Abstract

Nanomaterials provide different or additional features compared to bulk material. Their properties are often controlled by their size and shape. For several decades, more and more nanomaterials have found their way into various applications. Nanostructures are employed due to their specific properties or enhanced surface area, but also provide routes towards decreasing the size of devices.
An outstanding material for nanostructures is titania (TiO_2). It is a non-toxic, abundantly available semiconductor capable of resisting intensive chemical and thermal stress and its optoelectronic features are tunable over a broad range through relatively inexpensive methods. Hence, TiO_2 is useful for a variety of applications such as surface functionalization, photocatalysis, photovoltaics, photodetectors, gas sensing, data storage, and energy storage. There are many methods to generate TiO_2 nanostructures. This thesis deals with controlling the fabrication and properties of hydrothermally grown rutile TiO_2 nanorods.

First, a detailed introduction reviews known properties, fabrication methods, and manipulation techniques of these nanostructures.

Second, the hydrothermal growth process on selected substrates such as fluorine tin oxide (FTO), anatase and rutile TiO_2 films is described. Especially, anatase substrates exhibit a deviation from simple epitaxial growth processes. It is strongly assumed that anatase nanoparticles become chemically unstable after reaching a critical size and are converted into rutile growth seeds. In addition, the annealing temperature affects the density of grown nanorods significantly. Films annealed at lower temperatures consist of smaller grains and provide a higher density of nanorods. The films are fabricated using a sol-gel method, spray pyrolysis, sputter deposition, and electron-beam evaporation. Features are investigated by SEM, AFM, XRD, and TEM.

Third, besides nucleation and the early stage of nanorods, the growth itself is investigated in more details. Especially, the fine structure of these rods riddles scientists and their origin is not completely understood. An effect of the fibrous fine structure on optical and electronic properties has to be considered. In this work, a model is introduced describing the origin of the fine structure by a thermodynamic disequilibrium between the crystallization and energy minimization process. Several features of nanorods grown under different conditions are predicted by the presented model such as the reduction of the fine structure at elevated growth temperatures.

Fourth, the main challenge of this thesis was the finding of methods for position-controlled fabrication of nanorods. Here, new, fast, and inexpensive techniques are presented and compared with well-established techniques such as optical or electron-beam lithography.
A 2D lattice without employing lithography is achieved by placing a monolayer of polystyrene spheres (PSML) on a blank substrate. The PSML acts as a mask during the seed layer deposition and the nanorods grow on highly ordered seed islands.
A rather simple method is to sputter a thin SiO_2 layer on a rutile TiO_2 film that was deposited on a substrate with some trenches. Inside the trenches, the film becomes much thinner than on the flat surface. While thick SiO_2 films prevent the growth of nanorods on the untreated surface, the SiO_2 shell inside the trenches is too thin. Consequently, nanorods grow inside the trenches only. The trenches have been created by focused ion beam (FIB) milling.
Another newly implemented technique is a scanning probe method. In order to do so, anatase TiO_2 particles are generated as a primary stage for rutile seeds by scratching with a silicon tip across an anatase film. Since the particles do not move across the film, the growth of nanorods is triggered on scratched positions only.
Furthermore, a laser is employed to melt mixed phases containing titanium, silicon, and oxygen which are situated at the interface between anatase TiO_2 films and silicon substrates. These mixed phases are created by diffusion of atoms across the TiO_2/silicon interface during annealing. As the melt solidifies, rutile TiO_2 is formed promoting the local growth of rutile TiO_2 nanorods. The melting is performed using a frequency-doubled Nd:YAG laser at 532 nm. A continuous wave laser is applied to write individual structures on a wafer, while a pulsed laser is applied to create a large-area pattern by two-beam interference.

Fifth, optical characterization offers insights in light reflection and scattering of highly anisotropic TiO_2 nanostructures. These results give rise to the assumption that TiO_2 nanorods act as tiny dielectric antennas. In this context, the transition from single particle to effective medium behavior is discussed based on measurements performed with an optical microscope run in bright and dark field mode.

Sixth, current over voltage characteristics demonstrate the variety of adjustable electronic features achieved by different growth conditions or annealing in different atmospheres. It is known that the variation of the oxygen vacancy density changes the number of mobile electrons and even the band structure. This results in either highly insulating or highly conductive nanorods as shown in this thesis. Switching between ohmic and rectifying contacts at the nanorod/electrode interface is described as well. Both, charge trapping and ion migration, change the band structure, the spatial, and energy distribution of charges and trap states in TiO_2 nanorods during intensive voltage or current stress. These effects are characterized by time-dependent transient currents. All experiments were performed in a controlled and dry atmosphere.

Based on physical models and descriptions, this work gives a detailed instruction for the position-controlled fabrication of rutile TiO_2 nanorods and how to manipulate their optical and electronic properties.

Zusammenfassung

Nanomaterialien bieten unterschiedliche und zusätzliche Eigenschaften gegenüber weniger fein gegliederten Materialien. Ihre Eigenschaften werden oft durch ihre Größe und Form festgelegt. Seit vielen Jahren werden immer mehr Nanomaterialien in verschiedenen Anwendungen verwendet. Einerseits werden Nanostrukturen aufgrund ihrer spezifischen Eigenschaften oder relativ großen Oberfläche eingesetzt. Andererseits bieten Nanostrukturen die Möglichkeit Geräte und Bauteile immer kleiner zu bauen.
Ein hervorragendes Material für Nanostrukturen ist Titandioxid (TiO_2). Es ist ein ungiftiges, reichlich in Erzlagerstätten vorhandenes Halbleitermaterial, welches eine hohe chemische und thermische Beständigkeit aufweist. Seine optoelektronischen Eigenschaften sind über ein breites Spektrum mit relativ kostengünstigen Methoden abstimmbar. Somit eignet sich TiO_2 für eine Vielzahl von Anwendungen wie Oberflächenfunktionalisierung, Photokatalyse, Photovoltaik, Photodetektoren, Gassensoren, Daten- und Energiespeicherung. Es gibt viele Methoden, um Nanostrukturen aus TiO_2 zu erzeugen. Diese Arbeit beschäftigt sich mit der kontrollierten Herstellung und den Eigenschaften von hydrothermal gewachsenen Rutil-TiO_2-Nanostäbchen.

An erster Stelle wird eine detaillierte Einführung zu bereits bekannten Eigenschaften, Herstellungs- und Optimierungstechniken dieser Nanostrukturen gegeben.

Zweitens wird das Verfahren des hydrothermalen Wachstums auf ausgewählten Substraten, wie z.B. Fluor-Zinnoxid- (FTO) oder Dünnschichten aus Anatas- und Rutil-TiO_2, beschrieben. Insbesondere Anatas-Substrate zeigen eine Abweichung von einfachen epitaktischen Wachstumsprozessen. Es wird angenommen, dass Nanopartikel aus Anatas nach Erreichen einer kritischen Größe chemisch instabil und in Wachstumskeime aus Rutil umgewandelt werden. Zusätzlich beeinflusst die Temperatur beim Tempern der Schicht aus Anatas die Dichte der gewachsenen Nanostäbchen erheblich. Filme, die bei niedrigeren Temperaturen getempert werden, bestehen aus kleineren Körnern und liefern eine höhere Dichte von Nanostäben. Die Filme können mittels Sol-Gel-Verfahren, Sprühpyrolyse oder Sputterabscheidung hergestellt werden. Die Eigenschaften werden durch REM, AFM, XRD und TEM untersucht.

Drittens wird neben der Keimbildung und dem frühen Wachstumsstadium der Nanostäbe das Wachstum selbst näher untersucht. Vor allem die Feinstruktur dieser Nanostäbe wirft Wissenschaftlern Rätsel auf und ihre Entstehung ist bei Weitem nicht vollständig verstanden. Ein absehbarer Einfluss der Faserstruktur auf die optischen und elektronischen Eigenschaften ist zu berücksichtigen. In dieser Arbeit wird ein Modell eingeführt, das den Ursprung der Feinstruktur durch ein thermisches Ungleichgewicht zwischen den Prozessen der Kristallisation und der Energieminimierung beschreibt. Mehrere Merkmale von Nanostäben, die unter unterschiedlichen Bedingungen gezüchtet wurden, werden durch das dargestellte Modell vorhergesagt, wie beispielsweise das Verschwinden der Feinstruktur bei erhöhten Wachstumstemperaturen.

An vierter Stelle bestand die Hauptaufgabe darin, Methoden zur lokalen Herstellung von Nanostäben zu finden. Hierbei werden neue, schnelle und kostengünstige Techniken vorgestellt und mit bewährten Verfahren wie optischer oder Elektronenstrahl-Lithographie verglichen.
2D-Gitter lassen sich ohne Verwendung einer Lithographie herstellen, indem eine Monolage aus Polystyrolkugeln (PSML) auf ein Substrat aufgebracht wird. Die PSML wirkt als Maske während die Saatschicht aufgetragen wird. Somit wachsen die Nanostäbe auf hochgradig geordneten Saatinseln.
Ein weiteres, einfaches Verfahren zur Herstellung individueller Strukturen besteht darin, eine dünne Schicht aus SiO_2 auf eine Schicht aus Rutil zu sputtern, die auf einem Substrat mit einigen Gräben aufgetragen wurde. Innerhalb der Gräben werden die Filme viel dünner als auf der unbehandelten Oberfläche. Während dicke Schichten aus SiO_2 das Wachstum von Nanostäben auf der Oberfläche verhindern, ist die Hülle aus SiO_2 innerhalb der Gräben zu dünn dafür. Folglich wachsen Nanostäbe nur innerhalb der Gräben, welche durch Fräsen mit einem fokussierten Ionenstrahl (FIB) erzeugt wurden.
Als weitere neue Technik wird ein Rastersondenverfahren demonstriert. So werden Partikel aus Anatas als Vorstufe für Keime aus Rutil durch Kratzen mit einer Siliziumspitze über eine Dünnschicht aus Anatas

erzeugt. Da sich die Partikel nicht frei bewegen können, wird das Wachstum von Nanostäben nur an den verkratzten Positionen ausgelöst.
Außerdem wird ein Laser verwendet, um Mischphasen, die Titan, Silizium und Sauerstoff enthalten, zu schmelzen. Diese Mischphasen befinden sich an der Grenzfläche zwischen der Schicht aus Anatas und dem Siliziumsubstrat. Sie werden durch die Diffusion von Atomen über die TiO_2/Silizium-Grenzfläche erzeugt, während die Schichten aus Anatas getempert werden. Während des Verfestigungsprozesses der Schmelze wird Rutil gebildet, wodurch das lokale Wachstum der Nanostäbe aus Rutil gefördert wird. Das Schmelzen wird unter Verwendung eines frequenzverdoppelten Nd:YAG-Lasers bei einer Wellenlänge von 532 nm durchgeführt. Es wird sowohl ein cw-Laser zur Herstellung individueller Strukturen als auch ein gepulster Laser zur Herstellung großflächiger Muster durch Zweistrahlinterferenz verwendet.

Die optische Charakterisierung bietet Einblicke in die Lichtreflexion und Streuung der stark anisotropen Nanostrukturen. Diese Ergebnisse führen zu der Annahme, dass die Nanostäbe als winzige dielektrische Antennen wirken. Und so kommen sie als Nano-Streuer, Nano-Resonatoren, Nano-Polarisatoren, Nano-Gitter und Wellenleiter in Frage. In diesem Zusammenhang wird das Übergangsverhalten von Einzelpartikeln zu einem effektiven Medium diskutiert. Die Eigenschaften werden durch ein optisches Mikroskop im Hell- und Dunkelfeldmodus untersucht.

Zuletzt zeigen Strom-Spannungs-Kennlinien die Vielfalt an erreichbaren elektronischen Eigenschaften, die durch Tempern in verschiedenen Gasen oder durch die Herstellung mit unterschiedlichen Wachstumsbedingungen erreicht werden. Es ist bekannt, dass die Variation der Sauerstofffehlstellendichte die Menge der mobilen Elektronen und sogar die Bandstruktur ändert. Dies führt entweder zu stark isolierenden oder gut leitfähigen Nanostäben, wie in dieser Arbeit gezeigt wird. Ein Schalten zwischen ohmschen und Gleichrichtungs-Kontakten an der Nanostäbchen/Elektroden-Grenzfläche wird ebenfalls beschrieben. Sowohl das Einbringen von Ladungsträgern als auch die Ionenwanderung verändern die Bandstruktur sowie die räumliche und energetische Verteilung von Fallenzuständen in Nanostäben aus TiO_2 während hoher Spannungs- oder Strombelastungen. Diese Effekte werden durch zeitabhängige Messungen untersucht. Alle Messungen werden in einer wohldefinierten und trockenen Atmosphäre durchgeführt.

Auf der Grundlage von physikalischen Modellen und Beschreibungen liefert diese Arbeit eine detaillierte Anleitung für die kontrollierte Herstellung von Nanostäben aus Rutil und die Anpassung deren optischer und elektronischer Eigenschaften.

1 Introduction

As a nontoxic, chemically stable, and frequently occurring material with various valuable electronic and optoelectronic properties TiO_2 has great potential for innumerable applications. The broad range of properties and applications can even be extended by using nanostructured TiO_2 [1]. In addition, nanostructured TiO_2 systems offer a high surface area, single crystal structures, and shape related scattering facilities. In spite of intensive research on this material in the past, many properties which are essential for various applications are not yet understood or even controllable. In this thesis, fundamental questions of the growth mechanism, the position-controlled fabrication, and the optical and electronic properties of rutile TiO_2 nanorods$^\diamond$ are discussed. For a better understanding, terms marked with a diamond symbol ($\diamond$) are explained briefly in the glossary. Framed paragraphs emphasize important information and introduction graphics in the beginning of "results and discussions" chapters help the reader to keep the track. A lot of additional information and graphics are given in the appendix. The detailed chapters summarizing the state of research are supposed to help other young researchers to find a faster access to this topic.

TiO_2 was brought into the industry for the first time in 1923. In those days, it was used as a white pigment only, but soon its applications became more and more versatile. Today TiO_2 is indispensable in many branches of industry as shown in the first chapter. In addition, researchers opened various doors to new potential applications in recent decades [2]. A quite promising trend is to use nanostructured TiO_2 such as rutile nanorod array (NRA). Due to their appropriate electronic and optoelectronic properties, their simple fabrication methods, and high chemical stability [3–5], these arrays are beneficial for photocatalysis devices [3, 6–14] (using both anatase [15–19] and rutile [20–23] TiO_2), photocatalytic disinfection [24–28], intimately coupled photobiocatalysis (ICPB) [29], hydrophobic/superhydrophilic$^\diamond$ materials [30–36], gas sensors [37–46], gasochromic displays [47–49], electrochromic displays [50], biosensing [51, 52], transparent electrodes [50], photodetectors [53, 54], field emission devices [55, 56], nonlinear optical devices [57], hybrid solar cells$^\diamond$ [58–62], organic light-emitting diodes (OLEDs) [63–66], fuel cells [67], data storage devices [68], flexible data storage devices [69], field-effect transistors [64, 70, 71], flexible capacitors [72], supercapacitors$^\diamond$ [73], and lithium batteries [74–84]. Since TiO_2 is a non-toxic material there are applications in medical engineering as well. It was shown by Bjursten et al. [85] that TiO_2 nanostructures are a promising candidate for implant coatings to obtain a stronger adhesion between osteoblasts$^\diamond$ and the implant surface compared with conventional microstructured coatings. In many current applications, NRAs are fabricated by simple, fast, and inexpensive hydrothermal methods resulting in homogeneously distributed NRAs. Applications using defined distributions of rutile TiO_2 nanorods are rare, largely because of the absence of suitable techniques for the fabrication of locally confined arrangements. Confined geometries for NRAs are of great interest for locally increased gas-sensing, photocatalysis, hydrophobic/superhydrophilic characteristics, light scattering, or surface roughening as it is useful for lab-on-a-chip$^\diamond$ for instance [86–88].

The findings shown in this thesis are not only important for the integration of rutile TiO_2 nanorods into devices, but a significant part of the achieved knowledge could be transferred to other rutile nanostructures consisting of different metal oxides. In the following a brief overview of various rutile metal oxides and their applications is given to demonstrate the great significance of this research for the technical development in many fields. VO_2 shows a metal-insulator transition at 65 °C [89]. CrO_2 nanorods show temperature-dependent magnetotransport properties [90]. GeO_2 is used for infrared (IR) transparent glasses [91] and as a catalyst in the production of polyethylene terephthalate [92] and also available as nanorods [93]. MoO_2 has a low electrical resistivity of $88\,\mu\Omega \cdot \mathrm{cm}$ [94, 95], high chemical stability [96] and thus, it is used in a wide range of applications such as anode material in lithium batteries [97–102], field emission devices [96, 103], nanorod based photodetector devices [104] and catalysis processes such as the dehydrogenation of alcohols [105], the reformation of hydrocarbons [106] and biodiesel$^\diamond$ [107]. Furthermore, several fabrication techniques for nanorods are reported [94, 96, 96]. RuO_2 is used for catalyzing the Deacon process$^\diamond$ for chlorine production [108], as an active material in supercapacitors due to its high charge transfer capability [109–112], and as a resistive temperature sensor for low-temperature experiments [113]. Different recipes for RuO_2 nanorod fabrication are reported [111, 114, 115]. SnO_2 nanorods are used for resistivity based gas sensors [116–118], transparent electrodes for dye-sensitized solar cells (DSSCs)$^\diamond$ [119], and lithium ion batteries [120] as well as fully transparent transistors [121]. TeO_2 is used for fiber optics and waveguide applications due to its high refractive index [122] and as an acousto-optic material [123–125]. OsO_2 single crystals show metallic resistivity of about $15\,\mu\Omega \cdot \mathrm{cm}$ [126] and IrO_2 is used for microelectrodes for electrophysiology [127, 128].

In this thesis, the research focuses on rutile TiO_2 nanorods as a potential model system for all other rutile metal oxide nanostructures. In the beginning, a general overview on TiO_2 is given starting from the economic meaning, natural mineral deposits, extraction from natural minerals, morphologies, chemical and mechanical stability, and electronic and optical properties to the point of confinement effects on low dimensional systems (Chapter 2,3).

In the experimental chapter (Chapter 4), fabrication and characterization techniques are described. This includes the hydrothermal growth method of rutile TiO_2 nanorods as well as the processing of seed layers promoting the growth of such nanorods. For the methods applied in this thesis, the processing is described in detail. For the sake of completeness, further typical fabrication techniques are described briefly as well. Characterization techniques include methods to determine the surface topography (atomic force microscopy (AFM), scanning electron microscopy (SEM)), the atomic structure (X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX)), the optical properties (ellipsometry, ultraviolet-visible-infrared (UV-Vis-IR) absorption spectroscopy, optical microscopy), and the electronic properties (current over voltage (I-V), current over time (I-t), impedance spectroscopy (IS)).

To promote the growth of rutile TiO_2 nanorods on substrates without a rutile surface an appropriate rutile seed coating is needed [61, 129–131]. Typically, these seed layers are made of polycrystalline TiO_2 films that can be fabricated employing sputter deposition [132–134], electron-beam evaporation [132, 135, 136], atomic layer deposition (ALD) [137–141], sol-gel methods [142, 143], spray pyrolysis [144–147], or $TiCl_4$ treatments [148–150]. Besides TiO_2, fluorine tin oxide (FTO) appears as a polycrystalline rutile film as well. Usually, FTO films are made by sputter deposition [151] or spray pyrolysis [152]. Due to its high conductivity and transparency, FTO is often used as an electrode for photovoltaic applications [61, 153]. There are a lot of reports about the application of rutile TiO_2 nanorods, but only a few articles about the details of their growth process [61, 129, 153–167]. Usually, the as-grown nanorods consist of numberless smaller crystallites forming a mesocrystal rather than a single crystal [168]. So far, it is assumed that the grain boundaries separating these crystallites originate from point defects implemented during the crystal growth.

In this context, the new knowledge delivered by this work is a detailed overview of the structural properties of differently fabricated seeds (Chapter 5). In addition, a detailed relationship between the shape of the seed, the growth time, and the shape of the grown nanorod is described (Chapter 6). Besides rutile seeds, particular crystal formations on anatase surfaces are introduced as an alternative growth facilitator of rutile TiO_2 nanorods. A model is introduced explaining the creation of small crystallites inside the as-grown nanorods. It is demonstrated that the consequences of this model allow to control the density and shape of these crystallites and hence expand existing models with respect to important problems (Chapter 7).

A basic question in many electronic devices is to locate individual semiconductor structures precisely on a substrate. The position-controlled fabrication of semiconductor nanorods was applied successfully for different semiconductor materials in the past. The most common technique is to use lithography for selective seed layer deposition. A typical example is the patterning of ZnO NRAs, which share many properties and applications with TiO_2 NRAs. Common techniques to achieve submicron structures are optical immersion, deep UV, X-ray, nanoimprint, or electron-beam lithography [169–172]. These techniques can be used to create very localized seeds for the hydrothermal growth process. A simple option is to use optical lithography and accept a rather large minimal structure for a low purchase price. However, this technique is absolutely suitable for mass production [173, 174]. The smallest structures that are achievable with electron-beam lithography are about 2 nm wide [175–179], but this technique is too expensive and time consuming for industrial mass production. The resolution of extreme ultraviolet (EUV) lithography is 10 nm so far [180]. Although this technique is more suitable for commercial applications, it is also extremely expensive. Mi-Hee and Hyoyoung introduced nanoimprint lithography (NIL) to fabricate stripes and ordered islands consisting of ZnO nanorods [181]. Park et al. developed this technique further and demonstrated a pattern of parallel arranged stripes covered with ZnO nanorods by combining ultraviolet-assisted nanoimprint lithography (UV-NIL) and hydrothermal growth [182]. Another quite advanced technique is to generate local wetting gradients before the growth of ZnO nanorods [183]. Techniques of position-controlled growth of TiO_2 NRAs are found at rare intervals and dealing mostly with large area patterns [184–186]. However, it is possible to transfer many techniques listed for ZnO to TiO_2 nanorods.
In this context, the new knowledge delivered by this work includes mainly two further techniques – a scanning probe and a thermal lithography – to achieve submicron structures in a relatively fast and inexpensive way (Chapter 8-9). The new techniques are compared with optical and electron-beam lithography and a few derived techniques are discussed.

Related to their high refractive index, TiO_2 nanorods are efficient light scatterers. Because of this feature, they are applicable as nano-antennas [187, 188], nano-cavities [189–192], and nano-polarizers [193–196]. But there are hardly reports describing the scattering of small anisotropic accumulations of TiO_2 nanorods.
In this context, the new knowledge delivered by this work is the documentation of the transition from single nanorod scattering through collective nanorod scattering into non-scattering effective media consisting of dense NRAs (Chapter 10). To investigate collective nanorod scattering, highly anisotropic NRAs were grown on structures made by the above described position-controlled seed deposition techniques.

The ability to switch the electronic properties of TiO_2 in a controlled way turns this typically n-type semiconductor into an interesting building block for all kinds of electronic devices. The dominant intrinsic electron donors in TiO_2 are oxygen vacancies [197–203]. Their density corresponds to the number of mobile electrons and influences the position of the Fermi level. As a consequence, the limiting conduction mechanism is also fixed by the distribution of oxygen vacancies. The number and location of oxygen vacancies can be influenced by electrical fields

[204, 205], plasma [206], chemical [207–209], radiative [30, 210, 211], or thermal [212–214] treatments. Especially, the effect of the electrical field is used for data storage based on resistive switching [215–224]. Besides their electron donating nature, crystal defects can act as electron traps and charge the TiO_2 locally [225]. Of course, this feature affects the limiting charge transport mechanisms as well, but such charging is highly valuable for nanocrystal (NC) memory devices, where the electrical field of the trapped charges control the current flow through the channel of a field-effect transistor (FET) [226]. This effect was already applied in experiments employing silicon nitride as a charge trapping material and it is essential for decreasing the size of FETs [227, 228].
In this context, the new knowledge delivered by this work is a detailed description how the conduction mechanisms are influenced by certain chemical and thermal treatments of as-grown rutile TiO_2 nanorods (Chapter 11). In particular, the role and control of the density and distribution of intrinsic electron donors and traps are discussed.

In its entirety, this thesis can be split into two parts. On the one hand, there is the “hardware” part which covers new insights of the physical and chemical understanding of the hydrothermal growth of rutile TiO_2 nanorods, as well as the position controlled growth, which is essential for the fabrication of devices needing a spatially resolved functionality on a micro- or nanoscale. On the other hand, there is the “software” part, which deals with the physical understanding of optical and electronic properties of rutile TiO_2 nanorods and thus offers pathways to design optoelectronic properties for user-defined applications.

Introduction	C. 1	
State of Research	C. 2 C. 3	structural, optical, electronic properties hydrothermal growth of rutile TiO_2 nanorods
Experimental Methods	C. 4	fabrication and characterization
Results and Discussions: Seeds and Growth Mechanisms	C. 5 C. 6 C. 7	seed layers hydrothermal growth process on seed layers fine structure of rutile TiO_2 nanorods
Results and Discussions: Nanorods Grown in Controllable Confined Geometries	C. 8 C. 9	established position-controlled techniques, advanced scanning probe lithography, LASER-induced hydrothermal growth
Results and Discussions: Optical and Electronic Properties	C. 10 C. 11	from single nanorod to many body scattering conduction mechanisms in defect-rich nanorods
Conclusion and Outlook	C. 12	

Table 1.1: *Thematic overview of this thesis (C. = Chapter).*