FTO/TiO$_2$ interface.

TiO$_2$ NWs annealed in air block the transient current for electrical fields between -25 kV/cm and at least 100 kV/cm (see red line, Fig. 5.6a,b), which corresponds to the highest applicable bias in the employed setup. The IV-characteristics of the PtIr/TiO$_2$ interface become completely exponential and hence the transient current is limited by a Schottky emission across the whole measured bias range (see red line, Fig. 5.6b).\[256\] In contrast, the transient current of the NWs annealed in N$_2$ is not blocked at any bias, which indicates an almost complete vanishing of both Schottky barriers (see green line,
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Fig. 5.6b). Only at very low, negative fields up to roughly 2 kV/cm, we found a Fowler-Nordheim tunneling behavior for the electrons passing from the PtIr tip to the TiO$_2$ NW (see Fig. 5.6c). For larger field amplitudes, the transient current becomes linear, showing a relatively large ohmic resistance (see green line, Fig. 5.6a). However, the slope and thus, the absolute ohmic resistance depends on the applied voltage.

Our results show that different heat treatments change the nanostructure and the properties of hydrothermally grown rutile TiO$_2$ NWs significantly. In the following, the interaction of the structural changes on the properties will be discussed. As-grown NWs are intensively studied and used in many application and thus serve as a reference in this work. The detailed electron microscopic analysis showed that these NWs are rutile TiO$_2$, but contrary to many reports,[52] they are not single-crystalline.[48,167] Instead, they show a meso-crystalline structure that is built by a bundle of nanofibers and incorporate many crystal defects,[48] especially a high amount of O$_{\text{vac}}$.[167] The optical band gap of around 3 eV is in accordance with literature values for rutile TiO$_2$,[227] but the Urbach energy of 0.61 eV is much larger than reported for single-crystalline rutile TiO$_2$ nanoparticles,[257] and can be assigned to the high defect disorder of the O$_{\text{vac}}$ and other structural defects. In addition, the O$_{\text{vac}}$ influences the electronic properties, as they are prominent electron donors that tune TiO$_2$ into an n-type semiconductor.[258–260] The O$_{\text{vac}}$ in as-grown TiO$_2$ NWs have two effects on the electronic properties. In the first instance, the local donor density moves the Fermi level upward, closer to the conduction band minimum. As a consequence, the summit of the Schottky barrier between the metallic cathode and the TiO$_2$ drops with increasing electron donor density close to the interface. In addition, an increased number of O$_{\text{vac}}$ lowers the resistivity of TiO$_2$ by increasing the number of mobile electrons in the conduction band[261,262] and thus, the as-grown rutile TiO$_2$ NWs show n-type conduction.

As shown in a previous study, TiO$_2$ NWs annealed in air have a significantly reduced density of O$_{\text{vac}}$ in the crystal structure, as vacancy condensation takes place during the heat treatment.[167] The NWs are single-crystalline and the rutile crystal structure of the NWs annealed in air is almost O$_{\text{vac}}$ free. In addition, the vacancies close to the NW surface are vanished due to the oxygen atmosphere during the heat treatment, resulting in NWs that have only a 1.8 nm thick surface layer, which deviates from the perfect rutile TiO$_2$ environment, as shown by changes in the ELNES. These changes during the heat treatment influence the optical and electronic properties of the NW array, as both,
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the amount of trap states and electron donors incorporated in the crystal structure, are significantly reduced. This deduction is verified by the UV-vis measurements, which show that the band gap as well as the Urbach energy shrink. The reduced band gap can be assigned to less O\textsubscript{vac} in the crystalline rutile TiO\textsubscript{2}\textsuperscript{[206]} and a high Ti\textsuperscript{3+} concentration in the defective area surrounding each void.\textsuperscript{[167]} It is noteworthy that these NWs appear white although the band gap indicates absorption in the visible blue regime. This effect is related to a strong light scattering, which is caused by the high refractive index of TiO\textsubscript{2}.\textsuperscript{[59]} Furthermore, a reduced Urbach energy indicates less disorder. However, Urbach energy is still higher than expected for a single-crystalline rutile nanoparticle.\textsuperscript{[257]}

This deviation results from the 1.8 nm thick surface layer covering the NWs and a defective, Ti\textsuperscript{3+} rich area surrounding each void.\textsuperscript{[167]} Concurrently, the transient current is blocked over a broad range of electrical fields. Only for highly negative electrical fields, a Schottky emission limited current can be detected. These results are in good accordance with the discussion above. As the density of O\textsubscript{vac} is significantly reduced in the rutile crystal structure of NWs annealed in air, the Schottky barrier heights and the bulk resistance is expected to increase. Nevertheless, at high negative electrical fields the Schottky barrier can still be passed. We assume a constant work function for the PtIr tip and the FTO substrate for all experiments, so the Schottky barrier is mainly influenced by the Fermi level of the TiO\textsubscript{2} NWs. Structural inhomogeneity at the TiO\textsubscript{2} NW tip surface might influence the Schottky barrier, but SEM analysis showed that the surface of the NWs annealed in air is the smoothest, so we assume only a minor contribution of surface inhomogeneity on the height of the Schottky barrier.

Annealing in N\textsubscript{2} changes the distribution of O\textsubscript{vac} as well. According to the TEM results presented in this work, the NWs annealed in N\textsubscript{2} have a complex core-shell structure. From these results, it is reasonable to assume that the defect density in the core, which is riddled by voids, is similar to the defect density of the NWs annealed in air. Consequently, the electronic properties of the core, possessing a low defect density, are similar to the electronic properties of NWs annealed in air. However, the IV-characteristics measured for the NWs annealed in N\textsubscript{2} differ strongly from those, measured for the NWs annealed in air. Thus, the core of the NW annealed in N\textsubscript{2} has no significant influence on the conductivity in these NWs. The Fowler-Nordheim tunneling behavior that occurs at low electrical fields is supposed to be a result of a disordered surface layer (see Fig. 5.4a,c) covering the metal-like TiO\textsubscript{2-x} shell. For strong electric fields, the influence of this ultra-thin layer is negligible. Without this metallization, the Schottky barrier is much thicker and Schottky emission, as observed for the as-grown NWs, instead of tunneling dominates. The metal-like behavior of the shell is in good agreement with the black color of the NW
array, as absorption throughout the entire spectral range is common for metals. Several observations indicate that the metallization takes place in a confined volume. Firstly, the optical measurements are still dominated by the properties known for white TiO$_2$. It is known that the transmittance of light of thin metal films drops below 20 % for films being thicker than about 10-20 nm.\cite{263} As our NW arrays show a high transmittance, it is reasonable to assume that the metallic part in the NWs annealed in N$_2$ does not exceed 20 nm. In addition, the ohmic resistance measured for these NWs is relatively large. Such large ohmic resistances stem from the tiny cross-sections of the highly conductive part of the NW annealed in N$_2$. According to the TEM and EELS results, NWs annealed in N$_2$ are covered by a TiO$_{2-x}$ shell that contains a very high amount of O$_{vac}$, as the vacancies cannot be removed at the surface due to the slightly reducing environment of the N$_2$ atmosphere. Although an incorporation of N cannot be ruled out completely due to the EELS detection limit of around 1 at\%, we assume no influence of a potential N doping (which would be below 1 at\% of N) on the electrical properties. This assumption is based on the fact that changes in the electronic properties for TiO$_{2-x/2}N_x$ were only detected for N incorporation higher than 5 at\% N.\cite{264} Such high concentrations can be excluded due to the absence of an N-K edge in the EEL spectra throughout the NW, although it is not possible to confirm this result with other methods due to signal overlap. Nevertheless, even undoped but strongly reduced TiO$_{2-x}$, as found in the shell of the NW annealed in N$_2$, is highly conductive.\cite{249,260} Hence, it is reasonable to assume that the TiO$_{2-x}$ shell is responsible for the unusual properties of these NWs, but due to the small dimensions it is difficult to localize the origin of these effects within the shell. According to the TEM results, the shell can be divided in three parts, namely the disordered surface layer (2.2 nm), the crystalline TiO$_{2-x}$ shell (8-20 nm) and a defective interfacial area between the TiO$_{2-x}$ shell and the TiO$_2$ core (1.9 nm). The high Urbach energy measured for these NWs originates from the high degree of disorder in the surface layer. Similar surface layers were found in various black TiO$_2$ nanomaterials and seem to be the origin of the black color.\cite{240} This change in color is mainly related to the presence of a big Urbach tail at the upper part of the valence band.\cite{240} These results are in good accordance with the high Urbach energy which was measured for NWs annealed in N$_2$. The metallization and the high transient current might result from the entire shell but there are some indications that it is confined on the defective interface between the TiO$_{2-x}$ shell and the TiO$_2$ core. The EELS analysis showed a higher concentration of Ti$^{3+}$ at this interface, which might arise from a great amount of O$_{vac}$ confined at this interface. Both are electron donor type defects and can lead to high conductivity. Lü et al. found a similar conducting interface at the homojunction of a bilayer thin film. This homojunction is formed...
between an oxygen-deficient, amorphous TiO$_{2-x}$ layer with around 20 nm thickness and a comparable thick layer of anatase TiO$_2$.\cite{252} Our experimental setup does not allow direct proof of this assumption, but the results obtained in this study give evidence that not the entire shell, but a conductive interface might be responsible for the highly conducting properties of the black NWs annealed in N$_2$. In addition, there is a certain hysteresis of the IV-characteristics, which indicates that the O$_{\text{vac}}$ are able to drift through the TiO$_{2-x}$ shell. This effect is well known from resistive switching\cite{82,265,266} and might be the reason why the O$_{\text{vac}}$ cannot be detected by annular bright field STEM. Due to the high mobility of the O$_{\text{vac}}$, their density at the PtIr/TiO$_2$ and FTO/TiO$_2$ interfaces differ slightly, resulting in the observed asymmetry of the IV characteristics for positive and negative applied bias.

5.4 Conclusion

In this study, we propose heat treatments in different environments in order to manipulate the structure of hydrothermally grown rutile TiO$_2$ NWs in such a way that their optical and electrical properties can be tailored. The as-grown NWs incorporate a high amount of defects, especially O$_{\text{vac}}$, which are responsible for the n-type conductivity in these NWs. Independent of the environment, the heat treatment leads to a condensation of these vacancies and to the formation of single-crystalline, lattice defect free, rutile TiO$_2$ NWs that incorporate voids. The absence of O$_{\text{vac}}$ results in a blocking of the transient current and concurrently improves the optical properties by decreasing the band gap and Urbach energy. For an oxidizing environment, such as air, the resulting NWs are almost insulating. Although NWs annealed in N$_2$ contain up to around 80% of an insulating rutile TiO$_2$ core, their properties are completely different. They possess a black color and an almost metal-like conductivity. These properties are related to the slightly reducing atmosphere of N$_2$ during the heat treatment. It inhibits the vanishing of the surface-near O$_{\text{vac}}$ and thus a core-shell structure with a highly oxygen deficient shell is formed.
6 Fabrication and characterization of abrupt TiO$_2$-SiO$_x$ core-shell nanowires by a simple heat treatment

In this chapter a facile heat treatment at 1050 $^\circ$C is reported, which modifies the surface of TiO$_2$ NW by introducing a shell. In these TiO$_2$-SiO$_x$ core-shell NW arrays on Silicon substrates, the quality of the rutile TiO$_2$ core is improved by removing lattice defects. Concurrently, a uniform shell of amorphous SiO$_x$, which is several nanometers thick, covers the NW, but no intermediate phase is formed at the interface. Thus, the properties of the TiO$_2$ core are maintained, while the insulating shell suppresses undesired electron back transfer. In the following, these results, which are a modified version of a research letter published in APL Materials,[145] are presented.

6.1 Introduction

TiO$_2$ NWs combine the versatility of TiO$_2$ with the unique properties of 1D nanostructures, e.g., directed electron path and large surface area. Thus, TiO$_2$ NWs are a promising material for solar cells, photocatalysis, photocatalytic pollutant degradation, gas sensing, and ultra violet (UV) shield.[3] Most applications rest upon the UV-absorption and its associated charge generation and separation. However, these charges might be unintentionally transferred in opposite direction to the band alignment. This electron back transfer can lead to efficiency losses and a short life time of the device.[267] To avoid photo degradation of functional organic materials and high recombination rates in, e.g., hybrid solar cells, the interfacial recombination dynamics have to be suppressed. Hence coating of TiO$_2$ nanomaterials by an insulating material, e.g., Al$_2$O$_3$ or SiO$_2$, has attracted a lot of interest.[28]

SiO$_2$ coatings on TiO$_2$ are usually obtained by a sol-gel process. This process is suitable to coat the TiO$_2$ with a uniform shell, but the shells are 20-200 nm thick.[268,269] In the last years, other synthesis methods for the SiO$_2$ coating, such as chemical vapor deposition and hydrothermal flow reaction, have been developed.[269,270] Another possibility
to produce TiO$_2$-SiO$_x$ core-shell NWs is the heating of multilayered substrates, but the resulting NWs are not well aligned and the shell is thick and rough.$^{[271]}$

In this study, TiO$_2$-SiO$_x$ core-shell NW arrays were prepared by a heat treatment of TiO$_2$ NWs, which were hydrothermally grown on Si substrates. Uniform coating of TiO$_2$ NWs with a 3-4 nm thick shell is achieved by this simple and facile approach. The core-shell NW is investigated by electron microscopy to study the morphological changes, the structure of the shell and the local changes across the TiO$_2$-SiO$_x$ interface.

**6.2 Results**

SEM images in Figure 6.1 show that the morphology of the NWs changes during the heat treatment, but the thickness of the NW is constant within the error bar (as-grown: 130$\pm$27 nm, annealed at 1050 °C: 137$\pm$27 nm). These NWs grow along the [001] direction and the {110} surfaces are the main facets, as it was also observed in a previous study.$^{[48]}$

Significant changes occur at the NW top and at the surfaces of the NW. The NW top in the as-grown state has a fibrous structure, which is typical for hydrothermally grown rutile TiO$_2$.$^{[48,52,272]}$ For our synthesis conditions, this fibrous structure is caused by a V-shaped defect cascade$^{[48]}$ and was recently identified as recombination source.$^{[50]}$ The origin of the fibrous structure for our NWs is different to the one reported for branched TiO$_2$ rutile mesocrystals.$^{[49]}$ The latter were formed by self-assembly of nanofibers which were precipitated in solution in the initial stage.

![Figure 6.1](image-url)

**Figure 6.1:** Top view SEM image of a) as-grown TiO$_2$ NW array and b) TiO$_2$ NW array after the heat treatment at 1050 °C in vacuum. The pictograms next to the images show a simplified cross-section of the NW parallel (upper one, {110} cutting plane) and perpendicular (lower one, {001} cutting plane) to the NW growth direction.

The heat-treatment performed in the present work removes the nanofiber structure and forms a uniform NW tip with pyramidal faceted shape. The facet type and the core-
shell structure itself cannot be identified by SEM. The steps on the surfaces parallel to the [001] growth direction of the NW, which are visible in the as-grown state, are also removed after the heat treatment and new ones form perpendicular to the original ones. The resulting NWs have smooth {110} surfaces, which are connected by small {100} surfaces. The corresponding cross-sections of the heat-treated NW parallel to the {110} and {001} planes are shown in the pictograms in Figure 6.1b. The heat-treated NWs are much closer to the thermodynamical equilibrium shape proposed by Goldschmidt [273] than the as-grown NWs. Deviating from this ideal shape, steps perpendicular to the growth direction occur.

![Figure 6.2: a) BF TEM image of a heat treated NW and corresponding electron diffraction pattern. b) ABF STEM image of the NW tip with several faceted steps. c) HR ADF STEM image of the same NW showing the single crystalline core and the amorphous shell. d) EDS map of a core-shell NW.](image)
TEM investigations confirm these changes in morphology and give insight into which facets were formed. Figure 6.2a is a BF TEM image of a heat-treated NW and the SAED pattern of the NW, which corresponds to rutile TiO$_2$ acquired along the [110] zone axis, confirming the [001] growth direction. Thus, no phase transformation takes place during the annealing. This is in good agreement with the phase diagram of bulk TiO$_2$, which reveals that rutile is the thermodynamically most stable crystal modification.\cite{201} In comparison to as-grown NWs and NWs annealed at lower temperatures (e.g., 500 °C),\cite{167} the TiO$_2$ core of the NWs annealed at 1050 °C is free of lattice defects and does not incorporate any voids or other structural defects. The BF STEM image in Figure 6.2b shows that the \{110\} surfaces parallel to the [001] growth direction and close to the NW tip are interrupted by several steps. These steps are faceted and represent the \{111\} surface. At the NW top, the \{111\} surfaces built the pyramidal tip, which is slightly rounded. Similar morphologies have been observed for other rutile TiO$_2$ nanostructures.\cite{64,274,275}

![Figure 6.3: a) ADF STEM image of a TiO$_2$-SiO$_x$ core-shell NW with several defects at the surface of the TiO$_2$ core. The area marked is shown in higher resolution in b), which is a DF STEM image of one of these defects. The perfect encapsulation of the nanowire by an amorphous shell can be seen, including the area of the defect.](image)

From the bottom to the top, the NW is covered by a 3.7±1.6 nm thick, amorphous shell (see Fig. 6.2c). Moiré patterns in BF STEM image prove a complete encapsulation of the NW by the shell (see Fig. 6.2b). The shell even covers defects at the \{110\} surface of the rutile TiO$_2$ core (highlighted in Fig. 6.3). As shown in the elemental map, obtained by EDS analysis (see Fig. 6.2d), the shell consists of Si and O, indicating the formation of SiO$_x$. The core is pure TiO$_2$ (Ti:Si 1:0.15), as the amount of Si detected corresponds to the 3-4 nm thick SiO$_x$ shell that homogeneously covers the NW and thus also contributes...
6.2 Results

The interface between the rutile TiO₂ core and the amorphous SiOₓ shell is analyzed by EELS (see Fig. 6.4). For the core (9.8-2.2 nm away from the interface), the Ti-L₂,₃ and the O-K edge show the typical ELNES of rutile TiO₂.¹³⁹ The peaks of the Ti-L₂,₃ split into a duplet of t₂g and e₉ because of the tetragonal distortion of the [TiO₆]₈⁻ octahedra in rutile TiO₂. This t₂g-e₉ splitting also affects the O-K edge, which has a duplet with two main peaks at 531 eV and 534 eV. This duplet arises from the hybridization of the O 1s orbitals with the Ti 3d orbitals. The broad peak at 537-546 eV is formed by three
bands, which correspond to transitions from the hybridized orbitals of the O 2p orbitals with the s and p orbitals of the bonding partner (e.g., 4s and 4p for Ti).\textsuperscript{[277]} The Ti-L\textsubscript{2,3} edge changes close to the interface between the core and the shell (the outer 2.2 nm of the TiO\textsubscript{2}). The edge onset is shifted to lower energy losses, the peak width is decreased, and no $t_{2g}$-$e_g$ splitting is resolved. These changes arise from substoichiometric TiO\textsubscript{x}\textsuperscript{[138,167]} at the surface. As the Ti-L\textsubscript{2,3} edge of as-grown NWs shows the same changes at the surface (see Fig. 6.5), these changes are independent of the heat treatment and shell formation. The intensity of the Ti-L\textsubscript{2,3} edge decreases close to the surface, but the intensity ratio between the Ti-L\textsubscript{2,3} peak and the O-K duplet remains constant (see Fig. 6.6). Thus, no extended area (>1 nm) comprising a TiO\textsubscript{2}-SiO\textsubscript{x} solid solution\textsuperscript{[278]} with Ti-O-Si bonds is formed in the interface region.\textsuperscript{[279,280]} In the shell, no Ti can be detected and the shape
of the O-K edge changes significantly. The duplet (531 eV and 534 eV) disappears and the edge-onset is shifted to higher energy losses. The O-K edge for the shell has an edge onset of 534 eV and decays faster compared to the broad peak (537-546 eV) of the O-K edge in the TiO$_2$ core.

![Figure 6.6: a) EEL spectra of the Ti-L$_{2,3}$ edge and O-K edge, which are normalized to the peak height of the Ti-L$_2$ peak. The O-K edge is magnified in b) to show that the peak intensity of the O-K duplet (531 eV and 534 eV) remains constant at the TiO$_2$-SiO$_x$ interface (dark blue). This indicates that oxygen either belongs to the octahedrally coordinated Ti or to the tetrahedrally coordinated Si. Thus, no extended area with a TiO$_2$-SiO$_x$ solid solution is formed in the area of the interface.](image)

The Si-L edge (see Fig. 6.7) is detected all over the nanowire, as it is completely covered by the shell, but has a higher intensity in the outer region where the TiO$_2$ core is absent. Neither the edge-onset nor the ELNES of the edge changes at the interface. Figure 6.4d exemplarily shows an EEL spectrum of the Si-L edge, which was taken from the shell without the TiO$_2$ core. Starting with an edge onset of 103.8 eV, the edge consists of three distinct energy loss regions. In the ELNES two sharp and a broad peak arise. The sharp peaks result from Si 2p $\rightarrow$ 3s and Si 2p $\rightarrow$ 3d transitions. The delayed maximum starts at higher energy losses. It results from inner well resonances and appears frequently in Si compounds that are tetrahedrally coordinated by strong electronegative ligands like O.\textsuperscript{[146,147]} The extended energy loss fine structure starts above 150 eV, but its oscillations are weak and overlap with the Si-L$_1$ edge, which has a maximum at 157.2 eV. The second edge shown in Figure 6.4d is a reference spectrum of amorphous SiO$_2$. All features are visible for both edges, but the first peak in the ELNES, which arises from a 2p $\rightarrow$ 3s transition, has much lower intensity in the shell. In the literature, such shape of the Si-L$_{2,3}$ edge is assigned to the native oxide formed on Si wafers under ambient conditions.\textsuperscript{[281]}

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It is proposed that the native oxide is amorphous SiO, whereas our EDS measurements on the shell show a SiO$_{1.7}$ stoichiometry. Thus, the reduced intensity in the first peak, indicating less $2p \rightarrow 3s$ transitions, might result not only from a slight oxygen deficiency but also from additional electrons in the $3s$ states.

![Figure 6.7: EEL spectra of the Si-L$_{2,3}$ edge ranging from 15 nm inside the NW (yellow) to the surface of the TiO$_2$-SiO$_x$ core-shell NW (dark green). The intensity changes, but the edge onset and the shape of the edge remain constant.](image)

**6.3 Discussion**

Our results show that a high temperature treatment of hydrothermally grown TiO$_2$ NWs on a Si substrate is suitable to produce TiO$_2$-SiO$_x$ core-shell NWs with a single crystalline, defect-free, rutile TiO$_2$ core. Such 1D TiO$_2$ has advantages compared to the as-grown TiO$_2$ NWs, which have numerous defects and tend to split up in nanofibers.$^{[48]}$ The originally present free space between these fibers (around 14 % of the NW volume) is compensated by the faceting, which gradually thins the NW towards the top of the annealed NW. The volume loss of the annealed NWs is around 13 %, which matches with the free volume between the nanofibers. Our analysis indicates that the removal of the defects in the TiO$_2$ core occurs first and is completed before the shell covers the upper,
faceted part of the NW. Otherwise, one would expect cracks in the shell next to the kinks or SiO$_x$ inclusions in the TiO$_2$ core. Neither can be detected in the TiO$_2$-SiO$_x$ core-shell NWs. This conclusion is in accordance with previous results, which showed that the defect removal in TiO$_2$ NWs happens within seconds, as soon as a critical temperature is reached.$^{[167]}$

After the changes in the TiO$_2$ core, the SiO$_x$ shell is formed. As the vacuum in the heating chamber is not low enough to evaporate Si at 1050 °C,$^{[282]}$ the shell has to be formed by diffusion of Si along the sidewalls of the NWs. High mobility of Si at temperatures far below the Si melting point was shown before.$^{[283–285]}$ Si atoms of the substrate pass the TiO$_2$ seed layer most likely through the grain boundaries and diffuse along the contamination free sidewalls of the NW by a surface diffusion process. Due to the small concentration gradient we expect slow diffusion and the velocity of the shell growth is slow. The high temperature during the process is sufficient to avoid the formation of Ti-O-Si bonds$^{[286]}$ and consequently, the Si atoms are free to move, which enables formation of a uniform shell. The SiO$_x$ is formed after removing the samples from the oven in a process similar to the formation of native oxide layers on Si wafers.$^{[287,288]}$

### 6.4 Conclusion and outlook

In summary, we presented a method to cover TiO$_2$ NWs uniformly with a 4 nm thick SiO$_x$ shell by a thermal treatment at 1050 °C. Besides the shell formation, this treatment heals all defects present in the TiO$_2$ core of the as-grown NWs. The formed material is a core-shell material without intermixing between both materials. Therefore, the functionality of TiO$_2$ is preserved, while unwanted surface reactions, like recombination in solar cells or degradation of organic material, can be minimized.

In future, this procedure can be adopted to other photoactive metal oxides such as ZnO, and it can be used to produce Si shells around, e.g., TiO$_2$, if the material is handled in an oxygen-free atmosphere.
7 Deriving new morphologies from hydrothermally grown rutile TiO\textsubscript{2} nanowires by combining etching and heat treatments

The previous chapters focus on the influence of heat treatments in different environments and at different temperatures on the defect distribution in, and changes at the surface of TiO\textsubscript{2} NWs. Furthermore, the influence on optical and electric properties, as well as heat induced changes in the nanostructure are discussed. This chapter is dedicated on these changes in the nanostructure and shows how an aimed combination of hydrothermal growth, hydrothermal etching and annealing opens up the synthesis of new nanostructures. These structures preserve the 1D nature of the NWs, but possess higher surface areas. Meanwhile the fabrication of such morphologies is compatible with the heat treatments presented in Chapter 4, 5 and 6.

7.1 Introduction

Since the discovery of Honda and Fujishima\cite{2} that TiO\textsubscript{2} photoanodes can split H\textsubscript{2}O in hydrogen and oxygen, various photoanodes have been synthesized and steadily improved. For a long time mesoporous TiO\textsubscript{2} films were the favorite photoanode architecture.\cite{289,290} However, this random network of nanoparticles has several drawbacks. The electron transfer through such a mesoporous material is akin to a random walk of electrons, which requires usually much longer diffusion lengths than one would expect from a direct transfer along the shortest pathway to the substrate. On these long diffusion paths the electrons can encounter lattice defects, grain boundaries or traps that lead to the recombination of the electrons and loss of free charges.\cite{12,14,291} This trap-limited diffusion process of mesoporous TiO\textsubscript{2} films is a big drawback of such photoanodes.

There are various attempts to improve the nanoarchitecture of TiO\textsubscript{2} photoanodes, as for example the replacement of the mesoporous film by an ordered array of 1D TiO\textsubscript{2}
Due to the 1D structure and the confined volume in two directions they possess a direct electron path towards the conducting substrate.\textsuperscript{13,14} Consequently, there is less recombination and more charges can be collected. For this reason, the efficiency of cells based on these arrays, such as solar cells or devices for water splitting, should increase. 1D nanostructure arrays consist of either dense or hollow material with both morphologies offering advantages and drawbacks. Dense morphologies, such as NWs can be synthesized by various methods, but one of the most common is the hydrothermal growth on conducting substrates.\textsuperscript{52,293} In this way, highly crystalline NWs can be produced with a good electron mobility. Furthermore, they are almost free of grain boundaries, which further reduces the recombination probability.\textsuperscript{14}

Within the last years, a lot of research, including this thesis, was conducted to gain a better understanding about the properties of such NW arrays and it was found that the as-grown nanomaterial is full of lattice defects,\textsuperscript{48} which act as recombination centers, but can be removed by heat-treatments.\textsuperscript{50,167} Although the rutile TiO\textsubscript{2} NWs have a lot of advantages, especially their high crystallinity, they also possess disadvantages, such as a limited surface area. Several approaches have been developed to obtain 1D TiO\textsubscript{2} nanostructures with higher surface area, while conserving the advantageous properties of the quasi single-crystalline NWs. Among them, an increase in aspect-ratio,\textsuperscript{17,294} introduction of hierarchical structures\textsuperscript{18,20,22} and different etching routes\textsuperscript{294} are most promising. In the following, different approaches are presented in order to increase the surface area of solvothermally grown rutile TiO\textsubscript{2} NWs, while maintaining its unique 1D properties.

For the solvothermal synthesis H\textsubscript{2}O or ButOH were used as a solvent and the as-grown NW arrays were modified by different etching and heating treatments after the growth. The obtained morphologies, ranging from highly fibrous NWs, over NWs with tiny channels parallel to the growth direction to completely hollow nanotubes with squared cross-section, are presented. The underlying formation mechanisms are briefly discussed and its suitability for application is predicted.

### 7.2 Results

Figure 7.1a exemplarily shows a SEM image of a hydrothermally grown rutile TiO\textsubscript{2} NW. In average, these NWs have a diameter of 180±26 nm. The as-grown NW can be divided in three distinct areas, which are highlighted in the scheme of Figure 7.1b. The drawing represents a cross-section along a \{001\} plane of the as-grown NW. In the center, the NW is built by a bundle of nanofibers, which are Ti-OH rich at the surface and thus, connect with each other by hydrogen bonds.\textsuperscript{167} In the following, the term nanofiber bundle refers
7.2 Results

7 New morphologies for TiO$_2$ nanowires

Figure 7.1: a) SEM image of an as-grown NW and b) schematic drawing of a cross-section of the as-grown NW viewed in (001) direction that highlights the different parts of the NW: Nanofiber bundle, outermost nanofibers and surrounding wall.

to this part. This nanofiber bundle is surrounded by additional nanofibers, which show different properties and are termed as outermost nanofibers in this work. All nanofibers are embedded in a nearly single-crystalline surrounding wall.

In Figure 7.2 NWs after hydrothermal etching at 150 °C for 3 h using different concentrations of HCl from 3.7 M to 6.1 M are shown. For the lowest HCl concentration (3.7 M) (see Fig. 7.2a) the NW morphology is still visible, but first imprints of the acidic solution can be seen. The most affected part of the NW are the outermost nanofibers, which are etched away, while the 12.0 ± 2.3 nm thick surrounding wall and the nanofiber bundle (diameter: 131 ± 15 nm) withstand the acidic treatment. The etching of the outermost nanofibers results in a trench, which is 27.4 ± 8.9 nm thick. Using acidic solutions with higher HCl concentration for etching (4.3 M HCl, see Fig. 7.2b) the etching rate increases, but still the NW array remains intact. For this concentration, not only the outermost nanofibers, but also the nanofiber bundle is etched, while the 12.7 ± 2.3 nm thick surrounding wall still withstands the acidic solution. If the HCl concentration is increased further (4.9 M) the entire core (nanofiber bundle and outermost nanofibers) of the former NW is etched away while the 14.4 ± 3.2 nm thick surrounding wall remains (see Fig. 7.2c) and consequently, hollow nanotubes with a rectangular cross-section are formed. The inner diameter of these tubes is 164 ± 28 nm.

For HCl concentrations of 6.1 M or higher the acidity of the etching solution is too high, and the NW array collapses (see Fig. 7.2d). For these samples, no vertically aligned arrays
can be detected in the SEM. Instead, the remaining parts of the NW lie randomly on the FTO substrate. This observation indicates that also the dense TiO$_2$ seed layer described in Section 4.5 is affected by the etching. Nevertheless, for shorter etching times, it is possible to etch the NWs with 6.1 M HCl solution without destroying the array. Figure 7.3 shows the resulting NW array after 1 h, 1.5 h, 2 h and 3 h of etching. After 1 h the fibrous structure is much more pronounced and the individual fibers are clearly visible, due to the larger inter-fiber spacing compared to the as-grown state (see Fig. 7.3a). After 1.5 h the morphology is comparable to the one of NWs that are etched with 10.1 M HCl for 3 h. Again, there is a stable surrounding wall (10.7 ± 2.8 nm), which is separated by a 37.2 ± 8.7 nm thick trench from the nanofiber bundle (see Fig. 7.3b). However, the nanofiber bundle is also slightly etched, which results in a tapered shape. If the etching time is further increased, the NW array starts to collapse. In Figure 7.3c the array of nanotubes is mostly hidden by numerous fragments of detached nanofibers. After 3 h the FTO substrate is mostly uncovered and only some fragments remain (see Fig. 7.3d).
7.2 Results

New morphologies for TiO$_2$ nanowires

Figure 7.3: SEM images of NW arrays after etching under hydrothermal conditions with 6.1 M HCl solution at 150 °C for different times: a) 1 h, b) 1.5 h, c) 2 h and d) 3 h.

NWs after 1 h of etching are modified by an additional heat-treatment in air (500 °C, 4 h) and the evolution of the morphology from the as-grown to the etched and annealed NWs is shown in Figure 7.4. The fibrous structure is only barely visible in the SEM images of as-grown NWs (see Fig. 7.4a), but much more pronounced after etching (see Fig. 7.4b). When such etched NWs are additionally subjected to a heat treatment in air (500 °C, 4 h), the morphology is further modified (see Fig. 7.4c). Similar to the observations during the heat treatment of as-grown NWs,[167] the nanofibers merge, but as the spacing between the fibers is much larger after the etching, no continuous single-crystalline NW can be formed. Instead, highly porous NWs with channels, as shown in Figure 7.4d, are observed after the annealing in air. The NW fragment shown in the central part of the image is an etched and annealed NW that broke into pieces and depicts the channel network inside the NW. The channels have a diameter of 11.0 ± 2.8 nm and run along the [001] growth direction of the NW. In addition, there are also some vertical connections between the channels visible, which lead to a nanochannel network.

Another way to manipulate the morphology of rutile TiO$_2$ NWs is a combination of
solvothermal growth using ButOH as a solvent and a post-growth heat treatment. The NW array before and after the heat treatment is shown in Figure 7.5. This solvothermal growth leads to a much denser NW array and the fibrous structure of the NWs is built by a bundle of much thinner nanofibers and with larger spacing between the individual fibers. Thus, the nanofiber structure is more pronounced. Concurrently, the \{001\} surfaces are not smooth, but show many steps parallel to the growth direction. After the heat treatment at 500 °C for 4 h the NW tip changes. The nanofibers merge together and a complex structure is formed, with small channels facing inside the NW. These channels have a diameter of $7.0 \pm 2.1$ nm, but the depth of these channels cannot be determined from SEM, as no NW fragments, showing the inner part of the NW, could be found.

Figure 7.4: SEM image of the NW array in a) the as-grown state, b) after etching for 1 h with 6.1 M HCl solution and c,d) after etching and an additional heat treatment at 500 °C in air for 4 h.
7.3 Discussion

Using different concentrations of HCl for the etching experiments and different etching
times allows for drawing a conclusion about the chemical stability of the as-grown NWs
and enables the development of a model to describe these etching processes. In the initial
state, the as-grown NWs are built by a bundle of nanofibers,\(^{[48,167]}\) which are surrounded
by a nearly single-crystalline surrounding wall. These two parts are separated by a layer
of outermost nanofibers. The etching starts at the Ti-OH rich surface of the nanofibers,
which is highly active due to the free -OH groups. From this first etching step a much more
pronounced nanofiber morphology results. In a second step, the outermost nanofibers are
etched away, which results in the formation of a trench between the nanofiber bundle and
the surrounding wall. This step is followed by a complete dissolution of the nanofiber
bundle. The time-dependent study of the etching with 6.1 M HCl reveals a tapered shape
in an intermediate state of etching and thus, it is most likely that the nanotube is the
final state of the steadily increasing trench. For all these etching steps, the ordered ar-
ray of NWs or nanotubes is preserved, indicating that the TiO\(_2\) seed layer (see Sec. 4.5),
which covers the FTO substrate and connects the individual NWs after the hydrothermal growth, is not dissolved in moderate acidic solutions. However, if the HCl concentration increases (≥ 16.9 M) and etching is performed longer than 2 h, the NWs detach from the FTO substrate and a random distribution of NW fragments and individual nanofibers is obtained. As the NWs detach from the FTO, which is partly visible again, the compact TiO$_2$ layer between the FTO substrate and the NW array must be dissolved under these conditions. All these observations allow to derive a solubility sequence for the TiO$_2$ NW array, which is the following: nanofiber surface>outermost nanofibers>nanofiber bundle>TiO$_2$ seed layer>surrounding wall. Based on this sequence an etching mechanism, which is visualized in Figure 7.6, can be derived. Etching of hydrothermally grown rutile TiO$_2$ NWs was studied before,[24–27] but the mechanisms proposed in these studies suggest a slightly different etching mechanism, as the description of the as-grown NW did not consider the nanofiber bundle.[48,167] Most of the etching mechanisms reported in literature suggest that etching starts in the center.[24,25] The formation of a trench, which is located more close to the outer part and was clearly observed in the present study, was not taken into account. However, also Chai et al. show NWs with a trench, but this morphological change was not further discussed.[27]

![Figure 7.6: Schematic illustration of the etching process.](image)

Additional heating after etching was not studied so far, but the morphological changes that take place during the heat treatment are similar to those observed also for as-grown NWs (see Sec. 4.3),[167] and result from a merging of the nanofibers due to condensation of the surface -Ti-OH groups. As the total free volume between the nanofibers is much larger after the etching, this space cannot be compensated and channels arise. The assumption that the processes are the same, independently of the post-growth treatment, is confirmed by annealing of NWs that were grown with ButOH as solvent. These NWs also exhibit a strong fibrous morphology before the heat treatment and the merging of these
nanofibers during the annealing results in channels parallel to the growth direction. The only difference is the spacing between the nanofibers, which is smaller compared to the one of hydrothermally grown and subsequently slightly etched NWs. As a consequence, also the channels of the annealed NWs grown in ButOH have a smaller diameter.

Except for the highly acidic etching for long time, all the treatments, presented here, conserve the 1D structure of the NW array. Thus, one can assume that also the properties, which are related to this 1D structure, are preserved. In addition to the onedimensionality, higher surface areas can be gained. The smallest pores have a diameter of 7 nm and thus should be accessible by water (around 3 Å in diameter) and dye molecules (1-2.5 nm in diameter).[295] Admittedly, for polymers a complete filling is more challenging and even tubes with large diameters or mesoporous structures cannot be completely filled with the polymer due to insufficient wetting and spreading kinetics.[296,297]

### 7.4 Conclusion and outlook

This study shows that a combination of solvothermal synthesis, hydrothermal etching and heat treatment is a suitable approach to achieve new morphologies for 1D nanostructures. Etching in HCl is suitable to produce nanostructures with increased surface area ranging from highly fibrous bundles to nanotubes with rectangular cross-section. The etching study reveals that the weakest part of the as-grown NW is between the single nanofibers, but also the outermost nanofibers, located between an approximately 12 nm thick surrounding wall and the nanofiber bundle, can be easily etched away. The highest chemical resistance is found for the around 12 nm thick, nearly single-crystalline, surrounding wall.

Additional heat treatments offer to fabricate more complex morphologies. Here, slightly etched NWs are promising as they possess a highly porous structure with channels parallel to the NW growth direction after an additional heat treatment in air. However, similar morphologies can also be obtained by combining solvothermal growth in acidic ButOH with an additional annealing in air. The resulting NWs show a similar structure at the tip, but the depth of the nanochannels has not been determined yet.

In future, a combination of hydrothermally etched NWs with their large surface area and a heat treatment in N₂ or at 1050 °C in vacuum are promising, as these heat treatments manipulate the surface of the TiO₂, as shown in Chapter 5 and 6.
8 Summary and outlook

8.1 Summary

In this thesis, rutile TiO$_2$ NWs were hydrothermally grown and exposed to different post-growth treatments in order to tailor the (internal) nanostructure and defect distribution, which in turn influence the optical and electronic properties of the NWs. For the post-growth modifications heat treatments in different environments and hydrothermal etching were used. In order to understand the (internal) nanostructure and the defect distribution of these NWs, in-depth TEM studies were performed including (HR) imaging in TEM and STEM, diffraction, tomography and spatially resolved spectroscopic investigations by EDS and EELS. Additional heating experiments in the TEM allowed an in situ observation of changes in the internal nanostructure during heat treatments and completed the picture. Collectively, the obtained results shed some light on the interplay between post-growth modifications, defect distribution, material properties and stability. Thus, the presented post-growth treatments are suitable methods to tune the properties of TiO$_2$ NW arrays and the knowledge gained in this thesis can be utilized for targeted defect engineering of rutile TiO$_2$ NWs.

Annealing in air at 500 °C led to structural changes that are related to defects. In the as-grown NWs two types of defects dominate, namely planar or line defects and O$_{\text{vac}}$. The 1D and 2D defects, such as stacking faults and dislocations were the origin of the nanofiber bundle, which builds up the as-grown NW. They were removed at moderate temperatures above 250 °C. This temperature initiated a dehydratization, which resulted in the formation of new Ti-O-Ti bonds and the mesocrystalline NWs merged to single-crystalline NWs. At temperatures above 500 °C vacancy condensation took place and Wulff-shaped voids formed. The interior of these voids was covered with a Ti$^{3+}$ rich, amorphous TiO$_x$ layer. UV-vis measurements proved that the defect removal and the condensation of O$_{\text{vac}}$ led to a narrowed band gap (as-grown: $E_g=2.9$ eV, annealed $E_g=2.5$ eV) and a reduced amount of mid-band gap states (as-grown: $E_U=0.62$ eV, annealed: $E_U=0.49$ eV). In addition, the chemical as well as the mechanical stability of the NWs was affected by the heat treatment. Under acidic, hydrothermal conditions a much higher chemical stability...
Summary and outlook

8.1 Summary

for NWs that were annealed in air was found compared to the as-grown NWs. Moreover, the annealed NW arrays showed less deformation during scratching with moderate forces. However, the heat treated NWs fractured under very high forces, whereas the as-grown NWs only showed deformation at the tip.

In addition, the optical and electric properties were tailored by the use of different environments for the heat treatment at 500 °C. Two different heating environments with either oxidizing (air) or slightly reducing (N₂) properties were used and significant changes in properties arose. No matter, if the annealing was performed in air or N₂, a condensation of O_{vac} took place and single-crystalline, lattice defect free, rutile TiO₂ NWs that incorporate voids were formed. While the as-grown NWs with a high amount of O_{vac} showed n-type conductivity, the absence of O_{vac} after the annealing resulted in blocking of the transient current. Consequently, NWs annealed in air were almost insulating. However, NWs annealed in N₂ behaved completely different. They were of black color and showed an almost metal-like conductivity. These properties were related to the slightly reducing atmosphere of N₂, which inhibited the removal of the surface-near O_{vac}. Thus, a core-shell structure with an around 10 nm thick, highly oxygen deficient shell and an insulating rutile TiO₂ core was formed. The properties of the black TiO₂ NWs with metal-like conductivity were dominated by the small volume fraction of the shell and its surface and interface regions. The entire shell was oxygen deficient and thus enriched with Ti^{3+}, because no oxygen uptake from the slightly reducing environment of the N₂ was possible. Special interest was devoted to the surface of the shell and the interface between the shell and the core. TEM studies verified that the shell was covered with an out-of-plane ordered surface layer, which is the origin for the black color. In this layer the highest amount of Ti^{3+} was detected. In addition, the shell and the core were separated by a defective interface with also high Ti^{3+} concentrations, as proven by EELS. It is a strong indication for the formation of a conductive interface between the core and the shell, which might be responsible for the metal-like conductivity.

The previously discussed heat treatments were performed on NW arrays grown on FTO substrates. For another type of heat treatment utilized in this work the NW arrays were grown on Si substrate, which required some pretreatment of the substrate to facilitate the NW growth. The use of a Si substrate allowed to carry out a heat treatment at 1050 °C in vacuum, where the FTO substrate would have been already melted. The occurring diffusion processes were suitable to cover TiO₂ NWs uniformly with a 4 nm thick SiO_x shell without any intermixing between both materials. Therefore, the functionality of TiO₂ was preserved, while unwanted surface reactions were suppressed. Besides the shell formation, this treatment healed all defects of the rutile TiO₂ NWs, but in contrast to
the other heat treatments presented in this work, the core was not interspersed by voids. Instead, the free volume was compensated by an additional faceting towards the tip of the NWs. As this faceting is a fast process, whereas the shell formation exhibits slow kinetics, these structural changes did not affect the formation of a SiO\(_x\) shell, which homogeneously covered the TiO\(_2\) NWs.

Finally, some synthesis strategies, which combined hydrothermal growth, etching and heat treatments were presented and new morphologies for solvothermally grown rutile TiO\(_2\) NWs were derived. The big variety of morphologies were enabled as not only H\(_2\)O but also ButOH was used as solvent for the solvothermal growth. The obtained nanostructures ranged from highly fibrous NWs, over NWs with tiny channels parallel to the growth direction to completely hollow nanotubes with squared cross-sections. Based on a systematic etching study of hydrothermally grown TiO\(_2\) NWs a detailed etching mechanism was derived. This study also highlighted that the as-grown rutile TiO\(_2\) NWs were not a simple one-phase material but can be divided in several building units with different etching rates.

8.2 Outlook

The intention of this thesis was to shed some light on the influence of defects (especially O\(_{\text{vac}}\)) on the properties of hydrothermally grown rutile TiO\(_2\) NWs and to develop strategies to tune the defect distribution. Although the presented results revealed the interplay between defects, post-growth treatment, and properties, it is only a first step on the way to more efficient TiO\(_2\) devices. While this work contributes to a better understanding of defect mediated properties in rutile TiO\(_2\) NWs, it also raised new issues, which should be clarified in the future. Especially more \textit{in situ} experiments in the TEM, such as \textit{in situ} heating experiments to higher temperatures (up to 1050 °C or higher), with and without Si at the bottom of the NW, and conductivity measurements of single NWs are promising for an even deeper understanding of the involved mechanisms. However, such experiments are challenging due to stability problems of the NWs that arise, if high thermal or electrical stresses are combined with the illumination by high energy electrons.

In the future, the combination of the two key concepts of this work will be a promising approach to design even better materials: Etching to obtain high surface 1D nanostructures and surface manipulation by heat treatments in different environments. While the etching increases the surface area significantly, the heat treatment in N\(_2\) at 500 °C or in vacuum at 1050 °C produces an additional shell that improves the properties of the TiO\(_2\)
Furthermore, a natural extension of this work would be the effort to incorporate the obtained TiO$_2$ photoanodes in application, such as solar cells, water splitting devices or in photocatalytic water purification. In this way, TiO$_2$ has the chance to persist as the ruler of the Renewable Energy Age and make this age to a Golden Age.
Bibliography


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Danksagung

"Dankbarkeit zu fühlen und sie nicht auszudrücken, ist wie ein Geschenk zu verpacken und es nicht zu verschenken."

Adolphus William Ward


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