A study of electrical, dielectric and structural features as a route towards understanding a novel Transparent Conductive Oxide

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation vorgelegt von

Master of Science
Daniel Dorow-Gerspach
aus Neu-Ulm

Berichter:
Universitätsprofessor Dr. rer. nat. Matthias Wuttig
Universitätsprofessor Dr. rer. nat. Dieter Mergel

Tag der mündlichen Prüfung 29.03.2017

Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek online verfügbar.
Contents

Abstract I

Zusammenfassung II

1 Introduction 1

1.1 The Big Surprise - Discovery of TiO₂ as TCO . . . . . . . . . . . . . . . . . . . . . . 3
1.2 Some Material Properties of TCOs . . . . . . . . . . . . . . . . . . . . . . . . . . . 5
1.3 Structure of this work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 9

2 Fundamentals 11

2.1 Thin Film Preparation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 11
2.1.1 Reactive Magnetron Sputtering . . . . . . . . . . . . . . . . . . . . . . . . . . 14
2.2 DC Electrical Properties . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 16
2.2.1 Basic Concepts . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 16
2.2.2 Hall Effect . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 18
2.2.3 Effective Mass . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 19
2.2.4 Polaron . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 21
2.2.5 Insulators . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 24
2.2.6 Metal Insulator Transition MIT . . . . . . . . . . . . . . . . . . . . . . . . . . 26
2.2.7 Metal . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 28
2.2.8 Defect Scattering . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 28
2.2.9 Phonon Scattering . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 31
2.2.10 Ionized Impurity Scattering II . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
2.2.11 Additional Low Temperature Effects . . . . . . . . . . . . . . . . . . . . . . . 35
2.2.12 Magnetoresistance . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 39
2.3 AC Electrical Properties . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 42
2.3.1 Polarization Mechanisms . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 43
2.4 Electro Magnetic Waves . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 47
2.4.1 Low Frequencies: MIR/FIR . . . . . . . . . . . . . . . . . . . . . . . . . . . . 48
2.4.2 Medium Frequencies: NIR/VIS/UV . . . . . . . . . . . . . . . . . . . . . . . 49
2.4.3 High Frequencies: X-ray . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 54

3 Experimental Methods 57

3.1 Sample Preparation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 57
3.1.1 Sputtering Procedure . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 58
3.1.2 Sputtering Characteristics . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 63
3.1.3 After Deposition Treatments . . . . . . . . . . . . . . . . . . . . . . . . . . . 64
3.2 Electrical Measurements . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 65
3.2.1 Principles of Electrical Measurements . . . . . . . . . . . . . . . . . . . . . . 66
3.2.2 Hall-Effect and MR Measurement . . . . . . . . . . . . . . . . . . . . . . . . 70
3.2.3 Low Temperature Setups . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 72
3.3 Impedance Spectroscopy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 74
3.3.1 Special Sample Preparation . . . . . . . . . . . . . . . . . . . . . . . . . . . . 75
3.3.2 Impedance Meter . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 76
Abstract

It is impossible to imagine our contemporary every day life without techniques like flat screens and touch displays or the energy revolution without solar cells. What do these technologies have in common? Among others, the necessity of transparent and conductive materials as top electrodes for addressing individual pixels and collect the generated energy respectively. Transparent conductive oxides (TCO) are a fascinating class of materials which are able to fulfill these needs. They are transparent like electrically insulating glass but at the same time nearly as conductive as shiny metals. The most common oxide in industry is indium oxide (In$_2$O$_3$) usually doped with tin (Sn) due to its superior electrical conductivity. The growing demand and the rarity of In requires the search for alternatives. Such candidates are tin dioxide (SnO$_2$) and zinc oxide (ZnO) which are under investigation since several decades as well. Together with the first representative but toxic CdO (discovered 1907 [Cas11]), they form the group of the common binary oxides and are close to each other in the periodic table of the elements. One hundred years later titanium dioxide (TiO$_2$) doped with niob (Nb) has been found to possess also very good TCO properties [FHY+05]. This was highly surprising as Ti is located in a completely different region of the periodic system.

In this work TiO$_2$ films with outstanding quality have been prepared by reactive magnetron sputtering which enables the large scale production and boosts the applicability of this novel TCO. A post-deposition annealing step at much lower temperatures than usually and without the need of a reducing atmosphere has been sufficient to produce an outstanding quality. Highly transparent layers with a metallic conductivity behavior could be deposited with various amounts of Nb. Moreover, for the first time a similar behavior could be achieved for undoped films as well by a precisely controlled small amount of oxygen vacancies. By combining various analysis techniques along the complete frequency spectrum of electrical fields, including low-temperature measurements, a profound understanding of the relevant factors and characteristics could be acquired.

The comparison of a large number of TiO$_2$ samples of different Nb levels, including undoped ones, reveal several intrinsic performance limits and various sometimes counteracting effects.

Performing similar investigations on films of common oxides, especially ZnO:Al, and an additional broad-based literature study show several fundamental differences between TiO$_2$ and the standard TCOs. They affect the maximal transparency, electron scattering mechanisms, doping and mobility limits, and phenomena near absolute zero temperature. These distinctions can be explained as a direct result of the disparity of their chemical nature. Together with several other unique properties of TiO$_2$, these findings reinforce its high potential as a new TCO material for various applications and also point out the research issues for the future.
Zusammenfassung

Es ist unmöglich sich unseren heutigen Alltag ohne Flachbildschirme und Touch-Screens oder die Energiewende ohne Solarzellen vorzustellen. Was haben diese Technologien gemeinsam? Unter anderem, die Notwendigkeit eines transparenten und leitfähigen Materials als Top-Elektrode um individuelle Pixel anzusteuern beziehungsweise die erzeugte Energie einzusammeln. Transparente leitfähige Oxide (engl. transparent conductive oxides TCO) stellen eine faszinierende Materialklasse da, welche diese Anforderungen erfüllt. Sie sind transparent wie isolierendes Glas aber zugleich ähnlich leitfähig wie glänzendes Metall. Das am weitesten verbreitete Oxid in der Industrie ist Indiumoxid (In$_2$O$_3$), meistens dotiert mit Zinn (Sn), aufgrund seiner überlegenen elektrischen Leitfähigkeit. Der wachsende Bedarf und die Seltenheit von In macht die Suche nach Alternativen erforderlich. Zu den möglichen Kandidaten gehören Zinnoxid (SnO$_2$)und Zinkoxid (ZnO), welche ebenfalls bereits seit einigen Jahrzehnten untersucht werden. Zusammen mit dem ersten aber hoch giftigen Vertreter CdO (entdeckt 1907 [Cas11]) bilden sie die Gruppe der geläufigen binären Oxide, welche im Periodensystem der Elemente alle nahe beieinander stehen. Ein Jahrhundert später wurde entdeckt, dass Titandioxid (TiO$_2$) mit Niob (Nb) Dotierung ebenfalls sehr gute TCO Eigenschaften besitzt [FHY+05]. Dies war sehr überraschend, da sich Ti in einer völlig anderen Region des Periodensystems befindet.

Chapter 1

Introduction

TiO$_2$ is with 4.5 million tons one of the most often produced substances and is in commercial use as a white and nontoxic pigment since nearly one century now [GBGTV14]. 2002 it governed 60% of the worldwide pigment production and is used nowadays even as an economic indicator [Win03]. Although the main application is still as a pigment in paints, varnish or sunscreen, dozens of new technologies and additional fields of implementation are in use or evolving. The high refractive index, which is responsible for the bright white of the TiO$_2$ particles, is utilized in thin film technology to produce thin anti-reflex coatings on lenses. For such purposes the high mechanical stability and scratch resistance are further advantages of TiO$_2$.

One property which has gathered very high interest and is now utilized in many different fields of application was unwelcome in the beginning - the photocatalysis, especially of the anatase crystal phase. Irradiated with UV-light, TiO$_2$ starts electrochemical reactions which can lead to a degradation of the painted object. The long lifetime of the generated electron-hole pairs is the reason for the higher photoactivity in comparison to other materials with similar wide band gaps. Nowadays, one can make use of these reactions to produce water splitting devices (for hydrogen generation), self-cleaning surfaces, water purifier or chemical warfare decomposer where the chemical bonds of the organic substances are destroyed [HS11, DTG*03, UA, NVHC15, PM09, FKW+11]. This field of study becomes more and more relevant as there is a high demand of antibacterial surfaces in medicine or easy to use chemical and biological purification techniques in development and health industry [LZ15]. In all these fields the almost only industrial employable material is TiO$_2$ due to its high efficient photoactivity. Structuring can increase the photocatalytic efficiency even more, resulting in a very promising candidate for dye-sensitized solar cells, where nanostructured surfaces or nano-particles of TiO$_2$ are embedded in a dye [XBH+06, TWR12, ZT06]. Such nano-particles are also used to produce transparent but sun blocking cremes.

With the application in solar cells a complete new field emerges from the electronic properties of TiO$_2$ and has been attracting a lot of attention recently. To these fields belong the possibility to prepare sensors for UV, H$_2$, O$_2$ and NO$_2$ by nanostructured TiO$_2$ films [GSC00, CLE+13, RDA+04, PRL+16].

The field of so-called high-k materials is of vital importance to be able to reduce the critical dimensions of transistors or flash memories further and enhance the performance of computer

---

1Three nice reviews have been written for this topic: One by Linsebigler et al. 1995 [LLY95], another by Hashimoto et al. ten years later [HIF05] and in 2013 one by Scanlon et al. focusing on the difference between anatase and rutile structure [SDB+13].
chips. Compared to the still employed SiO$_2$ with a dielectric constant of 4 and the prominent new alternative HfO$_2$ with a value of 25, TiO$_2$ possesses a high potential in this field as it exhibits values up to 80 [Par61, CKG$^{+}$99]. However, a large variety of values for the dielectric constant of undoped TiO$_{2-x}$ can be found in literature, ranging from about 20 to 200 at room temperature [GRA59, BG78, Par61, YGC$^+$96, CKG$^+$99, BD05]. This scattering is much larger than in other comparable oxides, but nevertheless the parameter is of vital importance for the understanding of a variety of effects. Therefore, the correct value for sputtered films have been measured and the most important influencing factors causing the different values could be analyzed and understood.

Besides solar cells, there are several additional possibilities to gain energy and satisfy the increasing demand, of which one is to harvest thermal energy via thermoelectrics. Oxides such as TiO$_2$ show promising features as thermoelectric materials as well [LHS06, JGM$^+$13, Oht11] with a $ZT$ value of up to 0.35 [LMZ$^+$13]. In addition to energy production, the storage of electrical energy becomes more and more important. Besides storing energy chemically in accumulators like Li-ion batteries or producing fuels, the pure electrical storing by charging so called supercapacitors is a very fascinating technique. Often these supercapacitors achieve their high capacity of thousands of pF by nano-structuring resulting in large internal areas [AKH08]. Doped TiO$_2$ or TiO$_2$ based compounds offer a different approach by providing nearly temperature independent$^2$ dielectric constants of several ten thousands [HVS$^+$01, RMR$^+$11, HLW$^+$13, GCW$^+$14]. However, the production in these cases included a very high temperature sintering process. If such materials can also be produced by thin film deposition techniques and moderate temperatures is one question which will be answered in this thesis.

Albeit these fields of study are very interesting and progressive, the main focus of research, which has been conducted in this work, lies on the potential of TiO$_2$ as transparent conductive oxide (TCO). This is an unique and fascinating class of materials, which exhibit both optical transparency like glass and electronic conductivity similar to metals simultaneously. Modern technology cannot be imagined without them, as they are used as top contacts in practically every flat screen, computer and smartphone display and many photovoltaics. Furthermore, they are employed in energy saving low-emissivity or electrochromic windows [HPG11, GB00]. In$_2$O$_3$:Sn is the TCO with the best performance until now and therefore the most often used one. The very scarce and expensive material indium makes the search for alternatives essential. This is even more true as the demand for flat panel displays is increasing drastically. One of these possible alternatives has been discovered very late in the year 2005, namely Nb doped TiO$_2$ [FHY$^+$05]. In the following section the reason why it has been discovered so late will be given, which will lead to the question, how TiO$_2$ can actually be a TCO at all. In this thesis excellent conductive and transparent TiO$_2$ (:Nb) films on unheated glass could be prepared by reactive sputtering, which increases its usability drastically. Even more important, detailed characterizations and comparison to standard TCOs will help to understand its potential, properties, and performance.

All these facts combined, it is fair to say that TiO$_2$ is one of the most fascinating and versatile materials to study. TiO$_2$ indeed deserves its name, as titan comes from the Greek and stands for the mythological race of giants [GBGTV14].

$^2$This is in contrast to ferroelectric materials which are not suited for this type of application [HVS$^+$01, Hip50].
1.1 The Big Surprise - Discovery of TiO$_2$ as TCO

![Figure 1.1: Time line of the discoveries of the main TCO materials. It illustrates the unexpected and very late appearance of TiO$_2$ in this field. A nice comprehensive description of the history of the development of TCO materials can be found in [Bri07].](image)

A sketch of the chronology of some important steps in the development of TCOs can be seen in figure 1.1. The first transparent and conductive oxide has been discovered 1907 and was a thin film of CdO [Cas11]. Although it possesses a remarkably high conductivity due to its large electron mobility and low effective mass (see section 2.2.1), the toxicity prevents a practical usage usually. 1937 followed SnO$_2$ and both were prepared by oxidizing a metal film thermally after the deposition by sputtering or evaporation [Bri07]. Also in the case of In$_2$O$_3$ the same technique was applied 1954. In the first 50 years after the discovery of TCOs not much research was conducted and only few commercial applications had been invented. This changed thereafter and the remarkable development in the field of TCOs led to its wide spread employment in every flat display or top electrode of solar cells. Some more details about this early developments can be found in a review written by Bright [Bri07]. The next matrix oxide, which has been discovered in the 1970s, is ZnO typically doped with Al. The very good performance of this much cheaper oxide, compared to In$_2$O$_3$:Sn, triggered many studies on ZnO and a variety of dopants. Interestingly, until the 80s, the process control was difficult and a post deposition annealing step in oxidizing or reducing atmosphere was employed to control the film properties. The mixing of the basic oxides leading to ternary compounds, especially ZnO-In$_2$O$_3$, represents the next high intense research field. The performance reaches similar values like In$_2$O$_3$:Sn but the material can even stay amorphous, which is beneficial for some applications. In the late 90s, finally p-type TCOs have been detected, often based on CuAlO$_2$. Although these materials were and are still inferior by at least two orders of magnitude with respect to their conductivity$^3$ compared to the n-type ones, they enabled $p-n$ junctions constructed from TCO materials exclusively.

The experimental discovery of a complete new TCO material in the year 2005 was very surprising. It was TiO$_2$-$x$ doped with various concentrations of Nb and had been deposited epitaxially by pulsed laser deposition on SrTiO$_3$ [Bri07, FHY+05]. The conductivity, in such a first report, was very high and even competitive with In$_2$O$_3$:Sn. Because of this late discovery, TiO$_2$ is not included in most of the reviews available for TCOs [Min00, Gor00, CYL00, EPJ+04]. But even nowadays, it is still a material not often mentioned in literature regarding TCOs like for example a review from 2007 [Hos07] or 2011 [Cas11] and several other interesting comparative TCO studies [KE13, Bri07, LZ07]. The "Handbook of Transparent Conductors" written by Hosono, Paine and Ginley, also from the year 2011, mentions only very briefly the existence of TiO$_2$:Nb as an unconventional

$^3$Also with respect to the transparency they are by far not competitive [Bri07].
Figure 1.2: Schematic illustration of the different types of orbitals, which are occupied in elements up to the fifth group. The two colors represent different signs. Only one representative of the $p$ orbitals is shown. $p_x$ and $p_y$ are aligned along the other two directions analogously. Also $d_{x^2-y^2}$ and $d_{xy}$ are oriented analogously to the shown $d_{yz}$ (see [DMPW05] for more details).

TCO without giving many details of TiO$_2$ or comparisons to the conventional ones [HPG11]. However, the material attracts more and more interest recently, as one can see in a meta-study of Stadler, who determined the number of publications per year with respect to the studied element [Sta12]. But this study supports the impression that in comparison to the others is is still a rather unknown TCO material.

Why was this finding so surprising and why is TiO$_2$ referred, if at all, as an unconventional TCO? The reason is the underlying model with which the high mobility in common TCOs is explained. The conventional oxides are all composed of metal cations which belong to the same area in the periodic table, namely the subgroup II.A, the main group III. and IV. and the period 4 and 5. The valence electrons of elements in these groups consist of $s$-electrons at least partly, which are transferred to the oxygen during the oxidation. Therefore, the minimum of the conduction band consists in such oxides of the $s$-orbitals of the cations (see figure 1.2 for the different shapes of the orbital types). These orbitals had been occupied by the valence electrons with the lowest energy before the reaction and thus, they constitute the lowest unoccupied states in the oxide. Other oxides, which have also their valence electrons in the $s$-band, do not belong to the TCO group as they exhibit strong localization of electrons around oxygen vacancies leading to much lower mobilities. Furthermore, they form compensating defects which prevent sufficient high free charge carrier densities [MM12]. Also some oxides are not suitable because of a to small band gap below 3 eV, which is a necessary prerequisite to be optically transparent.

In Ti the valence electrons with the lowest energy have occupied $d$-orbitals and thus, the conduction band minimum of TiO$_2$ is composed of $d$-bands. Such highly oriented orbitals are not supposed to be able to have a large overlap to adjacent ones, which should lead to strongly localized electrons, no band transport and bad conductivities. Thus, nobody had expected to find such a very well conductive TCO material with Nb doped TiO$_2$ and indeed, till now no additional TCO showed up in the vicinity of Ti. Additionally, TiO$_2$ exhibits several crystal phases, but only one of them offers a high conductivity, making it a very odd finding.

Therefore, the investigation of this new and unconventional TCO material is of high interest. First of all, from a basic research perspective, in order to gain a better understanding of the

---

4 Throughout this thesis the oxides CdO, ZnO, SnO$_2$, and In$_2$O$_3$ are referred as common or conventional TCOs.
mechanisms influencing the conductivity in TCOs and perhaps to be able to find further new candidates. Secondly, from an applied research point of view, in order to be capable to utilize the many advantageous properties of TiO$_2$. In this thesis, it will be explained how very high quality films of TiO$_2$ can be prepared by reactive sputtering which is a common technique for industrial applications. The important factors necessary for a good TCO performance will be analyzed and explained with special focus on the electrical behavior. Temperature and magnetic field dependent measurements will give a deep insight into the differences of the electrical transport phenomena. By comparing the findings with the behavior of standard TCOs several very interesting distinctions will be found which follow from the unusual nature of TiO$_2$.

### 1.2 Some Material Properties of TCOs

<table>
<thead>
<tr>
<th>Property</th>
<th>In$_2$O$_3$</th>
<th>ZnO</th>
<th>SnO$_2$</th>
<th>TiO$_2$ ana</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{550,\text{nm}} = \sqrt{\varepsilon_\infty}$</td>
<td>2</td>
<td>1.9</td>
<td>1.9-2</td>
<td>2.5</td>
<td>[Szy01, FE00]</td>
</tr>
<tr>
<td>work function</td>
<td>4.8 eV</td>
<td>4.2 eV</td>
<td>4.9 eV</td>
<td>5.1 eV</td>
<td>[Gor00, SDB$^+$13]</td>
</tr>
<tr>
<td>etchant</td>
<td>HCl+HNO$_3$</td>
<td>acids/bases</td>
<td>Zn+HCl</td>
<td>HF</td>
<td>[Gor00, OSM01]</td>
</tr>
<tr>
<td>chem. stab.</td>
<td>middle</td>
<td>very low</td>
<td>high</td>
<td>very high</td>
<td>[Gor00, ZXF$^+$08]</td>
</tr>
<tr>
<td>thermal stab.</td>
<td>middle</td>
<td>low</td>
<td>very high</td>
<td>high</td>
<td>[Gor00, PGL$^+$09]</td>
</tr>
<tr>
<td>H-plasma stab.</td>
<td>low</td>
<td>high</td>
<td>low</td>
<td>very high</td>
<td>[WLS94, ABJ15]</td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td>5</td>
<td>4</td>
<td>6.5</td>
<td>6</td>
<td>[Gor00, ABBN01]</td>
</tr>
<tr>
<td>toxicity</td>
<td>middle</td>
<td>very low</td>
<td>low</td>
<td>very low</td>
<td>[Gor00, GBGT014]</td>
</tr>
<tr>
<td>costs</td>
<td>very high</td>
<td>low</td>
<td>very low</td>
<td>very low</td>
<td>[Gor00, ABJ15]</td>
</tr>
</tbody>
</table>

Table 1.1: A list of values of TCO parameters relevant for practical application of common oxides and TiO$_2$ in the anatase (ana) modification. Transparency and conductivity is highly depending on the preparation process and therefore not included here. The chosen criteria are based on the MRS Bulletin from 2000 [Gor00]. For the given work function the distance between vacuum level and conduction band has been taken. The costs are heavily influenced by the deposition method and necessary process steps.

The most important parameters for a TCO material are conductivity and transparency which are usually inversely proportional. But they are highly depending on the preparation process and vary over several orders of magnitude and will be discussed in detail later on. In this section more inherent properties of the relevant oxides shall be given. Table 1.1 gives some quantitative and qualitative comparisons of properties which are highly relevant for the application of TCOs. Whereby, only the anatase modification is considered as the rutile one exhibits much lower conductivities including exclusively insulating temperature behavior [TPS$^+$94]. The higher refractive index $n$ for example enables a higher number of charge carriers without becoming optically non-transparent due to a lower plasma frequency (see section 2.4.2). The work function is a very important value when it is applied in solar cells. A high value is suitable for connecting to $p$-Si, a low one to $n$-Si. Proper etchants are helpful for structuring the TCOs during the production of electronic devices. On the other hand, the very promising and cheap candidate ZnO is so easily dissolved by any diluted acid or base that it has to be protected even against the normal environment. Thus,

\[^5\]One possible formula to calculate a Figure of Merit is depicted in equation 7.1.
Figure 1.3: two main crystal structures of TiO$_2$. Left the thermodynamic stable rutile configuration is depicted and right the metastable anatase one. Both consist of Ti$^{4+}$ ions, each coordinated octahedrally with six O$^{2-}$ ions. Two Ti-O bonds are slightly larger than the other four, whereby, in anatase also these four lie not perfectly in one plane. In rutile adjacent octahedra are tilted by 90°. Schematics are taken from [Sch14] and were made using the database of the DIAMOND 3.2 software.

A good chemical stability is needed too for an usage without any special encapsulation or to be resistant against certain processing steps, which are needed later on. The temperature stability is denoted to oxidation and decomposition processes occurring in common TCOs. In the case of TiO$_2$ this includes additionally the irreversible transformation into the rutile configuration at high temperatures (both structures are visualized in figure 1.3). Although this temperature depends heavily on various details (see the review of Hanaor and Sorrell [HS11]) it is for thin films often in the range of 700 °C [Sch14]. Thereby, for TiO$_2$ and SnO$_2$ the softening of the glass substrate itself is of higher concern [Gor00]. Hydrogen plasmas are utilized, for example, during the production of amorphous silicon in solar cells in which, instead of or additional to ZnO, TiO$_2$ could be employed [NMY+06]. The high mechanical strength of TiO$_2$ is in use already as scratch resistance layer for lenses as mentioned above and could make protecting layers for TCOs superfluous. The very high toxicity and carcinogen effect are the key arguments why CdO is not used nowadays, although it can provide even better conductivities than In$_2$O$_3$ [Bri07, Cas11]. Indium itself is also somewhat toxic, whereas TiO$_2$ is so harmless that it is included as E171 as white pigment in food [GBGTV14].

The costs are not so easy to compare as they depend heavily not only on the quality of the raw material including its state (metal or oxide) but also on the deposition method and additionally applied process steps (annealing etc.). Indium is by far the most expensive one and SnO$_2$:F is usually denoted as the cheapest TCO material [HPG11], but not taking TiO$_2$ into account at all. In principle TiO$_2$ could feature even lower costs [ABJ15] depending on the necessary manufacturing steps. With pulsed laser deposition (PLD) on single crystalline substrates like SrTiO$_3$ this is certainly not the case.

Comparing TiO$_2$ for example with ZnO, the much higher work function and the better chemical, thermal and mechanical stability of the former are clear advantages. Therefore, TiO$_2$ could be employed for example as a top electrode without the need of any further protective layer and the
additional provided photoactivity would lead to a self cleaning surface, of course highly advanta-
geous for solar cells. This altogether shows the very high potential of TiO₂ as a TCO material and
explains the large motivation and the necessity for investigating this material.

For comparing the different oxides a variety of relevant physical properties are listed in table 1.2.
First the energies of formation are given. The recalculation with respect to one oxygen atom
illustrates the much larger reactivity of TiO₂ in comparison to the standard TCOs in an oxygen
poor atmosphere, as it is needed to produce highly conductive films. A specific type of crystal
structure is obviously no requisite for a TCO and the larger lattice constants of anatase give
reason to its Greek name, which means "extension" [ABBN01]. The cation density of TiO₂ is
quite comparable to the ones of standard TCOs which allows the direct comparison of doping
concentrations and resulting charge carrier densities. The ratio of the minimal distance between
the cations of the oxides and their respective ionic radius serves as a measure of the overlap
between the adjacent orbitals. The similarity of these values illustrates why the effective masses
of the common TCOs are alike and the low effective mass of TiO₂ would be no surprise, if it
would be a s-band instead of a d-band conductor. In section 7.1, I will take up this issue again
and give reasons for the observed deviations from the standard TCO model. It should be noted
that the values for effective masses scatter much more in literature than for example the lattice
constant. Additionally, the measured effective masses are influenced by a coupling to the ionic
lattice (polaron, see section 2.2.4). This effects are in particular important in the rutile TiO₂ and
lead to a tremendous variation of the values for the masses of \( m^*_\text{rutile} = 12 m_e \) to 130 \( m_e \)
maximumly and \( m^*_\text{rutile} = 20 m_e \) to 30 \( m_e \) most commonly [Fre61, TPS⁺94, BH53, GRA59].

To summarize, the most important differences of the physical properties between TiO₂ and the
common oxides are the d-band versus s-band character of the conduction band minimum, the higher
enthalpy of formation (including the oxides of the dopants), and the much larger permittivity (both
at static fields and optical frequencies). The generating of charge carriers is accompanied with the
formation of oxygen vacancies and the substitution of the host cation with the dopant. Very high
formation energies increase the necessary defect energy of such a vacancy and increase the tendency
of forming clusters of the higher valence state oxide respectively. Thus, a higher reactivity makes
it more challenging to generate high free electron concentrations.
## Important physical properties of the relevant oxides

The enthalpies of formation are given per molecule and per oxygen atom which is the better comparison in the oxygen deficiency regime present when depositing TCOs. The ionicity of the bonding is given according to equation (2.72). The minimal distances from cation to cation within each structure is given (d_{cat-cat}), together with the ionic radii with respect to the coordination number (KZ) and the ratio of these two distances as measure of the overlap. The given estimated values for the density of states (DOS) illustrate a key difference between the s-band of common TCOs and the \( d^- \)-band of TiO\(_2\). The values for the effective masses can scatter quite considerably and increase typically with larger dopant concentrations. Additionally, the measured values differ from the calculated ones and especially in the case of rutile TiO\(_2\) the values found in literature vary massively (up to \( 130\, m_e \)).

### Table 1.2

<table>
<thead>
<tr>
<th>Property</th>
<th>( \Delta H_{f} ) (kJ/mol)</th>
<th>( \Delta H_{f} ) (kJ/mol)</th>
<th>( \Delta H_{f} ) (kJ/mol)</th>
<th>( \Delta H_{f} ) (kJ/mol)</th>
<th>( \Delta H_{f} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{In}_2\text{O}_3 )</td>
<td>920/307</td>
<td>580/290</td>
<td>940/470</td>
<td>940/470</td>
<td>940/470</td>
</tr>
<tr>
<td>( \text{Sn}_2\text{O}_3 )</td>
<td>350/350</td>
<td>580/290</td>
<td>940/470</td>
<td>940/470</td>
<td>940/470</td>
</tr>
<tr>
<td>( \text{ZnO} )</td>
<td>250/250</td>
<td>250/250</td>
<td>250/250</td>
<td>250/250</td>
<td>250/250</td>
</tr>
<tr>
<td>( \text{TiO}_2 ) (anat)</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
</tr>
<tr>
<td>( \text{TiO}_2 ) (rutile)</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
</tr>
<tr>
<td>( \text{SnO}_2 )</td>
<td>2.80</td>
<td>2.80</td>
<td>2.80</td>
<td>2.80</td>
<td>2.80</td>
</tr>
<tr>
<td>References</td>
<td>[CKO91], [Szy01]</td>
<td>[Mar66], [OIAK01]</td>
<td>[Mar66], [ABBN01]</td>
<td>[Mar66], [OIAK01]</td>
<td>[Mar66], [ABBN01]</td>
</tr>
</tbody>
</table>

### References

1. Aachen University
2. RWTH University
1.3 Structure of this work

In this thesis TiO$_2$ has been investigated over the complete frequency spectrum of electro magnetic waves in order to explain some of the aspects of this unique TCO material. In figure 1.4 the different regimes of the frequency and wavelength spectrum of the electro magnetic waves are illustrated. In chapter 2 the theoretical background of sputtering (the preparation method applied for the films) and the important interactions within the different regimes are explained. First the direct current (DC) properties will be discussed, on which the main focus lays. Then the regimes with increasing frequencies follow. In chapter 3 the experimental methods are explained with the same sequential order. The results of the measurements within the different frequency areas are then presented in the following three chapters like shown in figure 1.4 complete with a summary at each end. In the last chapter 4 I will show how one can understand why TiO$_2$ can be a TCO material at all. A comparison and summary of important factors of TiO$_2$ and the common oxides could be gathered which illustrates the unique nature of this novel TCO.

Figure 1.4: Illustration of the different regimes of the frequency spectrum of electro magnetic waves. The areas investigated in this thesis are shown in blue (including the visible regime) together with the chapter numbers in which the corresponding results are presented.
Chapter 2

Fundamentals

In the following chapter, the necessary theoretical background for understanding the main issues for TCO materials and results of this work will be presented. The first section is dedicated to reactive magnetron sputtering, the thin film preparation technique that was used throughout this thesis. Here, important general concepts are explained while the practical details of the preparation process will follow in section 3.1.1.

The three subsequent sections will cover the whole frequency range, starting with the DC electrical transport properties in section 2.2, focusing on the most important phenomena in the range of conductivity measurements of TCO materials, including variations by applied magnetic fields and different temperatures. After that, the AC electrical properties and effects will be discussed in section 2.3. Several polarization mechanisms with their relevant frequency range are described which can contribute to the measured capacity and thus to the dielectric constant of the material which is an important parameter for understanding the properties of TCO materials and their limits. The interaction of such oxides with electromagnetic waves will be covered in section 2.4. Here, I will start with small frequencies and long wavelengths (MIR, FIR), which need to be explained, together with the AC measurements, in order to understand the dielectric behavior of a material. Then, I will continue with the middle frequency range of UV/VIS/NIR which is naturally very important when looking onto a TCO. Then, the chapter will be closed with information on the very short wavelengths of X-rays, with which the crystal structure and quality of thin films can be unraveled which influence significantly the electrical conductivity.

2.1 Thin Film Preparation

There are many different thin film deposition techniques all of which differ fundamentally in the way in which the material is delivered to the surface. The kinetic energy of the arriving particles, the diffusion time, and the distance which they can travel after their arrival and before they are getting buried below the next layer of material are particularly important for the resulting microstructure. The book ‘Materials Science of Thin Films’ by Milton Ohring [Ohr01] should be read by every starting thin films scientist as it contains a lot of important concepts and practical advices in the field of thin film preparation. More details on the topic of crystal growth mechanisms can be found in [Mar03].
Figure 2.1: Particles arrive at the surface of the substrate with kinetic energies depending on the deposition process. They first connect to the substrate only by a weak physisorption and some of them will desorb again. Depending on the impingement rate, the specific chemical interaction energies, the temperature, the remaining kinetic energy, the distance and time they are able to travel varies quite a lot. If this distance is long enough, they can reach positions of minimal energy like edges or kinks of, e.g., already growing nuclei. Of course, during the process also some impurities or for example inert gas atoms will reach the surface normally with much lower impingement rates, kinetic and binding energies and get incorporated into the growing film.

Figure 2.1 illustrates some fundamentals regarding the thin film formation process. More information of this field can be found in a paper by Reichelt [Rei88]. Different preparation parameters and the principles of the applied technique have a strong impact on the diffusion time and traveling distance of the particles until they get strongly, chemically bonded to the surface. This is due to the different amounts of energy the particles gather until they reach the substrate. The further the particles can diffuse freely along the surface the higher the chance that they desorb again or preferably find an energetic minimum, for example, at the kink of a growing nucleus. In the framework of these concepts, the differences in the microstructure and thus in the properties of differently produced films can be explained.

For example, the so called sol-gel process or spray method is very cheap as it doesn’t require any vacuum machinery and can achieve a good deposition rate. However, the developing structure is quite fluffy, including many voids and imperfections as the particles have a very low kinetic or thermic energy. This often results in insulating or at least higher resistive thin films [KBPA06, TMK+99, MSB+79, RDA+04, SYS+10]. Other techniques like pulsed laser deposition (PLD) or electron beam evaporation, which are relatively common in research, are not affordable or practical for industrial processes but achieve the best conductivities for a material [Gor00, Bri07, GRO+03, FHY+05]. On the other hand, the sintering process is necessitating expensive high temperatures and pressures to gain a dense structure. It also leads to very high resistive TiO₂, as the process is accompanied by oxidation and transformation to the rutile crystal modification [LMZ+13, Mac75]. In contrast, sputtering is a technique with a quite large energy of the incoming particles and usually a relative dense structure but without the need of high temperatures and therefore also heavily used in industry.
Section 2.1 Thin Film Preparation

Sputtering is a Physical Vapor Deposition (PVD) technique which is widely-used in research and also very popular in the coating industry. This is due to relatively high deposition rates, good structural properties and the possibility to scale up the process to substrates of several meters like in the case of glass coaters [KA00]. Additionally, it allows for fast and easy tuning of the structural and functional properties and actually even the composition. Chemical Vapor Deposition (CVD) techniques are not as flexible but also quite established and are able to produce high-quality deposits with a good coverage. However, they rely on higher substrate temperatures for the chemical reactions of the precursor gases to take place. In addition, the search for a suitable volatile precursor is quite cumbersome and severely restricts the selection and application of new materials.

For sputtering, a low pressure (typically 0.2 Pa to 10 Pa) is generated in a diode in which a glow discharge, often called plasma, of an inert gas (i.e. Ar) is ignited. The corresponding ions get accelerated by an applied voltage of several hundred volts onto a target consisting of the intended thin film material [Ohr01]. The electrons which gain speed in the opposite direction are sustaining the plasma by ionizing the gas. This self-sustaining discharge follows Paschen’s law [Pas89, Tow10]

\[ U = \frac{Bpd}{\ln(Apd) - \ln[\ln(1 + \gamma^{-1})]} \]  

(2.1)

with \( A \) and \( B \) being specific constants, the gas pressure \( p \), the target to ground (typically the substrate) distance \( d \), and \( \gamma \) the important secondary electron coefficient, representing the number of electrons which are released due to the bombardment with the Ar-ions. This coefficient is therefore heavily dependent, for instance, on the composition at the surface of the target and can change quite severely if the surface is oxidised. The effect can be seen by a changed target voltage that is necessary for the discharge. Interestingly, there are oxides with lower and others with higher \( \gamma \) values in comparison to their respective metal.

In principle, the alteration of the sputter process by the usage of a set of permanent magnets below the target can also be described by a change of \( \gamma \). The magnetic field (the configuration of which can be seen in figure 3.1) constrains the electrons to circular trajectories above the target due to the Lorentz force. This so called magnetron sputtering drastically increases the electron density and thus enhances the ionization effect, permits lower working pressures and boosts the sputtering rate. This can be interpreted as an increase of the coefficient \( \gamma \), but the electron density is not any longer homogeneous and thus also the erosion of the target isn’t uniform. This is the origin of the so called toroidal racetrack, which can be seen in figure 3.3. The “aging” of a planar target is a big issue as it changes the sputter rate, the target voltage, and the deposition profile over time, limiting the comparability and reproducibility.

The generated and accelerated Ar ions strike the target with energies in the range of hundreds of electron volts. Each hit is followed by a scattering cascade whereby atoms get knocked out of the target. The sputter yield which is the number of released target atoms in relation to incoming Ar ions was reviewed nicely by Sigmund [Sig69]. It is a material dependent parameter with numerous influencing factors.

The influence of \( pd \) and the applied power \( P \) on the resulting sputter rate \( Y \) as a first approximation
is given by
\[ Y \propto \frac{P}{pd} \propto \frac{IU}{pd}. \quad (2.2) \]
Details about the practical setup used during this work, including the parameters and characteristics, will be discussed later in section 3.1.1. If the sputter yield \( Y \) is only investigated in terms of small energies of the particles, it holds
\[ Y \propto (E - E_0)^{\frac{2}{3}}, \quad (2.3) \]
with a material constant \( E_0 \) corresponding to a surface binding energy. The increase of the energy of the ions raises the number of knocked out particles after each hit as well. However, the ions will also penetrate into the target more deeply with fewer particles being able to reach the surface. At some point, no additional atoms can leave the target causing the sputter rate to saturate \( [\text{Kap03}] \).

These released particles can then reach the substrate with energies in the order of 1 eV to 10 eV which is approximately one order of magnitude higher than for thermic evaporation \( [\text{Sev06, Brä14}] \). The way in which pressure and temperature alters the energetics and thereby influences the crystalline structure of the deposited film is illustrated in a diagram developed by Thornton \( [\text{Tho86}] \) which was updated and redrawn \( [\text{Ohr01, And10}] \). However, as the sputter conditions chosen in this thesis, resulted in TiO\(_2\) films which have been usually amorphous after deposition, his model is not applicable in this case. Details about the glowing discharge, pressure dependencies, etc., are also not particularly important here but can be found, for example, in the review articles written by Ellmer and Kelly in the year 2000 \( [\text{Ell00, KA00}] \) or in a more recent one by Bräuer \( [\text{Brä14}] \). The special case of reactive magnetron sputtering is however of vital importance for this work. Specialties of the structure formation in the case of reactive sputtering of transition metals can be read in \( [\text{NKMW04}] \).

### 2.1.1 Reactive Magnetron Sputtering

This technique has been used throughout this thesis in order to prepare the oxide thin films and the nitride capping. For this purpose, a conductive pure or alloy metal target like Ti or Zn:Al is utilized or in the case of Si\(_3\)N\(_4\) a silicon target. During the sputter process, a reactive gas like O\(_2\) or N\(_2\) is introduced into the chamber additionally to the sputter gas Ar. The discharge excites the gas and breaks up the molecules so that they can react with the metallic surfaces, like the target or the growing film. By this process, the desired oxide is produced.

The theoretical background for understanding the evolving characteristics and in particular the hysteresis of the O\(_2\) partial pressure (O\(_2\)PP) with varying oxygen flow was invented by Berg \( [\text{BBLN87}] \). An example of such a hysteresis is shown in figure 2.2. Berg and Nyberg later also provided a readable comprehensive review about the different parameters, the understanding, and modeling of the reactive sputter process \( [\text{BN05}] \).
The principle is illustrated in figure 2.3. The idea is a set of equations which account for the different consumers of the total amount of reactive gas \( Q_{\text{tot}} \) including also the pump \( Q_p \). The portion of compound covered \((\Theta)\) target \( A_t \) and chamber \( A_c \) surfaces also have to be considered.

The resulting fluxes of metal \( F_m \) and reacted compound \( F_c \) particles are also included. In the first model, there were a number of simplifications. For example, the target coverage was assumed to be only one mono layer thick and the complete compound would get directly sputtered away. Berg himself addressed later some of these restrictions, including preferential sputtering and sputter yield amplification [BK99]. In 2014, he presented an improved version of his model [BSN14] which accounts for several second order effects. Nevertheless, the original one is already very enlightening and explains the most prominent features of reactive sputtering.

The derivation is relatively straight forward and can easily be followed in the article by Berg [BN05]. It is based on several dynamic equilibria so that, for example, the increase of the reacted surface of the target or the collecting surface area is balanced by the corresponding increase of the metallic portion. In the end, the complete sputter rate from the target which is directly proportional to the deposition rate can be described by

\[
R_m = \frac{J}{q} Y_m (1 - \Theta_c) + Y_c \Theta_c A_t,
\]

with the sputter rates \( Y \) of the compound and the metal respectively. From the employed sputter current \( J \), the number of ions hitting the surface can be approximated by dividing it by the elementary charge \( q \). The coverage of target and collecting areas are explicit functions of the \( O_{2PP} \), especially, at the rising and falling edges of the hysteresis. Therefore, the stoichiometry of the film can be controlled by sputtering at a constant \( O_{2PP} \) with a fixed metal to compound
Figure 2.3: Illustration of the Berg-Modell and the variables needed to model the behavior of reactive magnetron sputter processes. a) focuses on the reactive gas consumers which are the pump and the still unreacted or uncovered portions respectively of the surfaces of the target and the remaining chamber including the substrates \((1 - \Theta)\). b) displays the fluxes of sputtered particles (metal or compound respectively) from the target to the collecting areas. (Adapted from [BN05]).

ratio. By using a relative point in the falling edge as a definition for this working point, samples of different runs, sputtering powers, and target compositions can be compared even if the absolute values of the hysteresis are changing.

2.2 DC Electrical Properties

In the following section, a few important solid state physics concepts are mentioned which are necessary to understand the effects and differences of TCO materials regarding resistivity measurements at negligible low frequencies. As high quality TCO films are degenerate semiconductors, the derivations will focus on this class of materials.

2.2.1 Basic Concepts

The following considerations about electrons in solids are based on the solid state physics books by Kittel [Kit93], Ashcroft and Mermin [AM07], and Singleton [Sin01] and can be followed there in greater detail. Good conductive TCOs are usually degenerate semiconductors and can be treated as metals as will be shown in chapter 4.5. Therefore, I start here by explaining the charge transport of this material class.

The first microscopic model to describe the electron transport in a metal was already developed by Paul Drude in 1900. With this model the conductivity of a metal can be expressed as

\[
\sigma = en\mu = \frac{e^2 n \tau}{m_e}
\]  

(2.5)
with $e$ as elementary charge, the charge carrier concentration $n$, the drift mobility $\mu = e\tau/m_e$, and the electron mass $m_e$. In this model, the scattering rate $\tau^{-1}$ represents the probability per unit time of the electron to suffer an inelastic collision. In other words, only collisions which include momentum relaxation are considered by Drude. This and the assumption that no interactions, much less collisions, between the electrons are present, can quite easily fail. Thus certain deviations from this simple picture can occur in experiments. Nevertheless, this formula is quite powerful and widely accepted and will also be used again when determining the mobility via Hall-measurements.

The theory was improved by Sommerfeld who included the quantum mechanical fact that not all electrons can have the same state in $k$-space which lead to the definition of the Fermi wave vector

$$k_F = (3\pi^2 n)^{1/3} \quad (2.6)$$

as the radius of the sphere of these filled states in $k$-space. Sommerfeld’s model does still not consider the periodic potential of a crystal and was tremendously improved by Bloch’s theorem and the Boltzmann transport equation. By describing the crystal as a periodic potential and treating it quantum mechanically through solving the Schrödinger equation, the picture of electrons in a solid was changed dramatically. The Bloch electron can be described as a wave function

$$\psi_{nk}(r) = e^{ik\cdot r}u_{nk}(r) \quad (2.7)$$

where $u$ is representing the potential structure of the lattice.

This wave function includes the lattice potential, but no concept like a scattering time. Thus Bloch waves aren’t scattering at the ionic cores of a metal, which form the periodic lattice. This is in contrast to the description of electrons in the model of Drude. In the Bloch model, every atom can be interpreted as the origin of a spherical wave and these different waves interfere with each other. Therefore, only the coherent waves which interfere constructively will remain, which in turn means that they don’t scatter at the metal atoms of the lattice. Instead, they get scattered at everything which disturbs the periodicity of the lattice. This contains crystal defects, like point defects, impurities, dislocations, grain boundaries, or surfaces but also phonons or distortions evoked by other electrons in polar crystals, so called polarons. This explains the experimental fact that the mean free path, which is typically in the order of the interatomic distance, can reach the mm or even cm regime for ultra pure crystals at low temperatures [Sin01]. In the Drude picture such differences could not be understood.

In this context, there is a simple, semi-classical concept with the help of which one can estimate if the concept of Bloch waves can be applied safely, should be used carefully, or is hardly employable at all. It was first mentioned by Ioffe and Regel in 1960 [IR60]. The more scattering occurs the smaller the mean free path $\lambda$

$$\lambda = \frac{\hbar\sigma}{e^2} \left( \frac{3\pi^2}{n^2} \right)^{1/3} = \frac{\hbar}{2e} \left( \frac{3n}{\pi} \right)^{1/3} \mu \quad (2.8)$$

becomes.
As long as the product $k_F \lambda$

$$k_F \lambda = \frac{\hbar \sigma}{e^2} (3\pi^2)^{2/3} n^{-1/3} \propto n^{2/3} \mu$$

is much larger than unity the concept of a Bloch wave is valid. The insertion of equation 2.5 shows that the mobility is even more important for a high value of $k_F \lambda$ than the charge carrier density. As we will see in section 4.5.2 for a typical metal, like silver, this can reach values of several hundreds ($k_F \lambda \gg 1$). For higher amounts of disorder and fewer charge carriers it gets reduced which is why TCO materials exhibit typical values of some tens or even down to unity. On account of that, additional effects known for "dirty metals" can evolve at lower temperatures like electron-correlations or weak localization which will be discussed in section 2.2.11 ($k_F \lambda \geq 1$).

For values smaller than unity ($k_F \lambda < 1$), the concept breaks down and the conduction can’t be well described by free electron waves anymore. At this transition the semi-classical concept itself starts to fail, thus the value of unity is not a sharp and universal barrier but can be slightly different for varying classes of materials. Large correlation effects reduce for example the kinetic energy of the charge carriers. The transition in these cases will occur at $k_F \lambda$ values slightly lower than unity [CG03]. Different kinds of hopping mechanisms are relevant for insulating samples as are shortly described in section 2.2.5. However, in this work the electrical properties of TiO$_2$ in the context of good conducting TCO materials are investigated, thus, these processes aren’t in the main focus.

### 2.2.2 Hall Effect

The prominent Hall effect to determine the charge carrier density of a sample is widely used, also in this thesis. E.W. Hall expected to see an increase in the resistance of a wire when positioning it perpendicular to a magnetic field by means of the Lorentz force but he couldn’t observe this [Hal79]. Actually, this so called classical magneto resistance (MR) does exist as a quite weak second order effect and will be briefly mentioned in section 2.2.12.

To explain his findings, he supposed that there had to be a counteracting force preventing the magnetic field from changing the measured resistance. This counteracting force had to be an electrical potential difference perpendicular to the direction of the measuring current and he indeed could measure it. The combined force of electrical and magnetic fields upon a moving electron can be described as $F = -eE - ev \times B$. For the change in velocity $v$, in the Drude framework, this leads to

$$\frac{dv}{dt} = -\frac{e}{m_e} E - \frac{e}{m_e} v \times B - \frac{v}{\tau}. \quad (2.10)$$

In the steady state case with no change of the velocity the left side equals zero and it can be concluded that

$$v_x = -\frac{e\tau}{m_e} E_x - \omega_c \tau v_y \quad (2.11)$$

and

$$v_y = -\frac{e\tau}{m_e} E_y + \omega_c \tau v_x \quad (2.12)$$
Section 2.2 DC Electrical Properties

with the cyclotron angular frequency \( \omega_c = eB/m_e \) and the directions \( x \) and \( y \) parallel and perpendicular to the applied current, respectively. In section 3.2 the used geometries and setups will be shown. Now, we set \( v_y = 0 \) so no current flows perpendicular to the one forced by our setup. Writing \( J_x = -env_x \), we can define

\[
R_{\text{Hall}} = \frac{E_y}{J_x B} \approx -\frac{1}{ne},
\]

which is known as the Hall coefficient. Interestingly, according to Drude, it is neither influenced by the magnetic or electrical field strength nor by the scattering time or mechanism. It has to be mentioned that this derivation is in principle not valid for semiconductors and even a number of metals don’t follow this scheme (like Aluminum or Indium for instance [Lüc66]). A much more sophisticated derivation can be read for example in a book written by Putley in 1960 [Put60]. He started with the Fermi-Dirac distribution to determine the charge carrier density and its change over time, temperature, or applied field which was neglected in the above derivation. There, the scattering time \( \tau \) is a measure of the time that is needed until the distribution, which was changed by a perturbation, e.g., the applied electrical field returns to normal. After several pages this leads Putley to a Hall coefficient \( R_H = -\frac{3\pi e}{8ne} \approx -\frac{1.18}{ne} \), so roughly the same like equation 2.13. He also states that the ratio between the mobility from a Hall measurement and the conductivity mobility is of great interest when investigating a semiconductor but extremely difficult to measure. Because of this and the fact that the formula determined in the Drude framework is nearly always applied in the literature regarding TCOs, it was also used throughout this thesis. For all samples where carrier concentrations or mobilities are given, it was checked with great care that the Hall coefficient has no dependencies on the magnetic field (up to 9 T) or on the applied current density.

Another important fact is that the above formula is only valid when there is only one type of charge carrier. This is, of course, not true for a typical intrinsic or lowly doped semiconductor where holes and free electrons can contribute significantly to the charge transport. Fortunately, in the case of typical TCOs like ZnO:Al, In2O3:Sn, SnO2:Sb and the material under question here, highly doped TiO2, the valence band maximum consists of strongly localized O 2p orbitals. Therefore, holes exhibit a much higher effective mass [MOI99, AC93] which is why the samples under test here can be described as exclusive \( n \)-type. Because of that the fabrication of \( p \)-type TCOs is very difficult and, to my knowledge, there is still no \( p \)-type oxide with a comparable electrical and optical performance as the \( n \)-type ones [Cas11]. This doesn’t necessarily mean that Hall measurements on these \( n \)-type Oxides are always easy. Some experimental pitfalls and tests that one has to keep in mind to obtain reliable results will be given in section 3.2.2.

2.2.3 Effective Mass

The concept of the effective mass is a very powerful tool in dealing with semiconductors. It doesn’t mean that the electron, seen as a particle, is indeed heavier or lighter in a semiconductor than in vacuum. Instead, it comprises the complete influence of the lattice potential on a band electron for a given energy and direction. Following Singleton [Sin01], it can be derived from the energy
change upon applying an external force which for the limit \( \delta t \to 0 \) leads to

\[
f = \hbar \frac{dk}{dt}.
\]  

(2.14)

As the velocity of a band electron can be described in terms of a group velocity \( \mathbf{v} = \frac{1}{\hbar} \nabla_k E \), its change over time can be linked to the applied force in an isotropic crystal by

\[
f = \frac{dv}{dt} \frac{\hbar}{2} \frac{dE}{dk^2}.
\]  

(2.15)

By converting this into Newton’s second law of motion \( F = ma \), the effective mass can be defined as

\[
m^* = \frac{\hbar^2}{d^2 E dk^2}.
\]  

(2.16)

This value remains constant (along a specific crystal symmetry) when changing the Fermi energy, as long as the curvature of the band in \( k \)-space is parabolic. Usually, this is safe to say for relative low carrier concentrations. For TCOs, the non parabolic nature can not always be neglected and there are several articles dealing with the change of the effective mass when increasing the amount of charge carriers [Ell01, PZL89, GB91]. Nevertheless, as this effect is relatively minute and hard to determine, a parabolic conduction band will be assumed generally when comparing the different materials and samples.

Perturbation theory suggests that for a semiconductor with a direct band gap, the effective mass is higher for materials with a greater band gap and, therefore, the ratio \( m^*_e / (m_e E_g) \) is more or less constant. As a rule of thumb this is true, especially for similar materials, e.g., comparing InSb, InAs and InP [Kit93]. In these materials the ratios are only 20% around 0.06 which is much smaller than the range of the effective masses which differ by a factor of 5. However, this concept is not expedient when trying to understand the differences between TCOs (SnO\(_2\), In\(_2\)O\(_3\), ZnO and even TiO\(_2\)). All TCOs have a band gap of around 3.5 ± 0.3 eV and effective masses around 0.3 ± 0.1 m\(_e\) [MOI99, Ell01, HAFD11]. The exact values differ also considerably between the authors and the measurements. Comparing the given values of the common TCOs in table 1.2 the contradictions became obvious. In\(_2\)O\(_3\) has a much smaller band gap than ZnO and SnO\(_2\) but a larger effective mass. TiO\(_2\) in the anatase configuration has a band gap in between the other mentioned oxides but a significant larger effective mass than they have. Also comparing anatase and rutile this concept fails as rutile has a slightly smaller band gap but a massively larger effective mass.

A concept which indeed will help us to understand several effects of the effective mass and mobility comparing different TCOs, structures, and preparation influences (see section 7.1) is the extend of the overlap between the orbitals which form one band. The overlap energy \( \gamma \) can explicitly at least be calculated for two 1s orbitals of two hydrogen atoms which is [Kit93]

\[
\gamma(Ry) = 2 \left( 1 + \frac{\rho}{\alpha_B} \right) e^{-\frac{\rho}{\alpha_B}}
\]  

(2.17)

with \( \alpha_B = 4\pi\epsilon_0 \hbar^2/m_e e^2 \approx 0.5 \, \text{Å} \) the Bohr radius. We see that the overlap energy (in units of
Section 2.2 DC Electrical Properties

Rydberg $R_y = m_e e^4 / 8 e_0^2 h^2 \approx 13.6$ eV) exponentially decreases with the distance $\rho$ between the atoms. For small wave vector $k$, (i.e., low energy) this leads to

$$m^* = \frac{\hbar^2}{2\gamma a^2}$$

(2.18)

with $a$ being the lattice constant. A high overlap energy therefore leads to a small effective mass of the corresponding band. An overview of the calculated values of different materials is given in section 1.2.

2.2.4 Polarons

Until now we considered the movement or propagation of an electron as a Bloch wave through a solid with a static lattice potential. This is principally not true, since thermal vibrations and moving electrons change the positions of the ionic cores. The disturbances of the periodicity by phonons are a very important scattering mechanism, especially for metals. In section 4.5.2, the temperature dependencies of the conductivity of several materials will show that the room temperature mobility is significantly lower than the one measured at e.g. 2 K. In metals the influence of these displacements of the ion cores is described by electrons scattering at phonons (see section 2.2.7).

In solids with a high ionic contribution the coulomb interaction between a moving electron and the lattice has to be considered. This leads to the concept of polarons and should be taken into account in oxides [IOT+01, Fre61, SBY+14]. They were first introduced by Landau 1933 [LP08]. A nice comprehensive book regarding the variety of issues in the field of polarons, was written by Alexandrov and Mott 1995 [AM95]. The interested reader can find more detailed descriptions of the following part in several reviews [AM01, Dev96].

An electron placed in the conduction band of an ionic material disturbs the position of the ionic core and a potential is generated by this displacement. The force on an additional not moving electron in the distance $r$ is of the order of $e^2/\epsilon_{stat} r^2$. If instead the velocity or frequency of the free electron is too high for the cores to react, only the contribution of the valence electrons $e^2/\epsilon_{\infty} r^2$ is present. With $\epsilon_{stat}$ being the static and $\epsilon_{\infty}$ the high-frequency dielectric constant respectively.

The measurement and concepts of these two parameters will be treated in section 2.3. Because of this difference $\kappa = (1/\epsilon_{\infty} - 1/\epsilon_{stat})^{-1}$ a Coulomb potential is formed, which traps the electron [AM95, Hol59a].

$$E_p = -\frac{e^2 (\epsilon_{\infty}^{-1} - \epsilon_{stat}^{-1})}{r_p 4\pi \epsilon_0} = -\frac{e^2 (\kappa^{-1})}{r_p 4\pi \epsilon_0}$$

(2.19)

is than the polaron energy or self-trapping energy, with $r_p$ the radius of the volume in which the electron wave is trapped (polaron radius). It can be much greater or comparable to the lattice constant. We see, the larger the difference between the two dielectric constants is, the stronger the trapping will be.

This radius subdivides the concept of polarons into the large ($r_p >> a$) and the small ($r_p \approx a$) ones. The electron can either move as a small polaron by thermally activated hopping, with $E_p/2$
as activation energy, or as a heavy but large polaron with the increased effective mass

\[ m^* \propto e^{\frac{Ep}{\hbar \omega}} \]  

with the characteristic phonon frequency \( \omega \). In this case the mean free path is still mainly limited by impurity, defect and phonon scattering.

For the radius of large polarons, in the case of strong coupling Alexandrov following Pekar (1946) gave the formula [AM95]

\[ r_p = \frac{16a_B}{5}, \]  

with \( a_B = \frac{\kappa^4 \epsilon \hbar^2}{m_e e^4} \) an effective Bohr radius\(^1\). From this he derived a ground state polaron binding energy

\[ E_0 = -0.146 \frac{1}{ma_B^2}. \]  

This can be compared to the ground state energy \((-0.5me^4 = -13.6 \text{ eV})\) of the hydrogen atom, which gives a ratio of 0.3 \( m/m_e \kappa^2 \). For \( \kappa \sim 4 \) and \( m \sim m_e \) a polaron binding energy of about 0.25 eV evolves [AM95, IOT+01].

The change in the effective mass of a large and strong-coupling polaron due to the retardation by the lattice distortion can be derived by starting from the lattice polarization described by a harmonic oscillator, subjected to an external force \( \propto D/\kappa \). Considering only small perturbations of slow moving polarons, so that the lattice deformation can follow, the mass for a large and strong-coupling polaron is

\[ m^*_{\text{strong-large}} \approx 0.02 \alpha^4 m, \]  

where \( m \) is the band mass and

\[ \alpha = \frac{e^2}{\kappa \sqrt{\frac{m}{2\omega}}} \]  

is the dimensionless Fröhlich coupling constant as a measure of the strength of the electron-phonon interaction (some values are given in table 2.1) and \( \alpha \gg 2 \) has to hold, so that the number of phonons forming polarons is large. On the other side it shouldn’t be too big, so that the polaron radius is still much larger than the lattice constant and a continuous effective mass and dielectric constant can be assumed.

Weak-coupling and large polarons were described by Fröhlich 1950, where \( \alpha \leq 1 \) and only very small displacements of the ions with respect to their equilibrium positions occur. For very slow moving polarons, where electrons interact with long wave optical phonons, this leads to a slightly different formula for the effective mass

\[ m^*_{\text{weak-large}} = \frac{m}{1 - \alpha/6} \approx m \left(1 + \frac{\alpha}{6}\right). \]  

As already mentioned, the first expression of equation 2.25 is only true for small values of \( \alpha \), since above 6, the effective mass would change its sign abruptly to negative.

\(^{1}\text{It differs from the typical } a_B^2 \text{ used e.g. in section 2.2.6 by employing } \kappa \text{ instead of } \epsilon_{st} \)
The second expression in equation 2.25 was derived for the intermediate regime, where $1 < \alpha < 10$ as shown by Lee-Low-Pines 1953 and others by different means, which are beyond the scope here. It is remarkable that regardless how large the Fröhlich constant is and which description or model is the correct one for a material, the increase in the effective mass for a large polaron will stay below 50\% for $\alpha \leq 3$ (here the before mentioned formulas give the same enlargement). Nevertheless, this concept is quite important in the field of TCOs and can lead to somewhat higher effective masses compared to the calculated ones. Imanaka et al. showed for example in ZnO an increase from the calculated $m^*_{\text{calc}} = 0.23m_e$ to $m^*_{\text{polaron}} = 0.29m_e$ due to the formation of a polaron [IOT+01].

Rössler derived 1968 with a new variational ansatz a formula, which in a way combines the ones mentioned before [Rös68] and is more accurate and applicable in a wider range of values of $\alpha$. It reads for the large polaron case

$$m^*_\text{complete-large} = m \left(1 + \frac{\alpha}{6} + 0.02362\alpha^2\right). \tag{2.26}$$

Using this formula and the value for $\alpha$ for TiO$_2$ given in table 2.1 it results in an enlargement of the effective mass of about 60\% compared to the one derived by band calculation.

It should be noticed that such an increased effective mass does not necessarily has to result in a lower mobility. The scattering probability of a heavy-massed polaron is successively reduced with increasing mass. So the scattering time can be proportional to the mass $m^*$ and $\mu$ would then be independent of the mass [See97, FCE+94].

If the coupling gets stronger, the polaron radius will at some point be comparable to the lattice constant and the assumption of an effective mass is inaccurate. Or more precisely, when the polaron energy $E_p$ gets larger than the half of the band width, the large polaron collapses into a small one, as it was shown by Holstein 1959 [Hol59b]. Small polarons are strongly localized and are attributed to carry electrical transport by temperature activated hopping (SPH). A typical non-degenerate semiconductor exhibits a strong increase of the charge carrier density with raising temperature (Arrhenius-like). In contrast for small polarons the mobility strongly increases with temperature and can be understood in the framework of variable range hopping. This was seen by several authors for ionic materials including rutile TiO$_2$ [AM01, HCVJ07, Mya01, YIM10].

The small polaron conductivity is supposed to be subdivided in two cases, the adiabatic and the non-adiabatic one. In the adiabatic case a high probability for hopping to an adjacent site exists, whereas it is quite small in the non-adiabatic one. The conductivity in the case of SPH can be expressed in the form [YIM10, FH63, AM01]

$$\sigma_{\text{SPH}} = \sigma_0 T^{-\alpha} e^{-\frac{W}{k_B T}}, \tag{2.27}$$

with an exponential pre-factor $\sigma_0$ and an activation energy $W$. The exponent $\alpha$ is 1 in the adiabatic and 3/2 in the non-adiabatic case. In practice, the distinction between the SPH mechanism in the case of small activation energies and a band transport of heavy particles can be quite difficult. This is due to the fact that the pre-exponential $T$ factor alters and can even dominate the exponential one quite severely in such a case [AM01]. It is important to note that this formula holds for the high temperature case, whereas a constant conductivity is predicted for low temperatures. This
is due to a transition from hopping to a band transport below half of the Debye temperature \( T < T_{\text{Debye}}/2 \) for SPH conductivity [AM01, FH63]. In section 4.5.1, this model will be tested to fit some conductivity data.

In the case of large polarons the increase of the effective mass, if any, is quite moderate, whereby in the small polaron case this can be very severe and is for example for rutile TiO\(_2\) in the order of 150 [AM95, AM01]. Alexandrov also states and dedicates a whole chapter to the fact that the concept of small polarons could explain, why highly doped semiconductors \( n > 1 \times 10^{20} \text{cm}^{-3} \) with very low mobilities even below the Ioffe-Regel limit (section 2.2.1) can be seen.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha )</th>
<th>Ionicity (%)</th>
<th>Material</th>
<th>( \alpha )</th>
<th>Ionicity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>0.31</td>
<td>4</td>
<td>KI</td>
<td>2.5</td>
<td>57</td>
</tr>
<tr>
<td>CdS</td>
<td>0.52</td>
<td>18</td>
<td>KBr</td>
<td>3.05</td>
<td>68</td>
</tr>
<tr>
<td>CdF(_2)</td>
<td>3.2</td>
<td>73</td>
<td>KCl</td>
<td>3.5</td>
<td>75</td>
</tr>
<tr>
<td>AgBr</td>
<td>1.6</td>
<td>23</td>
<td>GaAs</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>AgCl</td>
<td>1.8</td>
<td>31</td>
<td>GaP</td>
<td>0.20</td>
<td>4</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.43</td>
<td>18</td>
<td>SrTiO(_3)</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>ZnO [IOT(^+)01]</td>
<td>1.2</td>
<td>55</td>
<td>TiO(_2) [MJJ(^+)13]</td>
<td>2.5</td>
<td>59</td>
</tr>
</tbody>
</table>

Table 2.1: Some values for the Fröhlich coupling constant \( \alpha \) from [Dev96] if not stated otherwise. The ionicity calculated from equation 2.72 is given as well with the Pauling electronegative values applied. For a given metal one can deduce from this table a *qualitative* rule of thumb that the coupling increases when increasing the ionicity by replacing the anion by a more electronegative one. This rule can easily fail if comparing completely different materials like e.g. KI and ZnO, which have a quite similar ionicity, but different \( \alpha \).

Consistently, the reviews, books, and articles gave a value in the region of 1 cm\(^2\)/Vs and below for the mobility of small polarons due to the high effective mass. Since well conducting films, which are the major scope of this thesis, show greater mobilities and no increase but a decrease of the mobility with raising temperatures (see section 4.5.2), small polarons can be ruled out already in these cases.

It should also be mentioned that a mobility of 1 cm\(^2\)/Vs is also approximately the lower limit for the applicability of the Boltzmann theory, as the mean free path becomes otherwise smaller than the lattice constant. Moreover, at this point the Hall theory breaks down and it is not any longer a save technique to measure the transport mobility [AM95]. For completeness some other hopping processes are described briefly in the next section.

### 2.2.5 Insulators

Temperature dependent resistivity and Hall measurements are very powerful tools when a TCO material is investigated. For example, one can determine whether a crystalline sample is in the regime of a degenerate semiconductor or not. Although the precise determination whether a sample is insulating or metallic is experimentally not easily done, theoretically it is a rather simple concept. If the conductivity of a sample vanishes, when cooling down to approximately zero Kelvin
(\(T \rightarrow 0\) K), it is called an insulator, if not it is a metal. Some more details how this transition can be explained and experimentally determined follows in the section 2.2.6.

Non-degenerate semiconductors, for instance, are insulators, as the charge carrier density drastically depends on the measurement temperature and activation energies can be calculated by using an Arrhenius like \(\sigma \propto e^{-\left(\frac{E_A}{kT}\right)^x}\) dependency. A typical excitation process can be described with an Arrhenius law (so \(x = 1\)). At sufficiently low temperatures, the excitation from a defect or dopant level to the free electron like conduction band is no longer possible, leave alone from the valence band. The electrons are then strongly localized at for example an impurity and their respective wave functions are not any longer extended Bloch waves.

Instead the localization length is defined as the exponentially decaying envelope of the wave function. For such electrons several different hopping mechanisms, which differ mainly in the exponent \(x\), can describe the conduction process.

Hornung et al. observed, for example, in insulating Si:P a crossover from Mott variable-range (Mott VRH \(x = \frac{1}{4}\)) to Efros-Shklovskii variable range hopping (ES VRH \(x = \frac{1}{2}\)) [HIWL00] and Rosenbaum showed this also for undoped amorphous In\(_2\)O\(_3\) [Ros91]. Han et al. measured highly insulating ZnO:Mn and observed a transition from Arrhenius like activation of electrons at relative high temperatures to nearest-neighbor hopping below 18 K (NNH \(x = 1\) with \(T^{-1}\) added to the prefactor) [HSC+03]. And as a last example, Serin et al. found Mott VRH in sol-gel processed SnO\(_2\) [SYS+10].

As the theories often differentiate between 2 and 3 dimensional behavior an additional crossover can be seen performing a thickness series and at a specific temperature for one sample respectively. This was for example done by Vlekken et al. 1991 for amorphous TiO\(_{2-x}\), with such a low amount of oxygen that some of the samples revealed even a metallic performance due to metallic titanium paths, and no hopping anymore [VVvB91]. A very interesting study in this respect was done by Yildiz et al. 2008 [YLKM08]. They investigated undoped TiO\(_{2-x}\), sputtered with water vapor as reactive gas on heated substrates, as had been done also by Mardare et al. before [MBG+02]. This procedure increased the conductivity, compared to the complete stoichiometric TiO\(_2\), by several orders of magnitude and achieved values up to 2 \(\Omega^{-1}\) cm\(^{-1}\). Of course, such a value is still much to high for TCO-applications. For such high resistive samples, they observed normal Arrhenius behavior at high temperatures above room temperature and below that a crossover to 3D Mott VRH and below 100 K even another transition to ES VRH.

Nevertheless, the samples, which account for the majority of the ones investigated in this thesis, are two to three orders of magnitude more conductive than these high resistive ones. Also they don’t exhibit an increase in conductivity with higher temperatures not to mention an exponential one. Therefore, a more detailed description of these hopping mechanisms is not necessary here. To the interested reader, I point out to the already cited articles and to the books written by Gantmakher [Gan05] and Shklovskii and Efros [SE84].


2.2.6 Metal Insulator Transition MIT

Before discussing the origins of a MIT, one has to be able to distinguish a metal from an insulator. This can be done by performing a resistivity measurement to the lowest possible temperature and extrapolate it to \( T = 0 \) K. If it would have a conductivity there, which is still greater than \( 0 \) S, it is a metal as already mentioned in the section above. In an insulator at very low temperatures only hopping processes can exist, which are all temperature activated. Thus, a free electron transport is not possible at \( 0 \) K in such materials.

The usual way to extrapolate is either by [Gan05]

\[
\sigma(T) = \alpha + \beta T^{1/3}
\]  

(2.28)

or by

\[
\sigma(T) = \alpha + \beta T^{1/2}
\]  

(2.29)

which should be used on the "metallic" side. Details of the phenomena present in so called dirty or bad metals at low temperatures will be given in section 2.2.11. The extrapolation was for example used in P doped Si [TPR83] and in Ga doped ZnO [BTN06].

In principle, there are two possible reasons, why a crystalline semiconductor is an insulator (seen at very low temperatures). One is that in a perfect crystal there are too few dopants or in the intrinsic case even none. Therefore, the distance between them is too large and no overlap between the doping orbitals occur (see also eq. 2.17). So in the ground state the electrons are bound to the dopant. The bounding potential is a Coulomb potential of the form \( V(r) = \frac{1}{4\pi\epsilon_0\epsilon_{\text{stat}}} \frac{e}{r} \). It is screened by the other electrons and so the potential is changed to

\[
V(r) = \frac{1}{4\pi\epsilon_0\epsilon_{\text{stat}}} \frac{e}{r} e^{-\lambda_{\text{TF}} r},
\]  

(2.30)

with the \( r_{\text{TF}} = 1/\lambda_{\text{TF}} \approx 0.5(n/a_B^*)^{-1/6} \) Thomas-Fermi screening length for a quasi-free electron gas [IL09]. Thereby is \( a_B^* = 0.5 \Lambda\epsilon_{\text{stat}} m_e/m^* \) the effective Bohr-radius. This length becomes smaller for an increasing electron concentration until the potential well is so small that the electron can’t occupy a state there. Below this critical concentration it is bound to the impurity and strongly localized, above it is quasi-free, extended over the crystal even at absolute zero Kelvin. A more precise value, at which charge carrier concentration a semiconductor can become a metal, was given by Mott. Therefore, the so-called Mott-transition is a correlation phenomenon and reads [Mot61]

\[
a_B^* n^{1/3} \approx 0.25.
\]  

(2.31)

It can also be visualized as the concentration, at which the potentials of the individual dopants starts to overlap (as depicted in figure 2.4) and doing so, they form an impurity band where extended states can exist. This overlap can be understood in a similar way like in section 2.2.3 and it leads to a similar estimate of the Mott-criterion as the average distance between the dopants is \( n^{1/3} \) and the extend of one is the effective Bohr-radius \( a_B^* \).
Figure 2.4: A transition between a metal and an insulator can, in principle, be understood by two different means. In the Mott-transition picture the increasing number of perfectly ordered dopants leads at some point to the overlap of their states and is, therefore, a correlation effect. In contrast in the Anderson-transition a metal is formed by increasing the order of the dopants or also the matrix, as thereby the mobility edge is lowered. At some point this edge is below the Fermi energy, so that the electrons there are not any longer localized.

The second possibility is linked to the disorder in the material. For this so-called Anderson transition an additional concept is necessary; the mobility edge. It implies that even when the Fermi energy lies within the conduction band, the electron can be localized due to a high degree of disorder in the crystal (matrix and/or dopants). The energy above which the electrons can occupy extended states and exhibit a metallic behavior is therefore called mobility edge. The relative positions of the Fermi energy and mobility edge can be shifted with respect to each other by changing the amount of disorder. So by for example annealing an insulator can be converted into a metal, due to a reduced amount of disorder. The question which transition takes place in a practical experiment is hard to answer. For example, because the Mott assumption of a perfectly periodically ordered distribution of the dopants, even in a single crystal, is quite unrealistic, so there will always be some amount of changeable disorder. On the other hand also amount of disorder can be expressed in terms of the Bolz radius and by this nearly the same relationship as the one from Mott is derived [Gan05]. Because the two can hardly be disentangled by experiment these metal to insulator transitions are often called Mott-Anderson transition.

Of course, also a change in the crystal structure can occur and lead to a metal-insulator transition. For example, the crystallization of an amorphous film, or a phase transition to a different crystal structure at elevated temperatures, result in a drastic change of the band structure. In the case of TiO$_2$ for example, a good conductive anatase film will transform at high temperatures above $\sim 600 \, ^\circ\mathrm{C}$ into a rutile one [LiHM94]. However, therein the effective band mass is much higher and a metallic state can’t exist anymore [TPS+94].
2.2.7 Metal

Let us now discuss the most relevant case for TCO materials. For metals and degenerate semiconductors the conductivity can be described by Drude and Sommerfeld physics (see chapter 2.2.1) and equation 2.5. In these cases the Fermi energy doesn’t change much with temperature and therefore also the number of electrons at the Fermi edge is constant. Because of the Pauli principle, solely electrons at the Fermi energy can carry a current. This number is strongly influenced by the chemical composition e.g. dopant and impurity concentrations or in the case of oxides, the oxygen deficiency. To some extend also the microstructure impacts this concentration, as defects in a material can form states within the band gap and act as traps for charge carriers. This is why annealing of a sample, when reducing these defects, can lead not only to a higher mobility, but also to a somewhat larger charge carrier density, as experimental data will show later on in section 4.1. Therefore, the influence onto the mobility $\mu$

$$\mu \approx \frac{e\tau(E_F)}{m^*}$$

in $\sigma = ne\mu$ is of major importance [IL09]. This is especially true to understand the impact of temperature upon resistivity of a metal, as long as no permanent structural etc. changes occur.

The relaxation time $\tau$ is inversely proportional to the scattering probability and if different possible scattering mechanisms (e.g. scattering at different kinds of defects, phonons, other electrons etc.) are independent of each other, the corresponding probabilities can be added up (Matthiesen’s rule).

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{defects}}} + \frac{1}{\tau_{\text{phonons}}} + \frac{1}{\tau_{\text{other-interactions}}}$$

The following three subsections are dedicated to the different mentioned classes of effects out of which the resistivity of a sample is composed. Of course these processes are not limited to metals alone which is why they will be discussed in sections by their own but always with focus towards degenerate semiconductors.

2.2.8 Defect Scattering

The topic of defects in crystals fills hundreds of pages in different books and is an extensive research topic. In short, every deviation of the crystal symmetry is a defect in the sense of a scattering center for the Bloch wave (see sec. 2.2.1). Defects can be classified by their spatial extent in 0, 1, 2 and 3 dimensional ones.

Point defects (0 D) are for example foreign atoms (neutral impurities) or ions (ionized impurities), which are located either on substitutional (replacing a host atom) or interstitial sites (hollow space within the lattice). Also missing lattice atoms (vacancies), which can be charged as well, belong to this group. Especially, the ionized impurity scattering (IIS) is important in the field of doped TCO materials, as active and therefore charged dopants are unavoidable for good conductivity and will be treated separately in 2.2.10.
1D defects are stacking faults and dislocations in a crystal and their number and direction is primarily influenced by the preparation procedure, including the technique applied, growth parameters, post deposition treatment, substrate material used, etc. These defects are expected to have a negligible temperature dependence but are seen as the main origin of the residual resistivity at low temperatures in the case of metallic or degenerate semiconductor samples. Because of this, reducing the defect density is in principle a down shifting of the temperature dependent resistivity curves.

The lower and upper interface of the film belong to the group of 2D defects. As long as the film thickness is much larger than the mean free path, i.e., \( d \gg \lambda \), this type can be ignored. Reducing the film thickness result in an increase of the specific resistivity and such thickness series are often done for metal films like Ag [LB64] or Ti [SS72]. An extensive review about the numerous models to account for the exact behavior of this increase was written by Angadi 1985 [Ang85]. The key idea in all models is always that two different extremes of how the electrons become scattered back into the film can be distinguished. The scattering can be either treated more or less like a billiard ball getting reflected at a wall (specular) in which case the conductivity isn’t altered at all compared to the "bulk" material. Or it is more like light shining on snow covered winter land (diffusive). In this case the electrons, like the light, get scattered in every direction including the incoming one and the resistivity is elevated. Both cases, in a first approximation, are temperature independent. Surface roughness, seed layers, adsorbents and details of the micro structure at the interfaces are the key parameters controlling the degree of diffusivity of the scattering. The most prominent model for describing the thickness dependency of the specific resistivity is the Fuchs-Sondheimer Model [SON52].

The thicknesses of films used in TCO applications are in the range of several hundred nanometers and therefore, the much more important class of 2D defects are grain boundaries (GB) which occur in a polycrystalline material. Although the resulting formulas are somewhat different, in terms of understanding this mechanism can be treated qualitatively similar to the scattering at the upper and lower surface. This was for example done by Mayadas and Shatzkes [MS70, Ang85] introducing a microstructure dependent probability factor for a back reflection of an electron at a GB. The difference in the crystal orientation of adjacent grains embodies another mechanism of increased resistivities. The theory of this angle dependent resistivity was developed by Nakamichi [Nak96]. He proved the intuitive idea that the resistivity of a GB increases proportional with the angle between the two crystal orientations. Only at some special mismatch angles which are linked to the symmetries of the crystal structure the increase is abruptly lowered.

The above mentioned scattering approaches are used to explain the resistivity of metal thin films, influenced by grain boundaries and dislocations situated there [Bro77, CO06, CLGG14, KZN+10, KNZ+11]. It is quite intuitive to expect that for degenerate semiconductors like for metals the same kinds of GB scatterings are present. Although to my knowledge no quantitative attempts have been performed using the same formulas for TCOs too, qualitatively several authors state that preparation details which increase the grain sizes and crystal quality enhance the mobility due to fewer and "better" GBs. For example, Minami et al. and Choi et al. showed that improvements of the Hall mobility in ZnO with high charge carrier densities are caused by less GB and dislocation
Chapter 2 Fundamentals

scattering [MTMM05, CKK+05]. Also for SnO$_2$, GB and other structural defects were proposed to be the origin for lower mobility than expected by IIS and phonons alone [BCFM91].

To be able to disentangle intragrain mechanisms from GB scattering, one can compare mobilities measured electrically and optically. For not too small grains, the mobility determined by optical means is solely depending on the mobility within the grain as the electrons move back and forth. On the other hand, in a DC electrical measurement the electrons get affected by the GB as they travel along the complete film. Steinhauser, for example, could show that in ZnO above $1 \times 10^{20}$ cm$^{-3}$ the mobilities measured by these means are nearly the same [SFO+07], but differ greatly below this limit. From these results it can be concluded that above a critical carrier concentration the scattering at GB is dominated by intragrain effects. To further prove this point, the calculated mean free paths of the carriers (equation 2.8) can be compared with the typical grain size $L$ of the material, determined by SEM/TEM or similar techniques. Typically, the mean free path in TCO films is in the range of some nanometer and thus usually much smaller than the grain size. Thus, GB scattering is often stated as only a minute effect [CYL00, LYZ+06, SFO+07, ZM96, Min00, PST+01, GLL+13, BE14]. Of course, this is only true as long as the GB is not electrically completely insulating or showing high potential barriers. For example, some excess oxygen can form an insulating oxide layer (e.g. Al$_2$O$_3$) around conductive (ZnO:Al) grains which leads to a very high resistivity of the complete film.

In contrast to metals, grain boundaries in semiconductors can not be simply interpreted as interruptions of the crystal symmetry. In these cases GBs are also areas of dangling bonds and defects, which can result in a high number of trap states, which can be situated energetically within the band gap. These states become filled by free electrons and a depletion zone with a thickness

$$d_{\text{depl}} = \sqrt{\frac{2e\epsilon_0\epsilon_{\text{st}}E_B}{en}} \quad (2.34)$$

and a potential barrier $E_B$ is formed. This barrier the electrons have to overcome, by temperature, by tunneling, or by thermionic emission. For typical degenerate TCO materials the width of the barrier is only about an atomic layer [ZM96]. Seto derived a formula valid for non-degenerate semiconductors with enough carriers to fill all traps and assuming that the conduction in the crystallite is much higher than that through the boundary [Set75, Cro65]. The GB is thereby overcome by thermionic emission at low applied voltages which lead to

$$\mu_{\text{GB-Seto}} = L \frac{A}{(m^*)^2} e^{-\frac{eB}{kT}} \quad (2.35)$$

with $L$ the mean grain size and $E_B$ the energy barrier height. Bruneaux et al. changed the electron statistics from Boltzmann to Fermi-Dirac, whereby it can be applied to a degenerate material as well, in this case highly doped sprayed SnO$_2$ [BCFM91, ZM96]

$$\mu_{\text{GB-Bruneaux}} = L \frac{B}{m^*T} e^{-\frac{eB}{kT}}. \quad (2.36)$$
The barrier height for both of them can be calculated from the Poisson equation and reads

$$E_B = \frac{e^2Q_t^2}{8\varepsilon_0\varepsilon_{st}N_d^2}$$

with $Q_t$ being the trap density at the GB, $N_d$ the donor density far away from the depletion layer in the grain, $\varepsilon_{st}$ the static dielectric constant, and $A$ and $B$ constants. Bikowski and Ellmer claimed 2014 to have deduced a model for an arbitrarily high charge carrier density, thus, one has not to decide whether it is degenerate or not. Nevertheless, it is still analytically not too complicated to be applicable in practice and, last but not least, uses only few and physical meaningful parameters \[BE14\]. It reads

$$\mu_{GB-\text{Bikowski}} = \frac{4\pi em^*LkT}{n_{av}h^3} \ln \left(1 + e^{-\left(\frac{E_B}{kT} - \eta\right)}\right).$$

Where $n_{av}$ is the average charge carrier density including bulk and depletion layer and $\eta = (E_F - E_c)/(kT)$ is the reduced Fermi energy. Despite the differences of these formulas, they all have a strong even exponentially increase of the mobility with raising temperature in common, in contrast to the behavior of a metal.

For the sake of completeness, the 3 D case is also briefly mentioned. Voids or precipitations belong to this category. Voids emerge from bad crystal growth parameters when high deposition rates, high gas pressures, and/or low diffusivities are present during the growth. In the zone growth model of Thornton this is called Zone 1 \[Tho86\]. Therefore, preparation techniques like sol-gel deposition or spray-pyrolysis produce films with low electrical mobilities. The low energy of the particles accompanied with a high deposition rate in the case of these techniques generates voids and a weak contact between the grains \[KBPA06, TMK+90\]. This can also be seen as the reason why GBs have to be overcome by thermionic emission in such films including the characteristic temperature dependence even though the grains themselves are degenerate \[BCFM91\]. In contrast, sputtered particles exhibit higher energies which leads to compact films reaching nearly bulk densities. Thus, voids or loose contacts between grains are not such a relevant issue here. Precipitations on the other hand can always occur if the solubility of a dopant in its matrix is exceeded and enough time or temperature is provided. They reduce the mobility which is why the conductivity of a TCO exhibits in general a maximum at some dopant concentration, annealing or substrate temperature \[LYZ+06, BLV+10, HPG11\].

### 2.2.9 Phonon Scattering

After we have discussed defect scattering, which determine the residual resistivity at very low temperatures (in metallic films), we now switch to the most important and prominent temperature dependent scattering mechanism. It is the scattering by acoustic phonons for which the Bloch-Grüneisen (BG) formula \[Blo30\] is often used. This equation holds perfectly well for pure metals (see section 4.5.2 for Ag). A general version of this formula is \[AE93, BBR06\]

$$\rho_{BG}(T) = A \left(\frac{T}{T_{Debye}}\right)^n \int_0^{T_{Debye}/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx.$$  

(2.39)
Chapter 2 Fundamentals

Figure 2.5: Illustration of the predicted shape of the temperature dependency of the resistivity due to phonon scattering according to the BG formula. \( \rho \) has been normalized by \( A \) and the temperature by \( T_{\text{Debye}} \). The integral of equation 2.39 can be simplified for very high and very low temperatures with respect to the Debye temperature. In the insert a zoom of the very low temperature area is shown. It is nice to see that the high temperature behavior of the BG formula can be well described by the linear limit. On the other hand, the temperature range where the \( T^n \) relationship can be applied is very small.

Thereby, \( n \) can be 2, 3 or 5, depending on the details of the nature of the electron-phonon interaction and \( T_{\text{Debye}} \) is the Debye temperature, characterizing the phonon spectrum. \( n = 2 \) denotes temperature dependent electron-electron interaction and is usually not used with the integral. Instead it is often approximated as a \( \rho_{\text{elec- elec}} \propto bT^2 \) term with \( b \) being a fit constant, in a Matthiesen-like summation of several contributions. For materials with a dominant phonon assisted scattering of an \( s \) with an \( d \) electron, \( n = 3 \) is to be expected. It can be seen for several transition metals (Pd, Ni, Co, W [PAB81, WW57]) and their compounds as well, for example, CoSi \(_2\) [AE93]. Even when only employing them as dopants this influence can recognized, e.g., Cr in In\(_2\)O\(_3\) [LHSC12].

The most prominent case is \( n = 5 \) which is the common BG formula [Blo30] and represents the direct scattering of a conductive electron by an acoustic phonon. The temperature behavior of the resistivity of typical metals like Ag, Au or Cu [SON52] is explained very well by this equation. This holds also for samples with a reduced number of dimensions, e.g., Ag-wires [BBR06]. This model is also used for TCO materials, for example, SnO\(_2\)-F [GLL+13], In\(_2\)O\(_3\):Sn thin films [LL04, LCLW10, LL14], and also nanowires [CCL+09]. It’s worth mentioning that regardless which value is used for \( n \), the contribution approaches zero at low temperatures and at high temperatures \( T \gg T_{\text{Debye}} \) equation 2.39 simplifies to a linear increase with temperature. In figure 2.5, the predicted shape of the BG formula with \( n = 5 \) is shown including the resulting approximations of the integral for high and low temperatures, respectively. It elucidates how important it is to employ the complete integral and not a simple summation of the two limits when describing \( \rho(T) \) data for \( T < T_{\text{Debye}} \).

The variable \( A \) in equation 2.39 represents the intensity of the electron-phonon coupling and can be written as [PFC99, VCS02]

\[
A = \frac{\pi \lambda \nu k_B m^* T_{\text{Debye}}}{2 \hbar e^2 n}.
\]
Section 2.2 DC Electrical Properties

with \( \lambda_{ep} \) a dimensionless coupling constant, \( k_B \) the Boltzmann and \( \hbar \) the Planck’s constant divided by \( 2\pi \). Also the representation

\[
A = \frac{\lambda_{ep} \omega_{\text{Debye}}}{\omega_p^2},
\]

(2.41)
can be found in literature [BBR06] with

\[
\omega_p = \sqrt{\frac{ne^2}{m^* \epsilon_0 \epsilon_{\infty}}}
\]

(2.42)

being the Drude plasma frequency [HPG11]. This frequency is an important parameter for the optical properties of a TCO material as it defines the lower frequency limit down to which the material is transparent. It will be discussed in greater detail in section 2.4.2. As \( A \) should decrease for higher charge carrier densities, it is to expect that also the difference between the resistances at room and low temperature will become smaller. As Zhang and Ma mentioned 1996 [ZM96], some authors are using instead \( \mu = \mu_0 T^{-3/2} \) as the formula describing lattice vibrations. This concept can be used in normal semiconductors. However, it is not valid for degenerate systems as it uses Maxwell-Boltzmann statistics which are not appropriate under these circumstances.

2.2.10 Ionized Impurity Scattering (IIS)

Another unavoidable scattering mechanism in doped TCO films is the ionized impurity scattering (IIS) due to charged impurities. When dopants contribute one or several additional electrons into the conduction band, they have a higher valence state compared to the host cation and the resulting Coulomb potential acts as a strong scatterer to free carriers. Bellingham et al. identified this mechanism already 1992, together with the before mentioned plasma frequency (cf. section 2.4.2) as the "Intrinsic performance limits in transparent conducting oxides" [BPA92]. Several other authors since then and until now confirmed this as the fundamental limit for highly doped semiconductors, e.g., numerous reviews regarding TCO materials and the present status of the field [Min00, Gor00, EPJ+04, Cas11]. This is due to the fact that charged dopants are needed for charge carrier generation and thus will always be present even in a perfect single crystal.

On the other hand, there are several different models describing this interaction. An empirical approach was introduced by Masetti et al. [MSS83]

\[
\mu_{\text{IIS-MA}} = \mu_{\text{min}} + \frac{\mu_{\text{max}} \mu_{\text{min}}}{1 + \left( \frac{n_x}{n_{\text{ref1}}} \right)^{\alpha_1}} - \frac{\mu_1}{1 + \left( \frac{n_{\text{ref2}}}{n_x} \right)^{\alpha_2}},
\]

(2.43)

including in total seven independent variables and was invented for doped silicon. The variables have no deeper physical meaning but are able to describe the measured data and this model has been applied among others by Ellmer 2001 for ZnO [Ell01]. Conwell and Weisskopf derived 1950 a model in the non-degenerate case with uncorrelated collisions of truncated potentials which are
cut off at half the mean distance between the donors \(d = N_i^{-1/3}\) \([CW50, Ell01]\)

\[
\mu_{\text{HI-S-CW}} = \left(\frac{2\pi}{m^*}\right)^{1/2} \frac{128e_0^2\epsilon_0^2 (k_B T)^{3/2}}{e^3 N_i Z^2} \ln \left(1 + \frac{128e_0^2\epsilon_0^2 k_B T}{N_i^{1/3} Z e^2}\right)^2 .
\] (2.44)

Here, \(Z\) is the charge of the ion and \(N_i\) the concentration of such scattering centers. The other variables have their usual meaning. Zhang and Ma exchanged in principal in this expression \(kT\) against a temperature independent Fermi Energy \(E_F\) to account for a degenerate semiconductor \([ZM96]\). However, these formulas neglect the screening possibilities of a free electron gas and lead therefore to too low mobilities. Brooks and Herring included then a screening function to the non-degenerate formula from Conwell and Weisskopf \([Bro55, Ell01]\).

\[
\mu_{\text{HI-S-BH}} = \mu_{\text{HI-CW}} \frac{1}{F_{\text{HI}}(\xi)}
\] (2.45)

with

\[
F_{\text{HI}}(\xi) = \ln(1 + \xi) - \frac{\xi}{1 + \xi}
\] (2.46)

and

\[
\xi = \frac{96\pi^2\epsilon_0\epsilon_{\text{st}} m^*}{N_i} \left(\frac{kT}{he}\right)^2 .
\] (2.47)

Dingle \([Din55]\) derived then a formula often used for degenerate semiconductors including TiO\(_2\) \([FYH+07]\). This formula has also been applied by Bellingham et al. for ZnO \([BPA92]\) in order to calculate the intrinsic TCO limit

\[
\mu_{\text{HI-S-Di}} = \frac{3\pi\epsilon_0\epsilon_{\text{st}} h^3}{2Z^2 m^* e^3} \frac{n}{N_i} \frac{1}{F_{\text{HI}}(\xi_{\text{Di}})} .
\] (2.48)

He used the same screening function \(F_{\text{HI}}\) (equation 2.46) but with

\[
\xi_{\text{Di}} = (3\pi^2)^{1/3} \epsilon_0\epsilon_{\text{st}} h^2 n^{1/3} \frac{1}{m^* e^2} .
\] (2.49)

where now the free electron density \(n\) is included \([Din55]\). In the case of a partly compensated material\(^2\) \(N_i = N_A + N_D\) with the acceptor \(N_A\) and donor \(N_D\) concentration has to be used. Moreover, the free carrier concentration \(n\) in the formula has to be substituted with an effective one \(n' = n + (n + N_A)/(n + N_D)\). Often \(n = N_i\) is utilized by assuming that every incorporated dopant is ionized and that no electrons got trapped, for example, at grain boundaries, defects, etc., and so the measured electron density equals the one of ionized dopants.

An important issue is the value of \(Z\) which is unity for single ionized dopants (in comparison to the matrix cation) like Al in ZnO. Instead, it is often assumed to be two, if the doping mechanism is via oxygen vacancies. Values higher than unity can be present as well, if the dopants are not homogeneously distributed but had formed clusters. Because \(\mu \propto 1/N_i Z^2\) in all the formulas

\(^2\)Partly compensated means that not only donors \((N_D)\) are present in the material but also some acceptors \((N_A)\). Both types are ionized and thus increases the charged impurities but reduces the amount of free carriers.
Section 2.2 DC Electrical Properties

Figure 2.6: A sketch of the charge carrier dependency onto the mobility of the three models described above with two values for \( \epsilon_{st} \), 9 and 50 equivalent for a typical TCO material and TiO\(_2\) respectively. An effective mass \( m^* = 0.3m_e \), \( T = 300 \text{ K} \), and \( Z = 1 \) was used. First, the Brooks and Herring (BH) model for non-degenerate semiconductors is shown which has an unphysical mobility minimum at \( 10^{19} \text{ cm}^{-3} \) to \( 10^{20} \text{ cm}^{-3} \) and should not be applied above this minimum. Second, the Conwell and Weisskopf (CW) model with truncated Coulomb potentials and third the one from Dingle applicable for degenerate semiconductors including the screening effect by free carriers can be seen. Because of this screening mechanism the mobility decrease is eased drastically. Clearly, the higher dielectric constant of TiO\(_2\) leads to a much higher theoretical mobility limit.

Figure 2.6 shows calculated data which compare the three different models discussed above. The unphysical mobility minimum at \( 10^{19} \text{ cm}^{-3} \) to \( 10^{20} \text{ cm}^{-3} \) is a clear sign that the model of Brooks and Herring should only be applied for lower charge carrier densities. The tremendous effect of screening can be visualized by comparing the red and the blue curves where the first one describes a much stronger reduction in mobility than the second one. Additionally, the very beneficial effect of the higher dielectric constant of TiO\(_2\) in comparison to the common TCO materials in respect of the mobility limited by IIS can be seen.

2.2.11 Additional Low Temperature Effects

Cooling down a sample near to absolute zero can enable the detection of several quite fascinating effects. In the case of an insulator or a strong localized material the already mentioned hopping
mechanisms can give new insights 2.2.5. Different effects occur in the case of metals or degenerate semiconductors with a relative high degree of disorder but still dominant band transport. In these cases phenomena illustrating the wave nature of the electrons inside the solid can be detected. Due to their capability of interfering with itself or each other, temperature dependent changes in resistivity arise. Gantmakher wrote a comprehensive and relatively easy to understand book about the following effects [Gan05]. A thorough review can be read in the dissertation of Hanno Volker [Vol08], too.

Quantum Interference

The motion of an electron traveling diffusively can be visualized as a random walk and some possible paths, which lead back to the origin are shown in 2.7(a). The probability density function $p(r, t)$ to find it in a volume of $d^3r$ at the place $r$ after a time $t > 0$ can therefore be calculated via a Gaussian distribution [Gan05]

$$p(r, t) = (4\pi Dt)^{-d/2} e^{-\frac{r^2}{4Dt}}$$

where

$$D = \frac{v_F^2 \tau}{d} = \frac{\lambda h k_F}{m^*}$$
are two representations of the diffusion constant in a \( d \) dimensional sample. \( \tau \) is the elastic scattering time during which the electron was traveling with the Fermi velocity \( v_F \) \([LB02, SYS^{+10}]\). A graphical representation of the distribution can be seen in figure 2.7(b). If the temperature is low and the electron-electron interaction is weak enough, the dephasing time can get much bigger than the elastic scattering time \( \tau_\phi >> \tau \). In this case, electrons are able to scatter several times elastically before loosing their phase information. Some of them return to the origin and are still phase coherent. Because of time symmetry each loop comes as a pair (clock- and counterclockwise). Classically, the wave amplitudes would simply add up \( (|A_1|^2 + |A_2|^2 = 2A^2) \) and together with all other possible paths forming the maximum of the shown Gaussian distribution. Quantum mechanically, the amplitudes of the waves have to be added up due to the interference before calculating the squared modulus \( (|A_1 + A_2|^2 = 4A^2) \) which leads to a doubled backscatter probability as can be seen in figure 2.7(b) due to the interference term \( (2|A_1A_2|) \). If the spin-orbit scattering rate \( \tau_{-SO}^{-1} \) is higher than the dephasing rate, loops whose traveling times fulfill \( \tau_{SO} < t < \tau_\phi \) will suffer a destructive interference leading to weak antilocalization \([Gan05]\). Very small loops with lower times \( \tau < t < \tau_{SO} \) are instead still constructively interfering. The relation \( \frac{\tau_{SO}^{-1}}{\tau^{-1}} \) is proportional to \( Z^4 \) \([MT78]\) which is why spin-orbit scattering is often realized by doping with Au \([Ber84, Ova01]\).

The resulting quantum correction to the Drude conductivity and especially the temperature behavior is highly dependent on the dimensionality of the sample. The resulting correction in 3D is given by \([BTN06, MK85, Gan05]\)

\[
\frac{\delta \sigma_{3D}}{\sigma} = - \frac{C}{k_F^2 \lambda^2} \left( 1 - \frac{\lambda}{L_\phi} \right)
\]

with \( C \) a constant of the order 1 and \( L_\phi = \sqrt{D\tau_\phi} \) the dephasing or phase-breaking length. If instead the film thickness \( d_F \) is much smaller than \( L_\phi \) the 2D correction holds,

\[
\frac{\delta \sigma_{2D}}{\sigma} = - \frac{C}{k_F^2 \lambda d_F} \ln \left( \frac{\tau_\phi}{\tau} \right).
\]

A nice summary about the different relevant length scales can be seen in the article of Breznay et al. \([BVP^{+12}]\).

The temperature has its impact on these corrections via \( \tau_\phi \propto T^{-p} \) (for parabolic bands). \( p \) is a constant ranging from 1 to 4 depending on the dimensionality, amount of disorder, dephasing mechanism, phonon type, etc. \([Gan05, LMT87, BTN06]\). It is often assumed to be unity \([MG04, FKK^{+10}]\) which is often the result from fits \([MRG^{+02}, Ova01]\) as well. Therefore, the change in conductivity as a function of temperature, which is usually used as an indicator for quantum interference effects in 2D is

\[
\delta \sigma_{2D-QI} \propto b_{SO} \ln \left( \frac{T}{T_0} \right)
\]

with \( T_0 \) equals a characteristic temperature and \( b_{SO} = p \) for negligible spin-orbit scattering (WL) \( (\tau_{SO} >> \tau_\phi) \) or \( b_{SO} = - \frac{p}{2} \) in the opposite case (WAL) \([MC85]\). In 3D from equation 2.52, the
characteristic behavior is \[ \delta \sigma_{3D-QI} \propto b_{SO} T^{p/2}. \] (2.55)

It has been used successfully, for example, by Lin for amorphous In\(_2\)O\(_3\) with \( p = 1 \), neglecting \( b_{SO} \) [LHSC12]. Gao, on the other hand, calculated from his data on SnO\(_2\)-Sb a value of \( p = 3 \) [GLL+13]. Regarding the question if WAL is present in TCOs or not, Ovadyahu pointed out that spin-orbit scattering in In\(_2\)O\(_3\) without Au doping is rather weak [Ova01]. Also others found only signs of WL and not of WAL in, for example, In\(_2\)O\(_3\)-Sn [LCLW10, FKK+10] or SnO\(_2\) [DKBG11].

Electron-Electron Interaction

Besides the quantum interference effects described above, the electron-electron Coulomb interaction (EEI) has also often to be taken into account, when investigating the low temperature behavior. Due to the diffusive transport the interaction between the carriers gets much stronger. This is because the time increases in which they are close together and the Coulomb force

\[ F_{Coulomb} = \frac{1}{4 \pi \epsilon_0 \sigma_{st}} \frac{e^2}{r^2}, \] (2.56)

between the two electrons at a distance \( r \) is big. This changes the dephasing and also the density of states near the Fermi edge and is called the Aronov-Altshuler effect. It leads to similar corrections to the Boltzmann conductivity as WL with respect to the temperature dependency. In 2 D, the model predicts a correction which is proportional to [AAL80, SYS+10]

\[ \delta \sigma_{2D-EEI} \propto \left( 1 - \frac{3}{4} \tilde{F}_{\sigma} \right) \ln \left( \frac{T}{T_0} \right), \] (2.57)

with \( \tilde{F}_{\sigma} \) being a screening function. In the case of strong spin-orbit scattering \( \left( 1 - \frac{3}{4} \tilde{F}_{\sigma} \right) \) is substituted by unity. The result is then the same relationship like for WL with \( p = 1 \). In 3 D, the relation is [Gan05]

\[ \delta \sigma_{3D-EEI} \propto \sqrt{\frac{T}{T_0}}. \] (2.58)

The two principle effect types (localization and interaction) are assumed to be independent of each other and can therefore be added up. However, the temperature dependency is quite similar for both cases. In order to disentangle them, the change of resistivity by an applied magnetic field can be investigated (sec. 2.2.12).

Kondo Effect

Another many-body interaction effect was discovered 1964 by Kondo. It is a second order perturbation effect with which he could explain the origin of the resistivity minimum in diluted magnetic alloys [Kon64, AM07]. A nice modern review including the high importance in present research was written in 2001 by Kouwenhoven [KG01].
For this effect a coupling or exchange process between free or also called itinerant electrons and on the other hand localized spins is necessary. The electrons are getting scattered at the local magnetic moments which lead to a resistivity upturn in metals. The isotropic and not thickness dependent effect follows \[ \delta \rho_{\text{Kondo}} \propto J \ln \left( \frac{T}{T_{\text{min}}} \right) \tag{2.59} \]

with \( J \) being the exchange interaction which is negative for antiparallel spins \[ \text{Kon64} \]. This is normally the case and therefore the resistivity increases when reducing the temperature. \( T_{\text{min}} \) is a characteristic temperature near the resistivity minimum of such a metal alloy.

Several authors have found a Kondo effect in rare-earth-doped oxides, like Gd doped ZnO \[ \text{LDL}^{+13} \], or in diluted magnetic oxides, like Cr doped In\(_2\)O\(_3\) \[ \text{LHSC12} \]. Such elements have usually magnetic properties, i.e., when the total spin of all the electrons in the impurity atom is non-zero. Also a localized electron within a defect (e.g., a oxygen vacancy) or a 3\(d\)-impurity band can be responsible for this effect \[ \text{KG01}, \text{CVF05} \].

It is worth mentioning that this formula would lead to an unphysical prediction of an infinite resistance at very low temperatures \( T \to 0 \). Measurements instead have shown that a saturation occurs below the so called Kondo temperature \[ \text{KG01} \], which is typically around 1 K and below. This is due to a screening of the magnetic impurities by the free electrons. It could be explained by scaling theory invented by Anderson \[ \text{And70} \] and was proven by Wilson \[ \text{Wil75} \]. Their corresponding binding energy represents the Kondo temperature \( T_{\text{K}} \). Sometimes also \( T_{\text{min}} \) is called the Kondo temperature, which is quite imprecise, as around \( T_{\text{min}} \) the Kondo effect starts to dominate the resistivity behavior whereas at \( T_{\text{K}} \) it is screened and the resistance saturates \[ \text{GGGK}^{+98}, \text{Ham67} \].

### 2.2.12 Magneto Resistance

The investigation of the change of resistivity with magnetic field (MR) is a very powerful tool for differentiating between the before mentioned low temperature effects. The impact of the magnetic field onto the free electron transport is quite different from the one of strongly localized electrons. The discussion here is therefore limited to the former one. For the later one Dauzhenka \textit{et al.}, for example, is mentioning some MR characteristics in the hopping regime \[ \text{DKBG11} \].

First looking at high temperatures, only the classical magneto resistance should be present. This would lead to a small, positive, and parabolic behavior of \( \Delta R/R(B = 0 \text{T}) \) with magnetic field \( B \), as the strength of the low field MR scales with the cyclotron frequency and the relaxation time according to \( (\omega_c \tau)^2 = \left( \frac{eB}{m^*} \right)^2 \) \[ \text{BVP}^{+12} \]. Additionally, the MR data for different samples and temperatures would follow a universal curve, when plotted against the normalized magnetic field \( B/R(B = 0 \text{T}) \), called the Kohler rule \[ \text{Zim60} \]. Thus, the impact of the magnetic field onto the resistivity has to be checked at higher temperatures first. Corrections for the low-temperature data are necessary if the classical MR has to be taken into account.
Quantum Interference

In case of WL and WAL, the influence of the magnetic field is introduced via a phase shift proportional to the amount of magnetic flux flowing through the area enclosed by the traveling electron (see figure 2.7). This breaks down the time symmetry for the two paths as this shift is positive or negative depending on the direction. In the comparable case of Aharonov-Bohm effect all loops have the same size because of the chosen thin cylinder. This leads to oscillations of the resistivity with increasing magnetic field. In the case of WL and WAL in a thin film, there is no coordinated change between constructive and destructive interference as the sizes of the enclosed areas all differ from each other. Additionally, only the projection of each loop onto the plane, which is perpendicular to the field, is relevant for such a shift [Gan05]. This fact makes it even more unlikely that two loops will gain the same phase shift, thus, no oscillations occur. Instead, due to this additional dephasing mechanism, a negative MR which is symmetric around zero field is observed. The field $B$ introduces a magnetic dephasing time $\tau_B = \frac{\pi \hbar}{eBD}$ which replaces the before used $\tau_\phi$ in the moment when it gets shorter.

The complete theory, describing the magnetic field effects on the two dimensional quantum corrections, taking into account several scattering mechanisms, like elastic, spin-orbit, spin-flip, and inelastic scattering was derived by Hikami, Larkin, and Nagaoka [HLN80]. A description of this so called HLN-theory including some simplifications for special cases can be read elsewhere [Vol08, BVP+12]. For the scope of this thesis it is enough to mention the characteristic low field behavior with respect to quantum interference for the 2D and 3D case respectively [LHSC12, HLN80, Gan05]

$$\frac{\Delta \rho_{2D}}{\rho_0} \propto b_{SO} B^2, \quad \frac{\Delta \rho_{3D}}{\rho_0} \propto b_{SO} B^{1/2}$$

with $\rho_0$ being the resistivity at $B = 0$ T and $b_{SO}$ depends like before whether the spin-orbit scattering is weak ($b_{SO} = p$) or strong ($b_{SO} = -p/2$) with $p$ often assumed to be unity [HLN80]. In the case of 2D, the formula holds of course only for a field direction perpendicular to the film surface. If instead parallel to a true 2D film no change of the resistivity should be detectable.

A typical maximal magnetic field for which the formula from above could be applied is below 0.5 T to 1 T [LHSC12, SHE+14, DKBG11]. At higher fields the WL contribution is more and more suppressed as $\tau_B$ is approaching $\tau$ and the relative change saturates. The WAL effect is already annihilated at still lower fields than the WL. This is due to the fact that $\tau_B$ is smaller than $\tau_{SO}$ at even much lower field strengths.

It is worth noticing that there is no correction upon the hall effect originating from these quantum interferences so the calculated value of the charge carrier concentration should not get influenced [AKLL80].

Electron-Electron Interaction

The magnetic field effect upon the electron-electron interaction (EEI) is only due to spin-splitting effects and, therefore, quite small in comparison to the before mentioned WL [LR85]. This gives the
possibility to differentiate between EEI and QI, as moderately high magnetic fields can suppress QI efficiently.

On the other hand, the Hall effect is altered in the case of EEI but not in the case of WL. In EEI, the small but existing change due to a magnetic field also affects the Hall measurement according to Altshuler et al. [AKLL80]

\[
\left( \frac{\delta R_{HH}}{R_{HH}} \right)_{EEI} = 2 \left( \frac{\delta R}{R} \right)_{EEI}.
\]

Indeed, the effect is even twice as big as for the correction of the resistivity itself. Therefore, not only the mobility but also the measured carrier concentration will be altered if EEI is present.

**Kondo or s – d exchange Effect**

The impact of the magnetic field on the Kondo effect is supposed to be also destructive as the spin flip scattering is suppressed due to spin alignment. This negative MR takes into account a third order s – d exchange Hamiltonian as it can be seen in [Hew97, LDL+13, LHSC12]. A semi-empirical expression was proposed by Khosla et al. [KF70] and was used by several authors [LHSC12, ZL10]. It reads

\[
\frac{\Delta \rho_{\text{Kondo}}}{\rho_0} = -a^2 \ln(1 + b^2 B^2)
\]

\[
a^2 = A_1 J D_F \left[ S(S + 1) + \langle M^2 \rangle \right]
\]

\[
b^2 = \left[ 1 + 4 S^2 \pi^2 \left( \frac{2 J D_F}{g} \right)^4 \right] \left( \frac{\mu_B}{\alpha k_B T} \right)^2,
\]

with \(A_1\) a measure for the spin scattering, \(S\) the spin of the localized magnetic moment, \(J\) the exchange integral, \(g\) the effective Landé factor of the localized magnetic moment, \(D_F\) the density of states at the Fermi level, \(\langle M \rangle\) the average magnetization, \(\mu_B\) the Bohr magneton, and \(\alpha\) a numerical factor ranging from 0.1 to 10. The temperature behavior of the parameter \(b \propto 1/T\) is thereby supposed to be the hallmark for this MR mechanism [LHSC12, RFK+05, KF70].

**Positive MR in Degenerated Semiconductor**

If a material exhibits weak antilocalization, this will lead to positive MR which is very sharp around zero field, as mentioned earlier. Another mechanism gives rise to a positive MR also visible at somewhat higher field strengths. Assuming a two-band model, e.g., a conduction and an impurity band, the solution of the Boltzmann equation yields to a MR equation of the form [SW47, RFK+05, ZL10]

\[
\frac{\Delta \rho_{\text{twoBand}}}{\rho_0} = \frac{c^2 B^2}{1 + d^2 B^2}.
\]

Thereby are \(c\) and \(d\) functions of the conductivity and the concentrations of the two groups of carriers. In this case the MR will saturate for very high field strengths, be parabolic for lower ones, and be independent of the field orientation.
2.3 AC Electrical Properties

So far, we have considered the electrical properties of a material only for the DC-case. Or in other words, the frequency independent conductivity of a sample was investigated, as we applied only static currents. Nevertheless, for several concepts and formulas like the Coulomb force (equation 2.56), the ionized impurity scattering (section 2.2.10), or the plasma frequency (section 2.4.2), the dielectric function $\epsilon(\omega)$ is quite important. By measuring a capacitor, this function of the dielectric material between the metal electrodes can be evaluated by using $[\text{Vog97}]$

$$C(\omega) = \epsilon_0 \epsilon_{\text{st}}(\omega) \frac{A}{d}. \quad (2.64)$$

To determine the capacity precisely, impedance spectroscopy (section 3.3) can be used which utilizes the frequency dependent response of the device. In the limit of zero frequency, the dielectric function is represented by $\epsilon_{\text{st}}$.

By the help of the Clausius-Mossotti equation

$$\frac{\epsilon_{\text{st}} - 1}{\epsilon_{\text{st}} + 2} = \frac{N}{3\epsilon_0} \alpha, \quad (2.65)$$

with $N$ the density of dipoles with their corresponding polarizability $\alpha = q\vec{E}(t)$ (charge times their separation distance) the macroscopic dielectric constant can be linked to the microscopic polarization of charges. The variety of possible mechanisms are described in section 2.3.1.

The current response in an impedance spectroscopy experiment is due to a displacement of charge carriers or in other words, due to the polarization effects in the material. This is in contrast to the DC case where the response is governed by a long range movement. The induced polarization $P$ of the material can be described as

$$P = \epsilon_0 \chi_e E \quad (2.66)$$

where $\epsilon_0$ is the electric permittivity of free space and $\chi_e$ is the electrical susceptibility of the material which is a measure of how easy it gets polarized in an electrical field $E$. This leads to dipoles, with a moment $\mu = \alpha E$ where $\alpha$ represents the material constant polarization. Permanent dipoles have to be neglected therefore which is normally true for inorganic solids. The susceptibility of a medium is related to electrical permittivity $\epsilon_{\text{st}}$ by

$$\chi_e = \epsilon_{\text{st}} - 1. \quad (2.67)$$

The dielectric displacement $D$ can then be written as the sum of the electrical field in vacuum and the polarization of the material

$$D = \epsilon_0 E + P = \epsilon_0 \epsilon_{\text{st}} E. \quad (2.68)$$

In principle, the polarization is frequency dependent as there are several possible mechanisms with different time constants out of which the complete response of the material is consisting of. To consider also the direct current response, the dielectric function is complex and can be written as
the summation of the different polarization and charge transport contributions

\[ \epsilon(\omega) = \epsilon_0 \left( 1 + \sum_j \chi_j' - i \sum_j \chi_j'' \right) = \epsilon'(\omega) - i \epsilon''(\omega). \] (2.69)

Combining equation 2.68 and 2.69 it can be concluded that from the real and imaginary part of the measured complex displacement current one can deduce the components of the complex permittivity. The DC-conductivity is also part of the current response and therefore it is prudent to define an effective permittivity [Jon83]

\[ \bar{\epsilon}(\omega) = \epsilon'(\omega) - i \left[ \epsilon''(\omega) + \frac{\sigma}{\omega} \right]. \] (2.70)

The dielectric loss of a sample (the imaginary part of \( \bar{\epsilon} \)) is hence strongly effected by the conductivity. As one can see from the Kramers-Kronig relation for the real part which is given here as an evaluation for the case of zero frequency [Jon83]

\[ \chi'(0) = \frac{2}{\pi} \int_0^\infty \frac{\chi''(x)}{x} dx = \frac{2}{\pi} \int_{-\infty}^{\infty} \chi''(x) d(ln x), \] (2.71)

an increased imaginary part due to a too high DC-conductivity increases the calculated dielectric constant as well. According to equation 2.70, this effect diverges approaching zero frequency. This behavior is therefore a characteristic fingerprint when investigating the frequency dependency of the dielectric constant and it will be needed in chapter 5.1. Thus, only if the resistivity is high enough, the frequency dependency of an ideal capacitor is observed and the dielectric constant of the material itself can be reliably calculated. Well conducting TCO samples of TiO\(_2\)-x can, therefore, not be measured in this way. Nevertheless, in a first approximation it can be assumed that the \( \epsilon_{st} \), determined by impedance measurements, is a reasonable good value for the dielectric response of the intrinsic TiO\(_2\)-x crystal as well. In the following sections different types of polarizations are described and the results of several such impedance measurements are presented in chapter 5. From these results one can conclude which contribution of \( \epsilon_{st} \) is intrinsic for the TiO\(_2\) matrix and which is a extrinsic result of details of the film structure.

### 2.3.1 Polarization Mechanisms

Two different kinds of dipoles give rise to the dielectric properties of a material are, persistent dipoles and several kinds of induced ones. To this second group belongs the atomic or electronic polarization, the ionic one, the electronic-pinning, and the Maxwell-Wagner mechanism which will be discussed in the following.

The result of a dielectric medium inserted into a capacitor is shown in figure 2.8. The electrical field of the induced polarization counteracts the external one. The additional possibility of persistent dipoles can be neglected here as TiO\(_2\) exhibits no ferroelectricity. This is because the structure of TiO\(_2\) shows no asymmetry of the charges (see section 1.2), in contrast to some titanates like...
BaTiO$_3$, which is a quite common ferroelectric material [Hp50, SLC10, Mer56]. This lack of persistent dipoles rules already one mechanism out, the orientation polarization. There, the dipoles can align themselves according to the applied electrical field. This mechanism is, for example, in particular relevant for the molecules in liquid water and is the reason behind its quite high dielectric constant of roughly 80 [Lid04].

Figure 2.9 displays two polarization mechanisms relevant for TiO$_2$. The electronic polarization on the one hand is present in every material as it represents the shift of the electron cloud with respect to the nucleus and its equilibrium position [Jon83]. The second process sketched in figure 2.9(b) is very important for ionic compounds as TiO$_2$ or NaCl. According to Pauling [Pau60], the fraction of ionicity $f_{\text{ionic}}$ in a bonding of a diatomic composite can be calculated via

$$f_1 = 1 - e^{-\frac{(\Delta \chi)^2}{4}}$$

(2.72)

with $\Delta \chi$ being the difference in the electronegativities of the two elements. With the values of the Pauling scale this results in a $f_1$ of 59% for TiO$_2$ which is higher as the quite polar water molecules (32%) already and a bit lower than the prototype ionic material NaCl (71%). TiO$_2$ exhibits a higher ionicity than all standard TCOs, as can be seen in table 1.2. The ionic polarization is caused by the displacement of the positively charged metal cations against the negatively charged anions on their respective sublattices when a electrical field is applied. The different possible movements and orientations of this generated dipoles can be linked to thermal vibrations or phonons.\(^3\)

The three before mentioned mechanisms account for the complete $\varepsilon_{\text{el}}$ of a material, normally. However, there are several additional phenomena relevant for either doped materials or non ideal respectively inhomogeneous samples. Two of them which are relevant to TiO$_2$ are mentioned in literature in the field of supercapacitors or colossal dielectric permittivity [RMR11, WC88].

This very interesting new field of application tries to bridge the very fast response and high power density of normal capacitors and the slower ones of batteries or accumulators. In the former one

\(^3\)Due to this fact fourier transform infrared spectroscopy (FT-IR) measurements, with which these phonon modes can be excited and surveyed, are able to identify the ionic contribution to $\varepsilon_{\text{el}}$. 
the energy is stored purely electrically whereas in the later one the chemical energy storage results in a high energy density. Such a technology could for example decrease drastically the time needed to recharge an electrical car and increase thus their acceptance and practicability. To reach this goal, the capacity of standard capacitors has to be increased drastically. Equation 2.64 offers two possible routes to reach this goal. Either by geometrical means that is increasing the effective area and reducing the thickness maximum down to a Helmholtz double-layer, respectively [AKII08]. Or by using a dielectric material with a permittivity of several thousands or even ten-thousands [GCW+14, HLW+13]. The two mechanisms which are often used to interpret this tremendous values are electron-pinning and Maxwell-Wagner polarization.

Figure 2.10 illustrates these two effects. Important is that for electron-pinning several dopants with different valence states have to substitute the matrix ion-type for example the Ti-cation in TiO$_2$. As this also leads to oxygen vacancies and localized electrons, a multiplicity of different networks can form with huge electrical dipole moments because of the great length or separation distance. As only short range order is necessary to develop these dipoles, amorphous material can exhibit this effect and therefore a permittivity of several ten-thousands is possible. For example in Nb and In co-doped TiO$_2$ films this could be achieved and electron-pinning was supposed to be the possible source [GCW+14]. As these networks can easily reorganize themselves, this mechanism is in a way similar to the orientation polarization of molecules. For this mechanism different valence states are necessary but it should already work in a completely amorphous or homogeneous film. In contrast the Maxwell-Wagner effect is based on an inhomogeneous material consisting out of regions with relative high and very low conductivities. This can be realized for example by conductive grains which are separated by insulating grain boundaries [PP09, WC88]. In principle every other interface can act in a similar way and therefore the polarization caused by the Maxwell-Wagner effect is an extrinsic one and sensitive to details of the sample preparation. This is why the interface
between electrode and material is of big concern when measuring the dielectric impedance and a reason for varying experimental results.

2.3.1.1 Relevant Frequency Regimes

All the mechanisms noted above differ especially in their respective frequency range at which they resonate or relax. The first mentioned electronic or atomic polarization resonates at very high frequencies far above the optical spectrum. They are the main factor determining the optical refractive index of a material and the dielectric permittivity in this area is hence called $\varepsilon_\infty$. At frequencies even higher than this resonance, the dielectric permittivity reaches the value of vacuum, unity. The ionic polarization is in the THz (i.e., the far infrared) region as this is linked to the phonon-frequencies. Both of them show a resonating behavior for which the real part can be described by

$$\varepsilon_{res}(\omega) = \Delta\varepsilon \omega^2 \left(\frac{\omega_0^2}{\omega_0^2 - \omega^2}\right)^{\frac{1}{2}} + \eta^2 \omega^2.$$  (2.73)

Thereby denotes $\Delta\varepsilon$ the difference between the dielectric constants before and after their particular transition.

As the last mentioned effect, surface polarization, depends on rearranging charges, which is most often done by hopping mechanisms along relative far distances. This is a quite slow process and can already be seen below 1 MHz. Strictly speaking, a characteristic fingerprint of the Maxwell-Wagner polarization is the occurrence of two semi-circles in the imaginary against real permittivity plot [RMR⁺¹¹]. In other words, two relaxations with different time-constants can be observed because
of the two different regions in the sample. The real part behavior of an ideal, noninteracting dipole can be described in terms of the Debye relaxation [Jon83]

$$\varepsilon_{\text{relax}}(\omega) = \frac{\Delta \varepsilon}{1 + i\omega\tau_2}$$  \hspace{1cm} (2.74)

where $\tau$ is the characteristic relaxation time and $\Delta \varepsilon$ is again the shift of the dielectric constant between frequencies far above the relaxation and at much lower ones. Below the last relaxation process this equals $\varepsilon_{\text{st}}$. Figure 2.11 displays a sketch of a possible complete frequency dependency of the dielectric function. Here, the atomic and electronic resonance is accompanied with two relaxation processes in their typical frequency range.

![Figure 2.11: The delineated possible polarization processes exhibit characteristic frequency regions in which they typically relax or resonate. As orientation polarization is in solid crystals normally not possible due to the lack of dipoles which can rotate, surface polarizations are the only relaxation events measurable at the MHz-regime and below. The ionic and electronic polarizations are resonating at the THz regime and above the optical frequencies respectively.](image)

In summary, in the case of TiO$_2$ atomic/electronic and ionic polarization especially will be highly important. In the case of additional doping and/or inhomogeneous films also electron-pinning or Maxwell-Wagner polarization can be present.

## 2.4 Electro Magnetic Waves

Increasing the frequencies employed further, one reaches a region where the electrical field cannot be considered solely but together with the induced magnetic field as an electro magnetic wave (EM). The description of the interaction of such waves with a material are done with the help of
the Maxwell-Equations

\[
\nabla \mathbf{D} = \rho \quad \text{and} \quad \nabla \times \mathbf{H} - \frac{\delta \mathbf{D}}{\delta t} = \mathbf{j} \quad (2.75)
\]

\[
\nabla \mathbf{B} = 0 \quad \text{and} \quad \nabla \times \mathbf{E} - \frac{\delta \mathbf{B}}{\delta t} = 0 \quad (2.76)
\]

with \( \rho \) and \( \mathbf{j} \) being the charge and current density respectively, \( \mathbf{D} \) the electrical, \( \mathbf{B} \) the magnetic flux density, \( \mathbf{E} \) the electrical, and \( \mathbf{H} \) the magnetic field strength. The link between \( \mathbf{D}, \mathbf{E} \), and the polarization \( \mathbf{P} \) has already been given in 2.66 which is analogous to

\[
\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}). \quad (2.77)
\]

The response of a material is in general strongly frequency dependent. Thus, in the following sections several different regimes with their respective phenomena will be presented.

First the long wavelengths in the µm range of a FT-IR setup will be discussed (following ISO 20473: FIR: 1000 µm to 50 µm, MIR: 50 µm to 3 µm and NIR: 3 µm to 0.78 µm). In the regime of MIR and FIR, the absorption can be linked to the excitation of phonons and is a very powerful tool investigating such materials. In this work the main focus lies in their contribution to \( \epsilon_{\text{st}} \) due to the ionic polarization as described in section 2.3.1. As we are dealing with a TCO, the important optical regime (NIR/VIS/UV) will follow thereafter. In this regime the frequencies are quite above the ionic polarization and therefore one crucial material constant is \( \epsilon_{\infty} \) as it is directly linked with the refractive index by \( n = \sqrt{\epsilon_{\infty}} \) for materials with a negligible magnetic susceptibility. In the end of this section, the frequency will be increased even further so that the wavelength reaches the same order as the lattice constant. By doing so, the periodicity of the atomic arrangement, i.e. the crystal structure and its quality, can be investigated.

### 2.4.1 Low Frequencies: MIR/FIR

Light in the infrared regime is often imprecisely referred to as heat radiation, as at normal temperatures the intensity maximum of the black body radiation described by Plank’s law lies there. The temperature of a material, on the other hand, can be expressed in terms of vibrations of the lattice. As it has been shown in section 2.2.9, such vibrations can be treated as quasi particles called phonons and give rise to scattering of moving charge carriers. Additionally, such vibrations can be visualized as displacements from their respective equilibrium positions. Therefore, analyzing this vibrations in ionic materials like TCOs is a route towards determining the contribution of the ionic polarization upon \( \epsilon_{\text{st}} \) via the Clausius-Mossotti equation 2.65. As all oxides have a large ionic contribution, measuring the properties in this frequency regime can give large insight into TCO materials.

How to measure a spectrogram in the infrared will be explained shortly in section 3.4.1 including an example how it can look like. In principle, every vibration mode has one specific energy, at least, for a perfect crystal and so radiation with the corresponding energy will be absorbed. Every such
absorption peak can be treated as a harmonic oscillator following the line of thoughts of [KH07].

\[ m\ddot{x} + m\gamma\dot{x} + m\omega_0^2 x = q\tilde{E}_\text{local}e^{-i\omega t} \]  

(2.78)

with \(\omega_0\) the undamped angular frequency of the periodically moving mass \(m\) whose damping is expressed by \(\gamma\). The excitation is described by the right hand side via the frequency \(\omega\), the charge \(q\), and the local field strength \(\tilde{E}_\text{local}\). With the typical solution ansatz

\[ \tilde{x}(t) = \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \frac{q}{m} \tilde{E}_\text{local} e^{-i\omega t} \]  

(2.79)

the frequency dependent polarization \(\alpha(\omega) = q\tilde{x}(t)\) of the whole material can then be calculated as a sum of all different modes \(i\)

\[ \alpha(\omega) = \sum_i f_i \frac{q^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \tilde{E}_\text{local} e^{-i\omega t}. \]  

(2.80)

Thereby the variable \(f_i\) is the strength of the \(i\)th oscillator. Combining equation 2.65 and 2.80 the complex dielectric function is then

\[ \epsilon(\omega) = 1 + \sum_i f_i \frac{Nq^2}{m\epsilon_0} \frac{1}{\omega_{1i}^2 - \omega^2 - i\gamma\omega} \]  

(2.81)

with \(\omega_{1i}^2 = \omega_0^2 - \frac{Nq^2}{3\epsilon_0 m}\) the shifted resonance frequency. The influence of this oscillators on \(\epsilon_{st}\) can be seen by the real part of equation 2.81 for \(\omega = 0\)

\[ \epsilon(0) = \epsilon_\infty + \sum_i f_i \frac{Nq^2}{m\epsilon_0 \omega_{1i}^2}. \]  

(2.82)

We can conclude the very important fact that the impact of a phonon mode upon \(\epsilon_{st}\) gets stronger the lower the corresponding resonance frequency (i.e., wave number) is.

### 2.4.2 Medium Frequencies: NIR/VIS/UV

The properties of a film in the optical frequency range are naturally of fundamental importance in any discussion about a TCO material. In this optical regime, the material is usually characterized by the complex refractive index \(\tilde{n} = n + ik\) where the real part is the ratio of the speed of light in vacuum to the one in the material \(n = c/v\). The imaginary part represents the absorption of the EM-wave by the material like the electrical conductivity does it for the dielectric loss. For nonmagnetic materials it holds that \(\tilde{n} = \sqrt{\epsilon}\) and therefore the behavior can be expressed also directly in terms of the dielectric function.

With regard to the practical application of a TCO, the ratios of transmission \(T\), reflection \(R\), and absorption \(A\) to the incident light are used to characterize a material or a complete device. Using
the law of energy conservation, the desired quantity transmission can be expressed as

$$T = 1 - R - A. \quad (2.83)$$

A weighted average is calculated to concentrate a whole spectrum in one characteristic value for the transmissivity. The weighting function accounts for the fact that the human eye is not equally sensitive for all different wavelengths of light in the optical regime. Figure 2.12 displays this so called v-lambda curve or luminosity function [Int]. Additionally, the corresponding color

**Figure 2.12:** The luminosity function or also called v-lambda curve represents the wavelength dependent sensitivity of the human eye [Int]. With this function the measured transmission spectrum is weighted before calculating the average transmissivity.

**Figure 2.13:** a) displays an optical spectrum of a typical ZnO with T, R, and A. The important optical regime is between 400 nm and 700 nm. b) a schematic electronic structure of a TCO. The different features are explained in the following subsections. Taken from [HPG11].
impressions of the visible wavelengths are given. It is important to note that in order to be transparent for the human eye only the regime 400 nm to 700 nm is important.

Figure 2.13 shows a representative optical spectrum for, in this case, ZnO in which the typical features can be seen. They will be explained in the following subsections.

**Reflectivity**

In the field of optical reflectivity in TCOs, a very important phenomena is the already mentioned concept of the plasma frequency $\omega_P$ (see equation 2.42). It is derived starting from equation 2.78 but neglecting a restoring force due to the assumption of a free electron gas. Additionally the mass is exchanged by the effective mass to account for the crystal potential and instead of the damping concept the relaxation time $\tau$ is used. So with the contribution of the tightly bound electrons the dielectric function describing a material with quasi free electrons is $\epsilon(\omega)$ (2.84)

$$
\epsilon(\omega) = \epsilon_\infty \left(1 - \frac{ne^2}{\epsilon_0 \epsilon_\infty m^* \omega^2 + \frac{i \omega \tau}{\omega^2}}\right) \approx \epsilon_\infty \left(1 - \frac{\omega_P^2}{\omega^2}\right), \tag{2.84}
$$

with $\epsilon_0$ being the permittivity of the vacuum, $n$ the charge carrier density, and the other variables have their usual meaning. Furthermore, in the second representation the relaxation time has been neglected. For $m^* = 0.4 m_e$, $\epsilon_\infty = 4$ and $n = 5 \times 10^{20} \text{ cm}^{-3}$ a plasma wavelength

$$
\lambda_P = \frac{2\pi c}{\omega_P} = \frac{2\pi c}{e} \sqrt{\frac{m^* \epsilon_0 \epsilon_\infty}{n}}, \tag{2.85}
$$

of $\sim 2 \mu\text{m}$ is obtained. If the material is not to thin it will be totally reflective with respect to light with a wavelength larger than $\lambda_P$, or frequency lower than $\omega_P$ respectively. For metals, with their high charge carrier density, $\omega_P$ is above the visible light regime, and typically lies in the UV which explains their shiny optical appearance. In figure 2.13, this transition is marked with $\lambda_P$ as for wavelengths greater than this the reflectivity increases drastically. When dealing with TCOs, this frequency should not exceed the NIR regime to keep the film optically transparent and thus is limiting the maximum useful charge carrier density. This concept explains why the transmittance is reduced for highly doped TCOs in the infrared [HPG11, Cas11, CYL00, GB00].

Secondly, if the surfaces are smooth enough (in comparison to the wavelength) the diffusive reflection can be neglected, as will be shown in section 6.3.2. The remaining direct reflectivity is a function of the refractive index (or referring to the sections before $\epsilon_\infty$) and the Fresnel equations [Vog97, Gob78]. For the simplest case of a perpendicular incident from air to the dielectric material and negligible absorption this leads to [Bas09]

$$
R = \left(\frac{n - n_{\text{air}}}{n + n_{\text{air}}}\right)^2. \tag{2.86}
$$

A high index of refraction leads in this way to a higher amount of reflection in the optical regime. For typical float glass $n$ is around 1.5 (at 500 nm) which gives already a reflectivity of 4%. As

---

\footnote{Naturally, this is only true for materials with a band gap larger than $\hbar \omega$ of the utilized light.}
Figure 2.14: Example how to determine the interference free transmission $T_\alpha$ and reflection $R_\alpha$ from the measured spectra $T_{\text{measure}}$ and $R_{\text{measure}}$ based upon the envelopes $T_{\text{max/min}}$ and $R_{\text{max/min}}$ following the Swanepoel method [R S83].

usually TCOs exhibit higher refractive indices, the amount of reflectivity is also greater as one can see in figure 2.13 in the optical regime around 500 nm.

The usage of anti-reflex coatings is, therefore, quite important for every optical device like spectacles, lenses, or solar cells. There are several different approaches to achieve this, like index-matching, single or multi-layer interference and several more which is an interesting field of study but beyond the scope of this work.

For smooth thin films on a substrate, interference effects will additionally be present as well, due to multi reflections at the different interfaces. This can be seen as interference fringes in the optical wavelength regime in figure 2.13. As this is an extrinsic feature and strongly thickness dependent, it makes it difficult to compare the transmissivity of different samples. Especially due to the sensitivity function displayed in figure 2.12, the thickness dependent shift of the oscillations would lead to a considerable error when calculating the average transmissivity.

Swanepoel developed 1983 [R S83] a nice condensed formalism to explain these fringes and also to extract from them, besides others, an interference free transmission $T_\alpha$ and reflection $R_\alpha$. In practice, the method can be utilized by enveloping the measured spectrum so that maxima $T_{\text{max}}$, $R_{\text{max}}$ and minima $T_{\text{min}}$, $R_{\text{min}}$ curves are produced for transmission and reflection respectively. With the geometrical mean

$$T_\alpha = \sqrt{T_{\text{max}} T_{\text{min}}}$$

the interference free transmission and analogous reflection can be calculated. Figure 2.14 shows a representative example of a high transparent TiO$_2$ film together with the envelopes and the resulting interference free spectrum.
Absorption

In the field of absorption a variety of mechanisms can be present. The most important one, present in every transparent material, is the fundamental absorption of light with an energy larger than the band gap energy. This is, of course, a basic restriction as therefore the material has to have a band gap of at least 3 eV to be applicable as a transparent layer. This fundamental absorption edge can be seen in the 300 nm range of figure 2.14 and 2.13(a) as well. To measure the band gap optically the so called Tauc-method is usually employed [DM70, BLV+10]. Therefore, the relation

$$\alpha h\nu = C (h\nu - E_g)^x$$

of the absorption, often denoted as \(\alpha\) and calculated by equation 2.83, is used with \(h\nu\) being the energy of the incident photons and different exponents \(x\), depending on the type of band gap (1/2 direct allowed, 3/2 direct forbidden, 2 indirect allowed and 3 indirect forbidden [TGV66]). Then \((\alpha h\nu)^{1/x}\) vs. \(h\nu\) is plotted followed by a linear extrapolation to the abscissa. An illustration of this procedure can be seen in figure 2.15. In section 6.2.2 this method will successfully be applied to TiO\(_2\)−x thin films.

The height of the band gap is mainly dependent on the chemical composition and structure. For example, the anatase modification of TiO\(_2\) features 3.2 eV and the rutile one 3.03 eV [TPS+94, SDB+13, DPOK+14]. In addition, the number of free carriers can alter the band gap. Most prominent is the Burstein-Moss (BM) shift whose principle can be seen in figure 2.13(b). It was first encountered by Burstein and Moss independently for InSb in the year 1954 [Bur54, Mos54]. The simplest picture to explain this shift uses as a starting point that the conduction band is partly filled by free charge carriers. As consequence, the optical band gap, i.e. the energy a photon has to overcome to excite an electron to an unoccupied site, is increased [Gru10]. For a spherical
Chapter 2 Fundamentals

Fermi surface this shift can be calculated by employing [UMHK98]

\[ \Delta E_{g}^{\text{BM}} = \frac{\hbar^2}{2m^*_v c} (3\pi^2 n_e)^{2/3} \]  

(2.89)

with the reduced effective mass \( m^*_v \) calculated by

\[ \frac{1}{m^*_v} = \frac{1}{m^*_v} + \frac{1}{m^*_c} \]  

(2.90)

with the valence- and conduction-band effective mass respectively. This concept is heavily used in the field of interpreting the doping behavior of TCOs or to tailor the band gap and is widely excepted [HGB+84, SBJ+88, MOI99, UMHK98]. Lu et al. presented a nice overview of the different models and effects which are responsible for the alteration of the band gap with increasing charge carrier density including also band non-parabolicity [LFK+07]. He also gave different formulas to quantitatively understand the many-body effect of band gap narrowing and applied it to the case of ZnO. This narrowing comes into play when the charge carrier density exceeds the amount necessary for the semiconductor to metal transition (see also section 2.2.6). At this point, the conduction and donor band merge with each other. This results in an abrupt reduction of the band gap and counteracts the effect of the filled states in the conduction band by the free charge carriers [LFK+07].

Besides the absorption at the band gap energy, there are several reasons for the existence of states within the band gap. These states result in the partial absorption of light with energies smaller than the band gap. Structural defects or impurities can for example create such states. Moreover, surfaces, interfaces, depletion layers, or adsorbent molecules can also lead to states within the band gap, even if the bulk of the film is absolutely perfect. Luminescent techniques can be applied to detect their energy levels and concentrations [SBZY12, BLV+10, JLLS15].

2.4.3 High Frequencies: X-ray

As was explained in chapter 2.2.1, the periodicity i.e. the crystallinity of a material is of vital importance for the mobility of the electrons and thus for a good conductive TCO. The structural order of a relative large and thus representative sample area can be investigated by X-ray diffraction. Therefore, much higher photon energies in the keV range are used, as their wavelengths become comparable to the interatomic distances. The CuK\(_\alpha\) line of a copper tube, which is employed usually, has a characteristic wavelength of 1.542 Å. For comparison, the minimal distance between a Ti and a O atom in TiO\(_2\) is \(\sim 1.95 \text{Å} \) [AC93]. Much more details can be read in the book written by Birkholz et al. [BFG06].
Figure 2.16: a) Schematic representation of the Bragg diffraction at a crystal plane with the spacing $d_{hkl}$. A parallel beam of X-rays get scattered to some extent at the three dimensional lattice of the crystal. The path difference scales with $\sin(\theta)$ as sketched in green. If the crystal plane is parallel to the macroscopic surface plane, a corresponding reflex will occur at an angle $\Theta$ which fulfills the Bragg Condition. In b), the grating incident geometry (GIXRD) is illustrated which is utilized for polycrystalline films and employs a fixed and very small incident angle $\omega \sim 1^\circ$. By chance, every crystal plane family can fulfill in some of the randomly oriented crystallites the Bragg Condition when performing a $\Theta$ scan.

Necessary for any characteristic signal is the constructive interference of the waves which every excited atom radiates. For amorphous films, the missing long range order prevents such constructive interferences. In contrast, crystalline samples can exhibit strong reflexes at specific measuring angles. The two Nobel prize winners William Lawrence Bragg and his father William Henry Bragg developed the Bragg Condition, with which the occurring reflexes can be explained. Figure 2.16(a) displays the basic principle for which of course the angle $\Theta$ has to be larger than the total reflection angle. The angle at which a measurable signal due to constructive interference can occur has to satisfy two constraints. First, the emergent angle has to be the same as the incident angle $\Theta$. Second, the path differences between beams which get diffracted at different crystal plans with spacing $d_{hkl}$, have to be an integer multiple $m$ of the wavelength $\lambda$ of the radiation used. Thereby, $h$, $k$, and $l$ are the Miller indices of the corresponding plane.

This boundary conditions and some simple geometrical considerations lead to Bragg’s law

$$2d_{hkl} \sin(\theta) = m\lambda.$$  

(2.91)

Films whose crystallites exhibit a preferred orientation with respect to the surface normal, this so-called texture results in coherent reflexes according to Bragg’s law. This is due to the fact that the two $\Theta$ angles correspond directly to the angle between radiation source and detector to the substrate. This scan geometry is called $\Theta - 2\Theta$ scan or sometimes also Bragg-Brentano scan. However, if there is none such preferred orientation or, in other words, no link between surface and crystal orientations but a more or less random distribution of the crystals, then such a scan would lack of intensity and eventually no reflexes could be observed although the film is crystalline.

In order to overcome this challenge when investigating such untextured films, a different scan configuration can be utilized. The so called grazing incidence scan (GIXRD), which is illustrated in figure 2.16(b), uses a fixed incident angle with respect to the surface. This angle $\omega$ has to be low to guarantee a high interaction volume but above the total reflection angle and is usually around $\sim 1^\circ$. 

RWTH Aachen University
A very big interaction volume is obtained as it scales roughly with the increased illuminated surface area which in turn is proportional to the beam width and \(1/\sin(\omega)\). This results in an increase of the interaction volume of about a factor of 50 to 90 (for \(\omega\) equals 1° to 0.6° respectively). If the crystallites are truly randomly oriented in the film, some of them will by chance have the correct orientation to fulfill the Bragg condition for a specific crystal plane family. Therefore, the diffraction pattern should ideally look like the one for a powder sample. Any deviation of the relative intensities from such a powder diffraction pattern is attributed to an uneven distribution of crystal orientations in the film. As consequence, in the extreme case of a single crystalline film, in this GIXRD configuration it is most improbable to see any reflex at all, in contrast to the outcome of a \(\Theta - 2\Theta\) scan.

The lattice constants and thus also the distortion with respect to the ideal lattice can be calculated using the measured angles of the reflexes. The full width half maximum (FWHM) of the reflexes can be used as a measure of the crystalline quality of a film. As a first approximation one can say that the sharper the reflex, the larger the coherence length in the film and the smaller the variations of the lattice constants are.

In the field of X-ray analysis, a variety of different scan methods can be used to investigate details of the crystal structure. To do so, the concept of the reciprocal space is very powerful. Therefore, the wavelength and direction of the incident and diffracted beam are transformed into the reciprocal wave vectors \(\vec{k}_i\) and \(\vec{k}_d\) respectively. With the length of them being \(|\vec{k}| = \frac{2\pi}{d_{hkl}}\). The crystal planes with a distance \(d_{hkl}\) are points in this representation characterized by the reciprocal vector \(\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3\) with \(\vec{b}_i\) defining the unit cell. This unit cell is the smallest volume that contains all essential information about the structure and the symmetries so that a continuous repetition of this cell in every direction represents the material. The Bragg-Condition is in the reciprocal space transformation called Laue-Condition and reads

\[
|\vec{S}| = |\vec{G}_{hkl}|, \quad \vec{S} = \vec{k}_d - \vec{k}_i
\]

with \(\vec{S}\) being the scattering vector. More details about the reciprocal space and how, for example, one can transform the different kinds of lattice types into this space can be read in the book of Ohring [Ohr01].
Chapter 3

Experimental Methods

In the following section, the systems used during this thesis will be presented including typical parameters applied. The main focus of this work is to improve the understanding of TiO$_2$ as a TCO material the production of reproducible, homogeneous and high quality thin films is of tremendous importance. A lot of the contradictory results can be found in literature in the area of TiO$_2$. Many of these results can be explained by a too careless preparation and investigation of this quite sensitive material. Detailed experiments, rigorous testing and crosschecking revealed in the course of this work many practical insights in the pitfalls and challenges investigating this material.

As till now only general considerations and descriptions regarding the theory of the preparation and measurement techniques were given, the following chapter will deal with the practical details of the various methods, which were applied. Starting with the preparation of the films, including cleaning, sputter parameters, structures, seed and protective layers and the heating procedure. Following on from that, details of the electrical measurements are given, including contacting, setups, parameters and necessary things to keep in mind. The last section is designated to the setups and parameters for the investigation of the interaction of thin films with electro-magnetic waves.

3.1 Sample Preparation

First the correct substrate type for the different analysis has to be chosen. For samples, which are planned for electrical measurements, the substrates have to be several orders of magnitude higher resistive than the corresponding film, as the thickness of the film is below one thousandth of the one of the substrate. The optical transmission is of course a key parameter for a TCO material. Furthermore, the optical appearance of a sample is a very good and quick way to determine the amount of sub-stoichiometry of the oxide layer qualitatively. Therefore, the most often used substrate class are microscope cover glasses, whose electrically resistances are above the measurement limits of the setups used. The substrate from the type Thermo Scientific are made out of borosilicate glass from the company MENZEL-GLÄSER with the size #5, which represents a thickness of about 0.5 mm and with edge lengths of 20 mm × 20 mm. They are above 90 % transparent with a refractive index of $n = 1.52$ in the range from 550 nm to 590 nm.
As such glasses are intrinsically contaminated with different kinds of other elements. The most prominent ones are Na, K or B oxides with each about 7% but they also include 4% TiO₂, which could of course react with sub-stoichiometric film. Some experiments have been carried out on silicon wafers, with a SiO₂ layer on top, as they offer higher temperature stability and lower waviness. All wafers had a diameter of 150 mm and were single side polished. The standard relative conductive (1 Ωcm to 20 Ωcm) p-typ boron doped Si substrates were grown in a Czochralski process and cut in the <100> orientation in 675 µm thick wafers. The manufacturer Siegert Wafer had let grown in a wet oxidation process a 1 µm thick completely insulating pure SiO₂ layer. Additionally, some depositions were executed on high resistive undoped Si wafers. Their much higher resistance of >10 kΩcm were realized by a float zone growth and were only 300 µm thick, also with a <100> orientation.

The glass substrates were cleaned by placing them for 15 min upright in 40 °C warm isopropanol and into a ultrasonic bath and after that the same time in deionized water, with no drying in between. Then they were blown dry by nitrogen and checked against light if all visible particles were removed. To measure afterwards the thickness of the films a thin line was drawn with a permanent marker leaving the inner 1 cm² large area untouched for the subsequent analysis. Thus for all films a correct thickness could be measured and did not had to be assumed by former calculated deposition rates. The silicon substrates, instead, were cut into pieces of 20 mm × 20 mm and than only blown off by nitrogen to remove some small splinters, as the wafers were produced and cleaned before in a professional clean room. All substrates are one last time shortly blown off just before placing them face down into the sample holder which reduces the particle density drastically.

### 3.1.1 Sputtering Procedure

Examples of other techniques applied for producing TCO thin films and TiO₂ ones in particular are given in section 2.1.1 and 1.1. The technique used throughout this thesis was sputtering, as it is one of the few techniques, which can produce high quality dense thin films on glass and is also suitable for industrial applications without to high costs. The working principle and theory can be read in chapter 2.1. Here, the practical procedure and setup will be introduced.

In figure 3.1, a sketch of the chamber used is shown. The first version was build by Johannes Stollenwerk in the framework of his thesis in 1992 [Sto92]. This system was extended during the next years several times. One of the biggest advantages of this chamber is that one can change the desired material in-situ and therefore, one is able to produce multi-layered thin films, without contaminations. Because of this feature it is nowadays called MYTHIC, which is the abbreviation of Multi-LaYer THin FIlm Coater.

It includes six independent cathodes with a cylindrical 3 inch (75 mm and 6 mm thick) target of at least a 99.99% purity, each. By the help of a switching board, the operator can connect easily and safely one of several different generators to any desired cathode.
Figure 3.1: Sketch of the sputtering setup used in the course of this work. The vacuum chamber is evacuated by a membrane and a turbo molecular pump to a base pressure of $1.6 \times 10^{-6}$ mbar to $3 \times 10^{-8}$ mbar. Then Ar as sputtering gas and O$_2$ or N$_2$ as reactive gases are let in by computer actuated mass flow controllers. One of several possible generators capable of high voltages up to $\sim 1$ kV and currents of $\sim 1$ A is then connected to one of the six implemented water cooled magnetron cathodes. The magnetic fields lead to a higher electrons density above the target with a maximum at half the radius. 24 samples can be placed upside down above the target in the automatically rotatable substrate holder. The in situ change of the sputtering cathode enables multi layers without venting.

In this thesis a direct current (DC) generator type DC PINNACLE manufactured by Advanced Energy with two outputs of 10 kW each and, from the same company, a pulsed DC generator called DC PINNACLE plus were used. Figure 3.2 shows an image of the MYTHIC chamber. The cover includes an automatically rotatable sample holder and can be lifted by a crane. Several view ports are available for surveillance of the sputtering process and of the positioning. This is important to position each of the 24 possible samples exactly above the target. The substrate holders were used only for TiO$_2$ deposits in order to prevent re-sputtering of some undesired material, which is important at the beginning of the deposition, i.e., for thin films especially.

The diaphragm backing pump MD 4 NT build by VACUUBRAND together with the turbomolecular pump (TP) from Pfeiffer Vacuum, a TMU 521 P, which has at 833 Hz a pumping speed of $520 \text{ls}^{-1}$ N$_2$ can achieve a base pressure below $2 \times 10^{-6}$ mbar. To check the pressure starting at room pressure down to lowest possible ones a Pfeiffer Vacuum full range gauge is connected to the chamber. After reaching such low pressures, usually overnight, the pumping speed was reduced to 420 Hz and by computer controlled mass flow controllers (MFC) from MKS Instruments an argon 4.8 (purity 99.998 vol%) process gas and as reactive gases 5.5 O$_2$ and 5.0 N$_2$ respectively could be very precisely inserted into the chamber. The pressure during the process can realistically be chosen in a range of 0.2 Pa to 2 Pa to ignite a discharge. Typically, 1 Pa was dialed in and was monitored by a MKS Instruments baratron for a more accurate controlling. The important
oxygen content has to be directly measured which was done by a lambda probe manufactured by ZIROX. The principle is to convert the oxygen partial pressure difference between inside and outside of the chamber into an electrical signal via a heated ZrO$_2$ membrane, which is an oxygen ion conductor at this elevated temperatures.

After the gas pressure has been stabilized the generator was activated and it applied a power of 50 W to 500 W at the target, typically 300 W. A Ti target including the race track of previous runs can be seen in figure 3.3. It should be noted that all doping concentrations given in this thesis are related to the metallic alloy, i.e. ratio of atom numbers of the dopant to matrix cation, not counting the oxygen atoms in the evolving film.

In figure 3.3 a picture of a discharge above the target is shown as well. The area with a higher electron density can clearly be observed, as it induces a larger ionization probability and thus sputter rate. As a consequence a race track evolves after some time.

After at least 10 min of pre-sputtering in the pure metallic mode, a high amount of oxygen was introduced for at least 1 h. The oxygen changes the discharge color from cyan blue (middle picture of figure 3.3) to pink. This two stages of pre-sputtering cleaned the target, coated all surfaces with the desired oxide and heated up the chamber to a steady state temperature.

This is then followed by a reduction of the oxygen flow to zero and the oxygen hysteresis (see figure 2.2) is recorded by waiting at each gas flow for a value of the partial pressure which is stable.
for at least half a minute. For a known target this can be done automatically as the changes of the interesting gas flow values are rather minute. When approaching the edge leading back to the metallic regime, the last stable point is searched with a gas flow step width of 0.05 sccm.

The definition of the correct oxygen partial pressure ($O_{2pp}$) is of vital importance for the reproducibility and comparability of the preparation of conductive and transparent TiO$_{2-x}$ thin films and will be explained in detail in the next subsection. After the $O_{2pp}$ values of the desired working pressures (WP) are known now, the flow is again increased far into the oxidic mode and then reduced to the last stable value.

To be able to sputter in the unstable regime, an active process control (APC) is now activated which utilizes a feedback loop. On time scales of ten milliseconds the current $O_{2pp}$ is measured and the output power of the generator slightly adjusted. If the actual value is higher then the set one, the power is reduced and vice versa. In a stable process, the power variation should be smaller than 5% of the nominal set value. By this method the oxygen content can be controlled much more precisely and faster than by changing the valve position of the MFC. Usually, samples with different WPs are produced during one sputter run. It is important to note that throughout this thesis the sequence of the deposited layers are not linked to their respective WP. The reason is the following: If one would start for example the first sample with the lowest WP and would then for every subsequent sample continuously increase the oxygen content, it would not be possible to disentangle afterwards the effect of the oxygen from other time related effects, e.g., chamber temperature, residual impurity concentration, target aging, and drifting etc. Therefore, the sequence of the chosen WPs had always been randomized.
Table 3.1: Typical sputter parameters applied for the amorphous TiO$_2$-$x$ layer. Some experiments were also performed with lower DC discharge powers down to 100 W which had no significant influence besides lower deposition rates. Within the given O$_{2\text{PP}}$ window lies usually the optimal working point with respect to optical and electrical performance for a TCO. No intentional heating was done and the target to substrate distance $d_{T-S}$ was kept constant throughout all experiments.

**Finding The Working Point**

One of the greatest challenges with respect to the sputtering of TiO$_2$-$x$ as TCO is the correct choice and control of the working point (WP). Later on it will be shown how strongly all properties of these thin films depend on the WP within the falling edge of the hysteresis.

The oxygen window for TCO-like films is very small for this oxide, in the range of 2 mPa, with an even much smaller optimal regime. To be able to investigate the O$_{2\text{PP}}$ dependencies closely and profoundly, a reproducible sample preparation is absolute necessary together with a high number of samples in the relevant regime. To achieve this, a very close determination of the transition regime between oxidic and metallic mode has to be performed, which will be explained in the following.

Starting from the last stable oxygen flow, the influx is reduced slightly further which results in a slow drifting of the O$_{2\text{PP}}$. To illustrate how the O$_{2\text{PP}}$ and the target voltage change with time at such a constant oxygen flow an example is shown in figure 3.4. The drifting continues over minutes,

![Figure 3.4: Change of the target voltage and O$_{2\text{PP}}$ over time at a constant oxygen flow for a Ti:Nb 5 at% target. The flow is only barely below (0.01 sccm to 0.05 sccm) the last stable one. It is visible that the O$_{2\text{PP}}$ is slowly drifting downwards over several minutes whereas in this time the target voltage is still constant and at a high value. At a threshold value the O$_{2\text{PP}}$ collapses in seconds together with the target voltage. Both reach a new stable point in the metallic regime after several more minutes. The insert displays a zoom at the threshold value of O$_{2\text{PP}}$. In cyan the value is marked, at which the target voltage has dropped one volt. The corresponding O$_{2\text{PP}}$ value defines the 100% point, as here the target surface just starts to show metallic parts again.](image-url)
whereas the voltage stays constant, as it can be seen clearly in the insert of figure 3.4. Reaching a threshold value of $O_{2PP}$, both parameters collapse in a time frame of seconds and reach after several minutes a new stable condition, now a pure metallic one. In the insert the point, at which the voltage had dropped about one volt, is marked and the corresponding $O_{2PP}$ is defined as the 100 % value. The 0 % value is the stable one at the metallic side naturally. In the example shown in figure 3.4 this points are at 33 mPa and $\sim 11$ mPa respectively. Typically, the $O_{2PP}$ difference between these two points were about 18 ± 4 mPa.

**Sputtering Si$_3$N$_4$**

For the majority of the samples, whose data is presented in this work, a capping layer has been utilized. Silicon was sputtered together with nitrogen as reactive gas to form Si$_3$N$_4$. The material was already successfully used in the institute for the improvement of the temperature and heating stability of ZnO:Al [Rie10]. Furthermore, in the industry sputtered Si$_3$N$_4$ is known [SO83] for example as a good insulator in transistors [PEH81] or as diffusion barrier e.g. against Na diffusion. It is amorphous and highly stable against oxidation even up to 1000 °C [Sin76, Tom01]. Another application is as anti-reflection coating, because in SiN$_x$ the refractive index can be tuned between 1.6 and 2.7 by altering the deposition parameters [DMH+12, IMF+15]. For stoichiometric Si$_3$N$_4$ a band gap above 4 eV is known, which is significantly larger than the one of TCO materials [IMF+15]. Most commonly, it is prepared by plasma-enhanced chemical vapor deposition and not by reactive sputtering as it has been done here.

<table>
<thead>
<tr>
<th>I (p-DC)</th>
<th>f</th>
<th>Off</th>
<th>P</th>
<th>N$_2$</th>
<th>N$_2$/Ar</th>
<th>rate</th>
<th>d$_{cap}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>210 mA</td>
<td>100 kHz</td>
<td>1 µs</td>
<td>1.2 Pa</td>
<td>10 sccm</td>
<td>1/3</td>
<td>0.5 nm/s</td>
<td>$\sim$34 nm</td>
</tr>
</tbody>
</table>

Table 3.2: Applied sputter parameters for the amorphous Si$_3$N$_4$ layer, which was utilized as capping and sometimes as seed layer as well. It is a reactive pulsed DC-process, as otherwise the insulating Si$_3$N$_4$ on the semiconducting Si could not sustain a stable discharge.

Table 3.2 contains the sputter parameters to produce Si$_3$N$_4$ films which are dense enough to be an efficient protecting layer against oxidation (see section 4.1). On the other hand, the values were chosen to be as gentle as possible to the underlaying TiO$_{2-x}$ film, therefore, a relative high pressure was dialed in. The thickness was adapted to be big enough to be oxygen proof, but also thin enough to enable a contacting of the TiO$_{2-x}$ layer underneath by the wire bonder directly (see section 3.2). After a similar pre-sputtering as in the case of TiO$_2$, nitrogen was introduced into the chamber. To ensure stable conditions, a waiting period of at least 15 min before starting the deposition was allowed.

**3.1.2 Sputtering Characteristics**

In this section some results will be presented, which are connected to the sputter characteristics of Ti, depending on the power, the oxygen and the niobium content. In figure 3.5 the influences
of the applied power 3.5(a) and of different Nb concentrations in the metallic target 3.5(b) upon the hysteresis are shown. Raising the applied power shifts the transition region (TR) to higher oxygen flows as the sputter rate and therefore the oxygen consumption is increased. The behavior (slope of the O$_2$PP vs. oxygen flow) in the pure metallic or pure oxidic mode respectively is not altered which results in a larger jump of the O$_2$PP at the TR, if higher powers are used. The Nb content has a similar effect like an increased power, caused by two effects. As a heavier element it enhances the sputter yield of the complete target which results already in a small widening of the hystereses. This effect can also be seen when a larger sputtering power is applied. Secondly, Nb can react to Nb$_2$O$_5$ raising also the amount of consumed/necessary oxygen.

Sputtering in the same chamber Zn instead of Ti the behavior is dramatically different. In figure 3.6 two similar targets with a similar doping concentrations are compared. Although only approximately half the power was used for the Zn:Al target compared to the Ti:Nb one, the hysteresis is even at higher oxygen flows (see figure 3.6(a)). This is due to the drastically higher sputter yield of the soft ZnO$_x$ compared to TiO$_{2-x}$. The rate difference is caused by the disparity of the surface binding energies following equation 2.3. With respect to the pure metals the rate of Zn is even a factor of eight larger than the one of Ti [Nat27]. A closer look upon the influence of the chosen WP on the sputter rat in the case of TiO$_{2-x}$ can be perceived in figure 3.6(b). The influence of the Nb content was typically not significant in comparison to the one of the O$_2$PP and could not be disentangled clearly.

### 3.1.3 After Deposition Treatments

After the sputtering process was finished the samples were shortly placed in acetone in an ultrasonic bath to remove the permanent markers and by this "lift off" process create a sharp and precise edge for the thickness measurement.
3.2 Electrical Measurements

In this section some details about the electrical measurements will be given. To investigate the produced TCO samples produced their specific resistivity, temperature and magnetic field dependency and via the Hall-effect their charge carrier density and mobility was evaluated. As the electric field and the current density can’t be measured directly, some geometrical informations are needed to deduce them from the current $I$ and voltage $U$. Special care has to be taken that these characteristics are ohmic, i.e. the measured resistances are not influenced by the applied current. Especially in the low temperature regime the heating of the sample, due to the the applied measurement
current, can easily alter the resistivity and lead to wrong temperature vs. resistivity data. This is in particular true for high resistive or insulating samples.

In the following subsections the necessary interconnections and theories for measuring thin films will be presented including details about the Hall-effect measurement and the utilized low temperature setup.

### 3.2.1 Principles of Electrical Measurements

The most straightforward way to measure the longitudinal electrical resistance $R_{xx}$ of a wire, is to apply a known current and measure the resulting voltage drop over it $R_{xx} = U/I$. With the known cross sectional area $A$ and length of the cable, the material specific resistance $\rho_{xx} = R_{xx}A/L$ can be calculated. In the case of thin films a similar approach can be taken, for which a bar with known length $L$, width $W$ and film thickness $d$ has to be structured. Good conducting e.g. metal contact pads at the end of the bar have to be deposited to ensure homogeneous and parallel stream-lines in the film under investigation. This so called two-point or two-wire method is very useful, if the resistivity of the material is quite high. If this is not the case this method overestimates the resistance of the device, as the contacts and interfaces between the electrodes and the thin film are also contributing. Their share can be quite high due to the relative short and practically limited length of the bar.

To account for this, one usually makes use of a four-point method, which is sketched in figure 3.8(a). The current is also sourced at the ends of the bar, but the voltage drop is in this case measured between two inner contact pads. By using a high impedance voltmeter practically no current flows over these inner contact pads and therefore no additional voltage drop influences the signal. Of course this is only true as long as the contact resistances are not to high, otherwise
the potential at the contact pads is not any longer linked to the potential in the bar and the resulting resistances are random. Usually also a polarity reversal is needed in order to avoid errors due to local charging, thermoelectric, and other effects. If in addition two opposing contact pads are present, the potential difference between the two sides of the bar \( U_{xy} \) can be tapped which is needed for the Hall-effect measurement as described in the next section. The production of such structures can be done either by structuring the film after the deposition, or by using masks during the deposition.

The former approach was used only scarcely during this work, as it makes many more processing steps necessary, which can also alter the film properties (e.g. ion bombardment, chemical etching, heat treatments etc.). The later one can for example be done by using shadow masks above the substrate, or by structuring a photoresist primarily to the film deposition and a lift-off process afterwards. In figure 3.8(b) and 3.8(c) models of the inner 1 cm² of the masks used for the bar and the contacts respectively are shown. With the aid of them, two structures can be produced on one sample and the comparison can give insight about the homogeneity and the magnitude of the variation of the film. The area of 1 cm² was chosen as only samples of this maximum size fit into the low-temperature setup (see section 3.2.3).

If such structures are not feasible, for example because structural or optical investigations should be performed, or because an additional insulating seed layer is utilized, a technique called van der Pauw (vdP) method can be employed. It was developed in the year 1958 and is also a four-wire method, which is therefore insensitive to lead or contact resistances [van58]. He could show that for any homogeneous film regardless of its shape (e.g. figure 3.9(a)), without any holes and everywhere equally thick, the sheet resistance \( R_{\parallel} = \rho_{xx}/d \) can be determined by at least two four-wire measurements. Therefore, contact leads had to be attached at four points anywhere at the edge of the film.
Figure 3.9: If structuring is not feasible, another four point method for resistivity measurements can be applied. The so-called van der Pauw method can be used for almost arbitrary shapes (a). Usually a square with contacts at the corners is produced (b). Then a current is sourced along one edge (e.g. DC) and the voltage drop along the opposing one (e.g. AB) is measured. Afterwards this procedure is repeated for the configuration turned by 90°. For a perfect square and an ideal material, these two resistances should of course be the same. Even Hall measurements can be done, by applying the current along the diagonal (e.g. DB) as shown in (c).

Then a current is sourced for example between the contacts D and C and the voltage drop across A and B is measured, resulting in a resistance $R_{DC,AB}$ (figure 3.9(b)). Secondly, the configuration is rotated, so that the current is now sourced e.g. from A to D and $R_{AD,BC}$ is determined. The sheet resistance is then \[ R_{\square} = \frac{\pi}{\ln(2)} \frac{R_{DC,AB} + R_{AD,BC}}{2} F(Q), \] (3.1)

being $Q$ the ratio of the larger to the smaller resistance. $F(Q)$ is a correction function, which in principle accounts for the irregularity of the film shape and is implicitly given by

\[ \cosh \left( \frac{Q - 1}{Q + 1} \ln(2) \right) = \frac{1}{2} \exp \left( \frac{\ln(2)}{F(Q)} \right). \] (3.2)

If a square shaped film is measured (like pictured in figure 3.9(b)) the two resistances should be practically the same and $Q = 1$. For $Q$ being smaller than 2 the correction $F(Q)$ is reduced barely from unity to 0.96. Because of this, $Q$ can also be interpreted as a quality factor of the film, if the shape is quadratic. As long as the film is homogeneous with respect to the thickness and especially with respect to the local specific conductivity, without any anisotropy due to the preparation, $Q$ will be close to one. The higher $Q$ is, the more questionable the resistivity gets, as the film properties are only poorly defined in such cases. It is worth mentioning that the error of this method scales with the ratio of the contact size to their distance from each other. As a consequence, good conducting, point-like contacts should be used and their ohmic characteristic always be checked.
Section 3.2 Electrical Measurements

Figure 3.10: In (a) a part of the used wire bonder, a sample holder called "Puck" for the low temperature setup and the "User Bridge" can be seen, with this testing station and standard multimeters the bonded channels can be checked and the resistances of the sample be measured. The soldering points at the TCO surfaces are very strong. In (b) a SEM picture displays the remains of such a Al-wire bond. One such soldering point is only $\sim 50 \mu m$ in diameter.

Contacting

Typically, evaporated chromium-gold layers (Cr as an adhesion layer) are used as contacts. They had to be replaced in the case of TiO$_2$, due to the high diffusion of gold at the elevated temperatures necessary for the TiO$_2$ crystallization. Additionally, the adhesion of such contacts is reduced dramatically during the annealing due to the dissolving of the Cr layer. Instead a 100 nm Al or Ti layer has been sputtered for TiO$_2$.

As a protective, electrically insulating capping layer was used frequently, the electrodes had to be deposited first. For some surveys also seed layers were used, either to improve the crystal structure, or to ensure a pure, water and oxygen free surface, where also no contaminations can diffuse from the substrate into the TCO film. In such cases neither top, nor bottom electrodes can easily be realized.

In these cases and in order to guarantee good and point-like contacts (for vdP) an unusual routine was applied in this thesis for the majority of the films. The wire bonder HB06 from TPT was utilized (figure 3.10(a)) for connecting the contact pads of the sample with the measuring leads of the instrument or substrate holder. Via ultra sonic vibration a special needle, called wedge, solders a thin wire of Au or Al:Si, with a diameter in the range from 25 $\mu m$ to 33 $\mu m$, between two contact pads. The contact force of the wedge, the ultra sonic strength, and contact duration have to be chosen differently for every material combination. Also the substrate material and the layer thickness alters via the thermal conduction the optimal parameter set.

However, if such parameters are found, very strong and good conducting bonds can be formed reproducible. Even a complete 2 cm $\times$ 2 cm glass substrate can be lifted at such a single wire bond on a TCO layer. A SEM picture of the remains of a teared off wire can be seen in figure 3.10(b). It proves that the contact is even better than the yield strength of the wire itself.
This good contact makes the deposition of a metal contact layer redundant. Even if the surface of a thin film is oxidized or contaminated slightly during the sample preparation, the wedge penetrates such insulating layers and ensures a low resistive contact. This concept works so well that even a protective capping layer can be used on top of the complete TCO film.

The thickness of the Si$_3$N$_4$ layer of 30 nm to 35 nm was chosen deliberately to be thick enough to be tight and thus to be an effective oxygen protection. It is also thick enough, so that a measurement via a gentle usage of handhold test prods doesn’t connect to the conductive film. However, the force of the wedge can be dialed in to penetrate the capping but without scraping off the complete layer stack. To improve the contact even further, the Si$_3$N$_4$ layer is first specifically scratched by using the wedge first without the Al:Si wire.

Then three to five bonds were placed at every corner of a $\sim$ (1 cm x 1 cm) piece. At such a number of connections the two point resistance is barely reduced anymore by adding more bonds, thus suggesting negligible contact resistances. Nevertheless, the attainable complete contact area can be still smaller than the one by classical metal pads deposited via the usage of shadow masks. Therefore, the theoretical accuracy in a vdp measurement is improved and the expenditure for measuring a TCO thin film is drastically reduced.

As the alignment of shadow masks mentioned before is quite cumbersome and fault-prone the application of this wire bonding method provides an additional benefit.

### 3.2.2 Hall-Effect and MR Measurement

The theory behind the Hall-effect technique, with which the charge carrier density $n_H$ can be determined, was described in section 2.2.2, here some more practical issues will be discussed. If a magnetic field is applied additionally to the current sourcing electric field and perpendicular to the surface of the film, the Hall-effect will induce a transverse voltage difference $U_{xy}$, indicated in figure 3.8(a). It is important to note that the Hall-effect does not depend on the lateral geometry and thus employing the configuration shown in figure 3.8(c), also unstructured films can be used for Hall experiments.

The resulting voltage $U_{xy}$ and thus resistance $R_{xy}(B)$ is ideally zero at $B = 0$. However, due to small alignment errors and non perfect parallel current stream lines originating from e.g. inhomogeneities in the film, it holds that $R_{xy} \propto R_{xx}$. This offset voltage has to be subtracted before calculating $\rho_{xy} = R_{xy}(B) d$. In order to be able to conduct successfully a Hall-measurement, it is therefore important that $R_{xy}(B = 0) \ll R_{xx}(B = 0)$. Otherwise, MR effects of $R_{xx}$ will easily overwhelm the Hall-signal in particular at low temperatures.

To get rid of the remaining magneto resistance effects i.e. the influence of $R_{xx}(B)$, the measurement is extended to the reversed magnetic field orientation as well. The effects of a magnetic field upon the resistivity $R_{xx}$ are always symmetric and therefore the antisymmetric part $R_{xy,\text{antisym}}(B) = 1/2 [R_{xy}(B) - R_{xy}(-B)]$ has to be used for the Hall analysis. By the same token, the magneto resistance $R_{xx}$ has to be symmetrized before fitting any models to the data. Data of a ZnO:Al
Figure 3.11: Here data of a metallic \((k_F \lambda \geq 1)\) ZnO:Al sample is shown, measured in the vdP geometry. It exhibits a negative MR due to WL as described in section 2.2.11, 2.2.12 and 4.7.1. The relative MR is not perfectly symmetric as can be seen in (a). This is due to slight influence of the Hall-effect, which is increasing with temperature. On the other hand the transverse resistance \(R_{xy}\) is influenced by the MR as well, at least for low temperatures. If \(R_{xy}\) would not be measured from \(-B\) to \(B\) like in (b) this effect could not be subtracted and a large change of the charge carrier density would be falsely stated.

Especially when investigating high mobile TCO films with large magnetic fields to gain accuracy, the so called Hall-angle can become important. It is calculated by

\[
\tan(\theta_H) = \frac{E_y}{E_x} = B\mu
\]

and describes the angle between the direction of the current flow following \(E_x\) and the direction of the total electric field. The supposedly linear relationship between \(R_{xy}\) and \(B\) is only true and the simple interpretation only valid, as long this angle is small, or in other words, as long as \(B\mu\) and the change of the conductivity is negligible small. So even for metallic \((k_F \lambda \geq 1)\), good conducting materials care must be taken, when performing Hall-measurements.

It is worth mentioning that although the technique was used here with a DC current, the polarity was reversed with a low frequency, to avoid basically the same effects described in the previous section. The restriction upon DC currents results also in a lower practical limit of the mobility, which can reliably measured. If the mobility is lower than \(1 \text{ cm}^2/\text{Vs}\) to \(0.1 \text{ cm}^2/\text{Vs}\) the Hall-signal contains eventually no longer any information about the charge carrier density. Temperature and other drifting effects will mainly determine the measured values of \(R_{xy}(B)\), which is then no straight line anymore.

In such cases or generally if in doubt how stable the conditions or the sample is, at least one complete cycle of \(B\) (e.g. from \(-B\) to \(B\) and back again) should be measured to gain an idea about magnitude of the drifting etc. effects. Additionally, the influence of the charging rate of the magnetic field upon \(R_{xy}(B)\) should, at least in such cases, be investigated. Otherwise, the
resulting, but physically perhaps meaningless values of the charge carrier concentration, mobility and even carrier type are taken seriously.

3.2.3 Low Temperature Setups

In the course of this work two models manufactured by Quantum Design (QD) were used to measure the electrical properties of a max. 11 mm × 13 mm thin film sample, mounted on a Puck (figure 3.10(a)). The two are a Physical Property Measurement System (PPMS) and a newer one called DynaCool. Information can be found also in the different manuals from QD and in the dissertation of Hanno Volker [Qua, Vol08].

Both setups consist of a cryostat, which can control safely via several heaters and thermometers the temperature of the sample in range from 1.9 K to 400 K. The main difference in this respect is, how the cooling is provided. In the case of the PPMS a liquid helium reservoir of about 90 L, shielded by a liquid nitrogen jacket, is connected via several gas inlets and impedances to the evacuated sample space. Due to the low pressure the boiling temperature of the liquid helium is reduced from 4.2 K to <1.9 K. The DynaCool instead is combined with a compressor and a heat exchanger, which produce a very small amount of liquid helium in a closed cycle. As the PPMS, depending on the experiments performed, consumes roughly 45 L to 60 L liquid helium a week, such a cryogenic free system like the DynaCool has much lower running expenses and requires less maintenance work. The temperature regime can be extended by a Helium-3 Option or a Dilution Refrigerator which can be inserted principally in both setups and are able to reduce the temperature of such macroscopic samples down to 340 mK and 50 mK respectively.

They were rarely used in this thesis, as the heat load generated by measuring a large vdP sample gets easily too large. This is intensified by the fact that Al becomes superconducting below 1.19 K and can not conduct any heat anymore, but oxides can not be soldered with gold. Therefore, devices which were structured by photolithography and Cr/Au contact pads are needed for such temperatures. However, even in the basic setup with a minimum temperature of 2 K a sample is easily heated to higher temperatures than the thermometer is sensing when using a too large measuring current. This is indeed a very probable reason for any non-ohmic behavior or drifting observed in resistivity data, although the temperature is already thought to be stable. An example is given in figure [?] in the appendix. There an insulating TiO$_2$−$_x$ film is measured at nominal 2 K with different currents. A direct correlation between current and resistivity above a certain threshold can be seen. A too high current is heating up the film and thus the resistivity drops and on the other hand a too low current results in a bad signal-to-noise ratio. In this respect, it should also be mentioned that the temperature ramp has to be slow enough to allow thermal equilibrium between sample and thermometer.

Both setups are equipped with a 9 T superconducting magnet, surrounding the sample space which can be charged by maximum rates of 200 Oe/s. Such high rates however are not recommended for stable and controlled measuring conditions. Typically 100 Oe/s were chosen for good conducting samples in the high field range above 3 T and 50 Oe/s below. A practical fact worth mentioning is that for samples with a low mobility or high resistances drifting effects can be seen if the magnet is
charged up from or is charged down to zero field. Before performing a magnetic sweep measurement one should wait first for stable conditions in the fully charged state and then continuously change the charged state to the reversed field direction.

The systems provide manifold measuring opportunities. The first and most often used is the so called Resistivity Option. Although the excitation and measurement limits for the two variations build into the two setups differ slightly their principle is the same. A square wave of 0.3 Hz is sourcing a current which is limited by the user chosen current, voltage, or power limit. The amplifier gains etc. are then controlled internally, including frequent calibration measurements with build in resistors. The voltage resolution for both electronics is 4 nV and suitable currents ranging from about 20 nA to 500 µA were sourced usually. These options can measure only one channel (i.e. four leads for one 4-wire configuration) at the same time, but can switch periodically between a maximum of three channels. This has the advantage that all 12 leads can be connected to one sample, which has to be done for measuring "simultaneously" resistance and Hall-effect in the vdP geometry.

Another option is the Electro-Transport Option (ETO) which is able to use two channels independently and parallel unlike the Resistivity Option. The electronics are situated much closer to the cryostat which is why it is less sensitive towards noise caused by electromagnetic perturbations. The two channels can in principle only be connected to the same sample, if they share their source contacts. If instead a vdP measurement is performed, the sourcing of one channel changes in an unpredictable way the sensing of the other one. At both channels a sinusoidal current can be applied within a frequency range of 0.1 Hz to 200 Hz. It is important to note that the excitation frequency is not freely selectable in this range. Instead both channels provide nine different frequencies, whereby each of them differs slightly from the corresponding one of the other channel (e.g. 128.1738 Hz and 143.4326 Hz). As a warning signal for non-ohmicity etc., not only the signal at the applied frequency but also at the second and third harmonic is determined. In contrast to the Resistivity Option also a two-wire mode is available with an excitation voltage of up to 10 V to extend the resistivity limit from 10 MΩ of the four-point one to 5 GΩ. Additionally, it provides the possibility of determining I-V curves and differential resistances. Summarized: the ETO offers a higher signal-to-noise ratio, which is why it should be applied, if very low excitation currents are needed, like in the case of the Helium-3-Option or Dilution Refrigerator.

Intrinsically, the magnetic field is oriented perpendicular to the sample surface. However, in order to investigate the influence of the field orientation a Rotator is available and can be inserted in both systems. In this case one channel is required for measuring an additional thermometer directly below the changed sample holder. This is true also for another insert, which was developed by the author, using a commercially available base structure, the Multi Functional Probe (MFP). Besides the calibrated thermometer it’s centerpiece is an optical fiber especially chosen to be able to transmit UV light with low losses. Thereby photoconductivity measurements at low temperatures are possible. In this thesis a power UV-LED array OTLH-0480-UV from Opto Technology Inc. with a peak wavelength of $\lambda_{\text{peak}} = 365$ nm was used as a light source. At a maximum excitation current of 300 mA it can deliver a light power of 244 mW. Additionally, two special low temperature coaxial cables are also included. They extend the applicable frequency range for
two-wire impedance measurements, as the standard wires are too noisy above 1 MHz.

### 3.3 Impedance Spectroscopy

As described earlier in chapter 2.3, the measurements of the AC electric properties were performed in order to get insight into the dielectric function. To achieve this impedance spectroscopy experiments on capacitors were executed. A device with an ideal dielectric material (no DC-conductivity)

![Equivalent Circuits](image)

**Figure 3.12:** Equivalent circuits to describe the impedance behavior of a device. Thereby represents (a) a serial circuit, where the leakage current through the capacitor can be neglected. If the DC conductivity is not negligible, an additional parallel resistance has to be taken into account, as depicted in (b).

can be regarded as a *serial* connection (figure 3.12(a)) of a ohmic resistance \( R_{\text{serial}} \) (leads, electrodes etc.), a capacitative reactance \( X_C = -1/\omega C \) with the capacity \( C \) and an inductive reactance \( X_L = \omega L \) with \( L \) being the inductance. So the total electrical impedance is

\[
Z_{\text{serial}} = R_{\text{serial}} + X_j = R_{\text{serial}} + \left( \frac{\omega L}{\omega C} - \frac{1}{\omega C} \right) j. \tag{3.4}
\]

Of course the capacitance is usually much bigger, as the inductance is only due to the connecting leads or the electrodes and will get important for very high frequencies only. In the case of some leakage current through the dielectric an additional conductivity \( S_{\text{parallel}} = 1/R_{\text{parallel}} \) parallel to the capacity has to be included (figure 3.12(b)). This leads to (neglecting any inductance)

\[
Z_{\text{parallel}} = R_{\text{serial}} + \frac{S_{\text{parallel}}}{\omega^2 C^2 + S_{\text{parallel}}^2} + \frac{\omega C}{\omega^2 C^2 + S_{\text{parallel}}^2} j. \tag{3.5}
\]

The sinusoidal excitation voltage \( U = U_0 \sin(\omega t) \) applied at a capacitor will result in also a sinusoidal current, but with a phase shift. The imaginary part of the calculated \( Z \) corresponds as a first approximation \( X_C \). Fitting the measured frequency dependency of \( Z \) with the theoretical output of an equivalent network offers therefore the possibility to calculate a very reliable value of the capacity. This is especially true for employing the ETO with its limited and low frequency range.

The next section will deal with details of the sample and device preparation techniques which were employed to produce capacitors with TiO\(_2\) with different doping elements as dielectric material.
Figure 3.13: Sketch of the production sequence of a capacitor array. In a first step, the 100 nm thick bottom electrode is deposited via sputtering through a shadow mask (a). Then it gets exchanged by a material mask (b), which is used exclusively for every material. As a last step the electrode mask is used again, but upside down (c). By doing so, top and bottom electrodes are turned by 90° against each other. Small misalignments between the bottom and top layer are therefore not influencing the active capacitor area, which is 1 mm² and 3.24 mm² respectively.

This is followed by the description of the measuring setups and processes.

### 3.3.1 Special Sample Preparation

A simple sandwich structure was employed to produce the capacitors. The upper and lower electrodes were 100 nm thick sputtered metal films. In figure 3.13 the three shadow masks levels for producing a sandwich structured capacitor array is shown. Like for the Hall-bar mask (figure 3.8) the inner area of 1 cm × 1 cm is shown, although the complete mask is 2 cm × 2 cm big.

With this mask, on every sample four capacitors can be produced, two with an active capacitor area of 1 mm² and two with 3.24 mm². This increases the statistical certainty of the results, as the calculated dielectric constant of all four capacitors should of course be the same. By using two different areas, size effects of the absolute capacitance can be disentangled from material intrinsic ones. The same mask can be used for bottom and top contact by simply put it upside down. The advantage is that by this 90° turning between top and bottom electrode the always present misalignment between the two depositions steps, does not alter the active area.

The PVD technique reactive magnetron sputtering was also utilized for depositing the several hundred nanometer thick dielectrics of the capacitors. However, it is important to note that the chosen working point area was very different in this case, than for sputtering a TCO (chapter 3.1.1). For these dielectric measurements even a relative low DC conductivity is very harmful for investigating the imaginary part of the impedance. Therefore, most samples were produced far in the high resistive, oxidic regime (see figure 2.2). Few samples could be measured close to the last stable point (100%) also.

As for these experiments different doping elements should be tested, a different sputtering chamber
was utilized, called COSMOS (serial co-sputtering for functional multi component thin films). Here, the sputtering is done in a two stage process, although they take place simultaneously. The dopant element X is sputtered from a normal 3in-75 mm metallic (so called "secondary") target onto a big ring shaped (outer radius 300 mm, inner radius 150mm) rotating Ti ("primary") target. A second discharge is then reactively depositing TiO$_2$:X onto the substrates. The secondary cathodes are placed inside their own container, with their own atmosphere, which is ensured by a overpressure with respect to the main chamber, where the reactive sputtering takes place. To ensure gas separation of the auxiliary and the main chamber a higher pressure of 5 Pa is employed in the auxiliary one. A detailed description of the chamber and the sputter process can be found also in the dissertation of Rüdiger Schmidt [Sch14]. For the scope of this thesis, it is only important to note that by changing the ratio of the sputter rates of the primary target to the secondary ones, the dopant concentration can be adjusted. This rate-ratio is either changed by different sputter powers, but also by different oxygen flows for the reactive sputtering from the primary cathode. There, the sputter rate is reduced by adding more and more oxygen, which does not influence the rate of the secondary targets. The resulting doping concentrations (X/Ti in TiO$_2$) vary therefore between $\sim$3 at% to 6.5 at% and the used dopant targets were V, Nb and In$_{0.9}$Sn$_{0.1}$. These values are also based on the dissertation of Rüdiger Schmidt, which is why a lower pressure of 0.4 Pa has been used for these stoichiometric TiO$_2$ films.

The electrical characteristics of the resulting devices were checked and it was observed that only for samples with DC resistances of $\gg$ 10 kΩ the capacitative effect is strong enough to allow a reliable result of the dielectric constant. The devices have been measured in the as deposited state and also after annealing, in order to crystallize the TiO$_2$ and investigate the influence of the structural changes. The annealing procedure was the same as for the TCO samples (see section 3.1.3). For dielectric thicknesses of approximately 50 nm and below the crystallization/annealing led quite often to short circuits or i.e. drastically reduced DC resistivities. Therefore, thick layers of typically 400 nm but at least 230 nm and up to 460 nm have been deposited for impedance measurements.

### 3.3.2 Impedance Meter

As mentioned above, the ETO of the low-temperature setup is able to measure AC resistivities including the phase difference between applied voltage and resulting current. It is quite useful for devices with a not to high resistivity, as it is not able to excite high frequencies and was build to measure in a very precise manner ohmic resistivities $< 10$ MΩ. If the device has nearly no conductivity, the ETO is therefore not able to determine the phase angle and the impedance correctly. So in this case the measured data should be interpreted with a parallel equivalent circuit diagram, as it was shown in figure 3.12(b). Because of the limitations of the ETO in terms of frequency range and maximal resistivity a fitting was performed to extract the capacity out of the data. Some representative simulation data can be seen in figure 3.14, within the expected range of parallel conductivity, capacity geometry and dielectric constant. As $\omega = 2\pi f$ the maximum excitation frequency corresponds to $\omega \sim$ 1000 Hz. So if the capacity is reduced (lower $\epsilon_{st}$ or thicker
Figure 3.14: Impedance spectroscopy simulations for a parallel circuit of a 200 nm thick capacitor with an area of 1 mm² and different dielectric constants and leakage conductivities. In (a) the frequency response of the real part of the impedance is shown. The higher the capacity and the resistivity respectively, the lower the frequency, at which the capacitor reaches the same conductivity as the resistor ($\tau_{\text{Cap}} = 1/RC$). The imaginary part of $Z$ depicted in (b) shows a maximum at the frequency, at which $Z_{\text{real}}$ drops to zero. The height of the maximum is not influenced by the capacity but a measure of the conductivity.

layer) or the conductivity is enlarged (e.g. to small layer thickness), the maximum of $Z_{\text{im}}$ drifts out of the effective range of the ETO. In order to analyze the frequency dependency of the dielectric constant and to improve its accuracy an impedance meter was also used. The HP Agilent 4192A LF Impedance Analyzer from Hewlett Packard is able to provide frequencies in the range from 5 Hz up to 13 MHz and a maximal achievable capacitance resolution of $1 \times 10^{-12}$ F. This resolution is quite sufficient, if compared to the typical values of $1 \times 10^{-9}$ F to $1 \times 10^{-8}$ F that the produced devices could typically achieve. The oscillating amplitude of the source voltage can be in the range from $5 \times 10^{-3}$ V to 1.1 V, on top of which an additional bias between $\pm 35$ V can be applied. For every impedance value at one frequency an arithmetical average during one tenth of a second is calculated. In figure 3.15 the wiring is shown which was utilized in the case of the impedance meter. Especially an additionally shielding is worth mentioning, together with the independence of sourcing and measuring. Another important fact is that the systems allows a calibration for every frequency. Preliminarily a short and a open configuration including the same sample holder and connectors are measured and saved as configuration data. With

Figure 3.15: The 4-terminal configuration employed by the impedance meter. A current is sourced through the sample (DUT) and the vectorial voltage and current are measured. Coaxial cables were used and their shields were connected to the impedance meter as well in order to reduce stray capacitance and inductance (from [Hew]).
this configuration external influences upon the data can be minimized. The measurement was automated via a MATLAB routine and a GBIP-interface, with which not only the measurement frequencies could be programmed, but additionally also the temperature control of the PPMS.

### 3.4 EM Waves

This section will briefly describe the measurements systems used for analyzing the electromagnetic wave spectrum. First, the FT-IR setup, for investigating the long wavelengths of the infrared regime will be presented. Afterwards, the procedure for determining the transmissivity and reflectivity in the optical range will follow and in the end the X-ray diffractometer used to investigate the crystal structure will be explained.

#### 3.4.1 FT-IR

The spectrometer in question was a IFS 66v/S manufactured by Bruker Optik GmbH. Details of the procedure can also be read in [SKW+08, Kre09]. Here only the MIR regime (section 2.4.1) was investigated with an aperture of 12 mm. For this region (400 cm⁻¹ to 8000 cm⁻¹) a Globar light source, a KBr beam splitter and a DTGS detector had been employed. The measuring principle follows a Michelson-interferometer with two mirrors, of which one is movable.

A gold mirror serves as a 100% reference and the sample spectra were investigated in reflection mode within an evacuated space of 2 mbar. For that reason a 100 nm thick layer of aluminum as a mirror was sputtered underneath the TiO₂ layer which was similarly produced like the dielectric for the capacity measurements. The data gained from this measurements were afterwards analyzed with the software tool Code, developed by W. Theiss. It allows the simulation and fitting of the response of model layer stack. As the investigated samples did not exhibit any free carriers no Drude contributions were detected or beneficial for the fit. To describe the phonon modes several Tauc-Lorentz oscillators were utilized together with a constant background as representation of \( \epsilon_\infty \). These oscillators yield thereby the contribution of the phonon modes upon the dielectric function as it was described in section 2.4.1.

#### 3.4.2 Optical Wavelengths

To investigate the very important optical and ultra violet regime a Lambda25 UV/VIS from PerkinElmer Instruments was utilized. There are two different lamps to cover the complete wavelength range from 190 nm to 1100 nm. For the infrared and optical part a halogen lamp is in service. Below 326 nm the lamp is exchanged automatically against a deuterium one. The system embodies a two beam structure. Next to the beam which interacts with the sample, a reference beam is traveling along through the same space and the two are compared by the detector. Every perturbation due to the atmosphere or lamp intensity etc. is thereby canceled out. Two sample holders, one for transmission measurements, another for reflection ones can be inserted. In both
cases a reference called blank, is measured primarily to the actual samples. In the reflectivity case, a substrate coated with a sputtered silver film is employed, whereas a clean glass substrate is used for the transmissivity.

### 3.4.3 X-Ray Diffraction

In this work, a PANALYTICAL X’PERT PRO X-ray system from PHILIPS has been used for the xrd-analysis. It works with a copper tube, whose CuK$_{\alpha}$ radiation possesses a wavelength of 1.5405 Å. Different detectors, slits and scan modes are available, however several test measurements revealed no texture, as the films were amorphous as deposited. Therefore, only X-ray reflectometry (XRR) and grazing incidence (GI) are of relevance here. A detailed description of the setup which is build in Brentano geometry (source and detector are on one circle, the sample in the middle), can be found in the thesis of Hansjörg Weis [Wei03]. In the case of a XRR measurement (an example is shown in figure 3.16(a)), the incident and emergent angle with respect to the sample surface are equal and typically smaller than 2°. The critical angle, below which the X-ray beam is totally reflected, gives insight into the density of the film. Above this angle so called Kiessig-oscillations can be observed, which are due to the constructive and destructive interferences at the different interfaces, similar to the interference fringes in the optical regime (section 2.4.2). The analysis was performed with the software tool GENX, where also quite complex layer stacks can be defined and among other parameters, their thicknesses, densities and roughnesses can be fitted to match the measured data.

In the case of a GI scan, the incident angle is constant and slightly above the critical angle (in this thesis: $\omega = 0.7°$) to maximize the interaction volume. The detector angle $\Theta$ is varied between 20° to 80° as there are practically no reflexes beyond this range, with respect to the analyzed oxides and metals. Most of the samples were measured with such a full range scan, whereby five samples could automatically measured over night with 2.5h each. In figure 3.16(b), the powder
Chapter 3 Experimental Methods

diffraction pattern of TiO$_2$ in the anatase and rutile structure respectively is displayed (by 1999 JCPDS-International Center for Diffraction Data: PCPDFWIN v2.02). The square root scale was chosen to visualize also the reflexes with a quite low intensity. The relative intensities should be the same in a GI scan, if a perfect polycrystal without any preferential orientation is investigated. However, the two main reflexes are close to $2\Theta \sim 26^\circ$ and thus it is usually sufficient to scan from 20° to 30° to determine qualitatively the phase composition (amorphous, anatase and rutile).

3.5 Additional Setups

In total three different annealing setups were used. Mainly the already mentioned (section 3.1.3) tube furnace LINDBERG/BLUE M was in service. For higher temperatures a HERAEUS M 104 muffel furnace was employed, where no inert atmosphere can be applied. A preheating was done, which includes the substrate plate. After the annealing time the samples were removed and put on a silicon wafer To investigate the change of resistivity during the annealing process, a custom-built heatable vDP setup was utilized. In this case a vacuum chamber which can reach 1 mbar and is purged three times with argon. A KEITHLEY source meter 236 SMU and a AGILENT multimeter 34401A together with switching relays and a LabVIEW control software are utilized there. Care was also for these measurements taken that all characteristics were ohmic and the Q-factors were small enough. Due to the high quality source meter, with this setup also the amorphous state of TiO$_2-x$ can be measured accurately and so it enables the detection of the crystallization process and temperature. Several tests have shown that the contacts can easily fail e.g. during the crystallization at the elevated temperatures. Best results were achieved by bonding a 1 cm × 1 cm TiO$_2-x$ sample with several Al wires to an underlying 2 cm × 2 cm glass sample, where the metal contacts were deposited on (evaporated or sputtered). On these contact pads than the gilded contact needles, which include flexible springs, were pressed.

3.5.1 Profilometer

Naturally, the film thickness is an important parameter for investigating the electrical properties. As the change of the deposition rates in the transition regime are quite significant, the thickness of every sample has to be checked. As XRR is quite time consuming and in the case of several hundred nanometer thick samples or complex layer stacks not suitable, an other technique had to be used. For this purpose a stylus profiler DEKTAKXT from BRUKER was purchased. It is able to achieve a reproducibility below 1 nm and even films with thicknesses in the range of 15 nm could successfully be measured. To do so, the height differences along an up to 150 mm long line is measured. A sharp edge between substrate and film allows a high precision of the local film thickness, which procedure was described in chapter 3.1. Although, the layer is not uniform along the complete sample size, it could be shown that within an area of 1 cm$^2$ in the center of the substrate, the fluctuations are barely around 1%. Every film was measured at least three times along the inner 1 cm.
Section 3.5 Additional Setups

**Figure 3.17:** In order to calculated the correct layer thickness out of a 2D height profile, the waviness of the substrate has often to be taken into account. A 3D scan of a clean (a) Si and (b) glass substrate has been taken. It can be seen that the silicon piece is far less bent, than the glass substrate, although the variation is still several hundred nanometers along the complete 2 cm × 2 cm Si sample.

In order to determine correct results for a film thickness, especially if it is a thin one, the waviness of the substrate itself has to be taken into account. Figure 3.17 contains an example for a clean Si and glass substrate respectively. This 3D scans along the complete sample can be performed, by placing three corners on small steel balls. Otherwise the see-sawing motion of the sample during the scan of the stylus tip over the sample can lead to changed results. Although the Si sample is much flatter, the height varies macroscopically still several hundred nanometers.

Such and other influences can be removed from the data, which enables the operator to gain this mentioned nanometer accuracy. A nice example for this is shown in figure A.1. There a 3D scan of a Hallbar device with a mean thickness of roughly 80 nm, but with lateral dimensions of 1 cm can be seen. With these capabilities together with it’s very user friendly control and high sample throughput, it is a good supplement to AFM and XRR.
Chapter 4

DC Electrical Properties of TiO$_{2-x}$

In the following chapter, the main results regarding the conductivity of TiO$_{2-x}$ thin films will be presented. The first section 4.1 deals with the change of the resistivity upon annealing as it is necessary for crystallization. However, it will mainly deal with the influences and pitfalls one has to be aware of in order to get reliable and reproducible results and especially motivate the necessity of the usage of a capping layer. Otherwise, the film homogeneity and the link to the chosen sputter parameters is lost.

The data given there will already indicate the impact of the oxygen partial pressure and the Nb content on the conductivity and on the crystallization behavior. Both parameters determine the characteristics of the TiO$_{2-x}$ films and the influences are highly complex. Therefore, the two subsequent sections 4.2 and 4.3 are dedicated to their influences on the electrical properties. Their impacts on the film structure will be discussed later in chapter 6.3.

After this, the following sections will deal with electrical transport as a function of the measurement temperature. Thereby, a greater insight can be gained including many differences compared to standard TCO materials. This will start with chapter 4.4 by discussing more thoroughly the transition between insulating and metal-like films. As highly conductive TCO films are of the main interest here, the sections thereafter will deal with the effects of such degenerate semiconductors. This encompasses in chapter 4.5 the intermediate temperature regime and thereafter in chapter 4.7 low temperature effects including the change upon magnetic fields. For this low temperature effects the dimensionality of the film is of crucial importance which is why the thickness dependency of the resistivity, mobility and charge carrier density and its intermediate temperature behavior is investigated before in chapter 4.6.

The last section 4.8 contains some conclusive remarks and suggestions of further experiments to continue and underpin the results in the field of electron transport achieved here.
4.1 Annealing Behavior

Later in chapter 6.3 the structural properties of the films will be discussed. At this point, it is only important to mention that with the employed sputter parameters, especially the chosen O$_2$PP within the hysteresis, the TiO$_{2-x}$ films are always amorphous as deposited regardless how thick, how much Nb, or oxygen they have been incorporated. In order to crystallize the sputtered samples an annealing step has always to be performed. During such a heat treatment several foreign influences can alter the film stoichiometry and homogeneity. In order to be able to characterize reliably the intrinsic electrical properties of TiO$_{2-x}$ films, the impact of these external parameters has to be investigated.

It is commonly excepted in the field of TCOs that oxygen vacancies can act as donors and insert up to two additional electrons per vacancy into the conduction band [EPJ$^+$04, Ell00, Hos07]. This enables the possibility to use the charge carrier density as a measure of the sub-stoichiometry of undoped films. Measuring the resistivity during this heating procedure reveals several interesting facts and can be seen in figure 4.1(a) in an exemplary manner. It should be noted that the effects which will now be described at a small selection of examples could be seen repeatedly and are indeed very significant, although on the necessary log scales they sometimes can be overlooked.

First interesting side remark is that TiO$_{2-x}$ is not suitable as an amorphous TCO. This is in contrast to common TCO materials like In$_2$O$_3$ or ZnO which are very conductive in the amorphous phase as well (see figure 4.17). Even the very sub-stoichiometric 50% films, which are not really

---

1The discussion about the crystallinity and the data to prove the statements about the structure of the films given in this chapter will follow later on in chapter 6.3 as its own section.
2Instead, in these cases the challenge is to prepare an amorphous film. This can be achieved reliably only by mixing two or three binary oxides [HKUK96, NOT$^+$04, KE13].
Figure 4.2: The influence of $O_{2}\text{PP}$ in (a) and Nb doping in (b) upon the crystallization temperature. All samples were capped and 100 nm thick. At every annealing step a 30 min holding time was applied. In the parameter range investigated here, the minimal crystallization temperature was for every sample approximately $250 \pm 10 ^\circ C$. This temperature is tremendously lower than in literature of single conductive $\text{TiO}_2^{-x}$ films which utilize $500 ^\circ C$ to $600 ^\circ C$ usually [FHY+05, OSJ+14]. However, it can be observed that reducing the oxygen content or increasing the Nb concentration the crystallization gets impeded slightly. See section 6.3 for details and the data about the structure.

transparent anymore, exhibit resistivity values of $1 \Omega \text{cm}$ which are several orders of magnitude to high to call them an amorphous TCO, not to mention the transparent $\sim 70\%$ films.

It is remarkable, how large the difference between the amorphous and the crystalline state is. At room temperature there lay three to four orders of magnitude between these two states\(^3\). Additionally, the amorphous phase exhibits a clearly negative temperature coefficient of resistivity (TCR), whereas the crystalline phase possesses for not to low oxygen contents a positive one.

The most important fact here is that a capping layer is mandatory in order to prevent degradation during the crystallization process. Samples without a $\text{Si}_3\text{N}_4$ capping layer deteriorate during the annealing compared to the protected ones. The example of a sample prepared at 60% in the hysteresis evince that the diffusion of residual oxygen from the inert Ar atmosphere into the $\text{TiO}_2^{-x}$ lead to severe oxidation and complete deterioration of the lateral conductivity in the 50 nm film.\(^4\) This is clear as for a good conductivity some degree of sub-stoichiometry, i.e., some oxygen vacancies, is needed as otherwise the number of free electrons is not sufficient. Thin and uncapped films with high oxygen contents decline so severely that they could not be precisely measured anymore with the setup in use here. For higher sub-stoichiometric or thicker films the relative amount of filled oxygen vacancies and thus the measured deterioration is less catastrophically but can still be recognized.

Actually, this can be recognized not only electrically but also optically. A larger transparency after the annealing without a capping can be seen even with naked eyes. For instance, in the case of the 100 nm thick film prepared at 50%, which is shown in figure 4.1(a), a brightening can

\(^3\)The black curves in figure 4.1(a) represent samples which did not crystallize fully and the effect will be shown in more detail in chapter 6.3.1.

\(^4\)Employing such relative thin layers around 50 nm to 100 nm, enables a much easier detection of the external influences.
be observed. This easily superimposes other influences one wants to study like seed layers, other annealing procedures, or the O$_{2PP}$ employed during sputtering.

Several experiments have shown that the same holds in the case of additional Nb doping. Typically, an O$_{2PP}$ of maximally 50 % was necessary for samples without a capping to get at least "measurable" conductive samples afterwards. Instead for samples with a capping an O$_{2PP}$ of 90 % to 70 %, depending on the amount of Nb, is sufficient already. Of course, conductive films without a capping are then highly inhomogeneous due to the diffusion profile and the changing oxygen content in the atmosphere. Therefore, a thickness series should be performed and the specific resistivities compared when investigating TCO films. With this series the impact of such external factors like oxygen diffusion and variations during the sputter deposition can be evaluated and minimized respectively. By such experiments it can also be proven that the capping employed is indeed an effective oxygen barrier (see section 4.6).

To investigate the crystallization behavior more closely, experiments have been performed to find the necessary temperature $T_c$. In figure 4.2, the results of such studies are shown exemplary. All samples have been capped and were 100 nm thick but with different compositions. At every temperature step a holding time of 30 min has been utilized. However, the resulting change in resistivity is remarkable different for the various samples and annealing steps. For not too low oxygen contents (see chapter 6.3), the minimal crystallization temperature, i.e., first drop in resistivity, is for every sample approximately 250 ± 10 °C. This temperature is far below the values which are stated in literature to be necessary to produce high conductive and transparent TiO$_2$−x: Nb films. There often vacuum or hydrogen atmospheres with temperatures between 500 °C and 600 °C have to be utilized [FHY+05, HUF+07, OSJ+14].

Half an hour is usually not enough time to finish the process and at the next higher temperature the resistivity reduction is much larger due to an increased crystal growth velocity. Comparing in figure 4.2(a) the temperatures at which the largest drop of the resistivity occurred, a clear trend is visible for samples with different amounts of oxygen. The lower the oxygen deficiency is, the lower also this temperature threshold gets. The influence of Nb is similar to the one of oxygen deficiency. The "impurity" Nb clearly impedes the crystallization kinetics due to its larger ionic radius and the resulting induced strain (figure 4.2(b)). The precise oxygen control and the protective capping layer used in this work are the reasons why higher temperatures and reducing atmospheres are needed in literature typically.

Some authors applied seed layers successfully to reduce this necessary temperature to about 400 °C [HYH+08]. In order to see whether there is a potential of reducing the crystallization temperature here as well, some tests with seed layers were performed too. Figure 4.1(b) shows exemplary the influence of a crystalline, stoichiometric, and insulating TiO$_2$ layer which was deposited and annealed first. Then the conductive TiO$_2$−x film has been sputtered in a second step on a pure glass substrate and on top of the TiO$_2$ seed as well. However, the crystallization kinetics are not significantly altered by such a seed. Albeit, the conductivity seems to improve a bit by the usage of a crystalline TiO$_2$ seed layer. More investigations are necessary to clarify the extend of
Section 4.1 Annealing Behavior

Figure 4.3: Annealing at increased temperatures (in the muffel furnace for 2 h), whereby (a) depicts the absolute resistivities. For a better visibility in (b) the relative changes due to the higher temperatures are shown with the 300 °C value as reference. The same legend is valid for both plots and all films have been capped. The sample with 2.5 at% Nb at a high O_{2PP} degraded by several orders of magnitude after the annealing at 500 °C and no Hall signal was measurable afterwards.

this improvement and also other consequences of a TiO\textsubscript{2} seed like stability at higher annealing temperatures should be tested in the future.

This is necessary, as a close look upon the graphs of the annealing cycles in figure 4.2 and 4.1(b) reveals that temperatures above 300 °C are often slightly harmful to the electrical properties even if a capping layer is provided. Therefore, some first experiments were performed to study the changes upon higher temperatures. A selection of these results can be seen in figure 4.3, where several capped samples were annealed subsequently to higher temperatures (400 °C and 500 °C in air). First thing to note is that the annealing behavior of TiO\textsubscript{2−x} thin films is rather complex. An improvement of the conductivity would be expected due to the healing of defects, as long as the material is not decomposing. However, in the case of crystalline TiO\textsubscript{2−x}, some films improve and some deteriorate. To provide a better overview of the alteration of the resistivities which are given in figure 4.3(a), the relative changes are plotted in figure 4.3(b). These first results indicate that at low O\textsubscript{2PP} (but still crystalline and transparent) an improvement with higher temperatures can be seen. Instead, samples with a bit higher O\textsubscript{2PP} and better conductivities at the beginning are deteriorating.

A possible reason can be concluded from tests where an amorphous Si\textsubscript{3}N\textsubscript{4} layer was used additionally also under the TiO\textsubscript{2−x} film. In these cases an improvement can be observed also in the case of films with a rather high O\textsubscript{2PP}. This effect is particularly intense for high Nb concentrations. The behavior of two films sputtered at the same O\textsubscript{2PP}, one with and one without a seed layer is shown for instance in figure 4.3(a). This suggests that a some small amount of oxygen can diffuse from the substrate into the film at higher temperatures.\textsuperscript{5} If the films are rather low in oxygen, this is not really harmful, but can on the contrary even be beneficial.\textsuperscript{6} In the opposite case, the oxygen results in a reduction of the oxygen vacancies and by this a decrease of the carrier concentration.

\textsuperscript{5}Water contaminations, which could in principle be on the substrate at the beginning of the sputter process, can not explain the deterioration with respect to the 300 °C state when applying higher temperatures afterwards.

\textsuperscript{6}In chapter 7.1 it will be explained that a too low oxygen content leads to lower mobilities.
Figure 4.4: Hall measurements were performed to clarify the effect of higher annealing temperatures. Whereby (a) depicts the relative change in the free carrier concentration $n$ and (b) the one of the mobility $\mu$, compared to the 300 °C case.

For clarification additional Hall-measurements were performed on these samples and the relative changes of $n$ and $\mu$ are shown in figure 4.4. They support the interpretation given above. The charge carrier concentration is reduced if no additional diffusion barrier of Si$_3$N$_4$ is provided. For samples with a low O$_{2PP}$ together with Nb doping, the net effect is not significant or completely clear as they have a very high charge carrier and defect density. The mobility in these samples is improved due to the typical process of lowering the amount of scattering defects. In the case of Nb doping and rather high oxygen contents the mobility is strongly reduced which is not the case for undoped TiO$_{2-x}$.

A possible explanation for this discrepancy would be that part of the Nb reacts with the additional, in a manner of speaking, excess oxygen and forms Nb$_2$O$_5$. The amount of Nb which is bound in this compound is incapable of acting as a dopant whereby the carrier concentration is reduced in the TiO$_{2-x}$ film. Such precipitations disturb also the periodic lattice, scatter the Bloch waves, and thus lower the measured mobility. These effects will be investigated in more detail later on.

As a consequence from all the data discussed so far one can conclude that the amount of oxygen is an absolute crucial parameter which alters the behavior of a TiO$_{2-x}$ thin film in a non trivial manner. Therefore, the next sections are dedicated to the influences of the O$_{2PP}$ and the niobium concentration upon the electrical properties after annealing 2 h at 300 °C.

Most importantly one has to note that the annealing of TiO$_{2-x}$ films even in a relative pure and inert atmosphere of Ar, not to mention in air, will result in an oxidation and degeneration of its conductivity, if no protective capping layer is utilized. For thick and very sub-stoichiometric films annealing without a capping is of course a possible route to create conductive films. However, the properties are in such cases naturally highly inhomogeneous, thickness dependent, non optimal and precise studies of influencing factors are not reliable.

The large heat of formation of TiO$_2$ and Nb$_2$O$_5$ per oxygen atom (see table 1.2) leads to a much stronger tendency to fully oxidize sub-stoichiometric TiO$_{2-x}$ films and deteriorate their electrical conductivity than in the case of typical TCOs.
4.2 Influence of $O_{2PP}$ on Undoped TiO$_{2-x}$

![Figure 4.5](image-url): $O_{2PP}$ dependency of $\rho$, $n$, and $\mu$, measured by 3T Hall measurements at room temperature for a series of undoped TiO$_{2-x}$ films. All films were capped and approximately 250 nm thick. The 45% sample is nearly completely black and opaque and most probable metallic Ti starts to be present below this point.

The resulting electrical properties of an oxygen series can be seen in figure 4.5. First thing to note is that a clear minimum of the resistivity can be observed, in contrast to the behavior of typical TCO films [Ell00]. As first approximation, in these cases the resistivities increase monotonically with increasing the oxygen content in the sputtering gas. The reason is that the increasing amount of oxygen leads to a reduced number of oxygen vacancies and also active dopants. The free carrier concentration is therefore continuously decreased. In fact this trend can also be seen in figure 4.5 in the case of TiO$_{2-x}$. A logarithmic scale for $n$ had to be chosen, in order to be able to visualize the strong increase of the carrier density when the $O_{2PP}$ in the hysteresis is reduced.

Between $\sim$55% to 75% the increase is approximately linear on a log scale and is even drastically intensified below. The reason for this could be the forming of metallic Ti filaments, i.e. the film does not consist solely of TiO$_{2-x}$ anymore, but also of metallic Ti. This argument will be supported by the structural analysis in section 6.3.

The reason for the evolving resistivity minimum, although $n$ is continuously changing with $O_{2PP}$, has to be a second opposing effect. It can be seen in the alteration of the mobility depicted also in figure 4.5. Down to 65% it is more or less constant and with 14 cm$^2$/Vs quite high. This is usually also the case for standard TCOs, whose mobilities are not strongly effected by the oxygen concentration. However, in the case of TiO$_{2-x}$ a clear and rapid deterioration of the mobility can be seen below 60%. In the case of 50% it could still be measured accurately, but it was only 0.06 cm$^2$/Vs, more than two orders of magnitude lower. The reason for this drastic drop of the mobility lays in a deterioration of the crystallographic structure as it will be shown in chapter 6.3.1.

Another interesting fact is that the carrier concentration above 75% starts to stabilize and even films sputtered at a value of 100% still exhibited free electron densities in the same range of
1 × 10^{19} \text{ cm}^{-3}. This leads to the idea that we reach here a kind of an entropic stabilized oxygen vacancy concentration. If this is a reasonable thought, a lower boundary of the amount of sub-stoichiometry can be determined by using the carrier concentration of such undoped TiO$_{2−x}$ films. The molar mass of one TiO$_2$ particle is $M = 79.9$ g/mol and with a nominal density of the anatase structure of 3.9 g/cm$^3$ [ABBG01] a formula unit density of $2.9 \times 10^{22} \text{ cm}^{-3}$ can be calculated. Assuming that every oxygen vacancy generates two free electrons, the measured carrier concentrations of $1 \times 10^{19} \text{ cm}^{-3}$ to $8 \times 10^{19} \text{ cm}^{-3}$ (till to the resistivity minimum) correspond to values of $x$ in TiO$_{2−x}$ of $\sim 1 \times 10^{-4}$ to $8 \times 10^{-4}$. A vacancy concentration of at least 0.1% is therefore present in TiO$_{2−x}$ if not sputtered in the oxidic mode i.e. in the oxygen excess region. In other words the stoichiometry for conductive TiO$_2$ is in the range of TiO$_{1.9999}$ to TiO$_{1.9992}$.

The knowledge of the amount and dependency of carriers, which get generated by oxygen vacancies, will allow us to disentangle the origin of the free electrons (Nb doping or oxygen vacancy) in doped films and, therefore, the doping efficiency.

### 4.3 Niobium Doping

![Figure 4.6](https://example.com/fig4.6.png)

**Figure 4.6:** The O$_{2pp}$ of the sputter gas atmosphere with its impact upon the resistivity (a) and the charge carrier density (b) is shown (for $\mu$ see figure 4.8). Measured at room temperature for ~250 nm thick and capped samples. A remarkable minimum in the resistivity of 620 $\mu$Ωcm at O$_{2pp}$ of about 55 % can be seen. Whereas, $n$ is in principle monotonically decreasing with an increasing O$_{2pp}$. This trend is shifted upwards to larger values with additional Nb doping. For visualization of these two aspects the colored area is introduced as guide to the eye.

Also for Nb doped films the O$_{2pp}$ is one of the most important factors and, therefore, its influence upon the electrical properties has to be thought of as well.\(^7\) As mentioned earlier, all dopant concentrations given in this work are calculated as ratio of the number of dopant atoms to the one of the matrix cation (i.e. Nb/Ti). This definition is better suited to calculate and compare the dopant efficiencies, as an efficiency of 100 % means that every Nb atom injects one additional electron into the conduction band.

\(^7\) As motivated in the section 4.1 the films have to be capped for any reliable result and have been annealed at 300 °C for 2 h if not stated otherwise.
Section 4.3 Niobium Doping

Figure 4.7: The electron mobility as function of the free electron density $n$ for the different doping concentrations is plotted. Here, samples with an $O_{2PP}$ down to the resistivity minimum have been taken into account, including also some higher annealed ones and the few 1 at% Nb films. It can clearly be seen that in this representation the different compositions populate more or less separated regions. The vertical lines mark the highest electron densities which can be achieved most probable with the corresponding Nb concentration. The blue line represents the mobility limit of TiO$_{2-x}$:Nb which is indicated by the data.

In figure 4.6(a) the resulting resistivities are depicted and a minimum can be observed, as it has been seen before in the undoped case. First great result is the remarkable low resistivity of about 620 $\mu\Omega$cm, in particular without any expensive substrate, deposition technique or procedure and with a quite low annealing temperature of only 300 °C. For example Sato et al. reported a value of 1300 $\mu\Omega$cm for DC-sputtered films but with 6.4 at% Nb and annealing at 400 °C in vacuum [SAKS08].

The good resistivities here could be even improved further to 600 $\mu\Omega$cm and 550 $\mu\Omega$cm by post-deposition annealing processes to 400 °C and 500 °C in argon flooded atmosphere respectively.\(^8\) It is worth mentioning at this point that although these samples were not produced altogether in one run, not even in the same year, or with the same sputtering power, they fit together quite nicely, when using the relative point in the hysteresis as an ordering scheme.

In order to understand the behavior of $\rho$ with the oxygen and also the Nb content, the charge carrier concentration is displayed in figure 4.6(b). As expected, $n$ is reduced with higher amounts of oxygen (less oxygen vacancies), whereas it is gradually increased by additional Nb doping. Therefore, the resistivity minimum is achieved with the highest used Nb concentration of 5 at% (Nb/Ti ratio). But surprisingly, the resistivity at the minimum of the 5 at% samples is not simply halved compared to the 2.5 at% ones as one might expect. Moreover, the free electron density does not at all exhibit a maximum but increases continuously with lower values of $O_{2PP}$.

To explain these discrepancies the alteration of the mobility with the free electron density has to be taken into account. Therefore, a $\mu$ versus $n$ graph is drawn in figure 4.7, as it is quite usual in

\(^8\)For the improvement at higher annealing temperatures also Si$_3$N$_4$ seed layers have to be employed.
the field of TCOs, and examples can be seen in [EPJ+04, Ell01, PZL89, RTM+13, PBRS13]. It has to be noted that here samples with an \( O_{2\text{pp}} \) much lower than the resistivity minimum have been neglected. The reason for this will be explained in section 6.3. On the other hand, some higher annealed samples and, especially, the few samples with a Nb concentration of 1 at\% have been included.

This graph illustrates some very interesting facts. The specimens with different doping concentrations populate different regions in this plot. Although they can possess the same carrier concentration and a similar mobility, they rarely have both in common at the same time. So one can already conclude that the mobility of \( \text{TiO}_{2-x} \) is not such a direct function of the carrier concentration as it can be seen for example in ZnO:Al [Ell01, BE14, HPG11] or In\(_2\)O\(_3\):Sn [PBRS13]. This means that, in contrast to common TCOs, in \( \text{TiO}_{2-x} \) additional effects have to be present which significantly influence the mobility, not only the charge carrier concentration.

The inserted vertical lines denote an approximation for the maximum \( n \) which can be achieved at the different doping levels. Varying approaches like Si\(_3\)N\(_4\) seed layers, lower sputtering powers, or higher annealing temperatures have been tested, especially in the case of the two higher Nb contents. However, they seem to reach a fundamental limit which a \( \text{TiO}_{2-x} \):Nb film can maximally obtain and not only regarding the carrier concentration, but as indicated by the blue line, also regarding the mobility.

<table>
<thead>
<tr>
<th>Nb at%</th>
<th>( n_{\text{limit}} ) [cm(^{-3})]</th>
<th>( \mu_{\text{limit}} ) [cm(^2)/Vs]</th>
<th>( \nu_{\text{Nb}} ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 1 \times 10^{20} )</td>
<td>20</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>( 3.2 \times 10^{20} )</td>
<td>15</td>
<td>76</td>
</tr>
<tr>
<td>2.5</td>
<td>( 8 \times 10^{20} )</td>
<td>12</td>
<td>96</td>
</tr>
<tr>
<td>5</td>
<td>( 14 \times 10^{20} )</td>
<td>9</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>( 27 \times 10^{20} )</td>
<td>6</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 4.1: List of the approximated limits of \( n \) and \( \mu \), which arose from figure 4.7. The efficiency \( \nu \) of the Nb doping was calculated, by subtracting \( 1 \times 10^{20} \) cm\(^{-3}\), which was assumed to be the maximum contribution of intrinsic oxygen vacancies. The 10 at\% values are a prediction, assuming the blue line holds and \( \nu = 90 \% \) persist. This would result in a resistivity of about 390 \( \mu \)Ωcm. The lower efficiency of the 1 at\% run is most probable due to a lack of optimized samples.

These limits are summarized in table 4.1. It also includes the doping efficiency \( \nu \) which the incorporated Nb could achieve. Hereby, the carrier density limit of the undoped case (\( 1 \times 10^{20} \) cm\(^{-3}\)) was subtracted from the electron densities of the doped films assuming a constant maximum contribution of oxygen vacancies. Otherwise, the efficiency would reach and even overcome a value of 100\%. Even so the calculated efficiencies are around 90 \% and above, which is quite outstanding for reactively sputtered TCO films, especially without employing high temperatures or hydrogen treatments. For example in the case of Al in ZnO:Al efficiencies of typically 50 \% are achieved [Szy01]. Even films produced very elaborately and exhibiting mobilities and conductivities in the highest possible regime [HOW+14, Som15], reach only roughly 75 \% by neglecting the contribution of oxygen vacancies.
Figure 4.8: The mobilities $\mu$ as a result of the used O$_{2pp}$ and the doping concentration with lines as guidance to the eye are presented. The resistivity and charge carrier density for these samples were shown in figure 4.6. In the undoped case the mobility is arising and saturating, when increasing the amount of oxygen. Whereas, if Nb is present, the mobility drops drastically adding more oxygen.

The approximation of the relation between mobility and dopant concentration, given by the blue line can be used to predict the outcome of a further increase of the Nb content. Such an extrapolation to 10 at% is also given in table 4.1, supposing a stable doping efficiency of 90%. Although the maximal mobility is supposed to decrease further, the higher charge carrier density could reduce the resistivity of such films to 390 $\mu$Ωcm. Reaching such low values via a reactive sputter process on glass at room temperature and only moderate annealing requirements would be a huge advancement.

At the end of this section the impact of the amount of oxygen upon the mobility of doped and undoped TiO$_{2-x}$ films has to be discussed. As mentioned before, one can observe that samples with varying Nb concentrations populate different regions in figure 4.7. These regions form bands in the viewgraph and are located on top of each other.

The fact that the maximal mobility, which samples of one Nb doping level can achieve, becomes reduced by increasing the Nb concentration, as indicated by the blue line, can be understood quite intuitively. Most importantly, the Nb atoms with their larger ionic radius distort the lattice which lowers the mobility.\(^9\) Secondly, after they have donated effectively an additional electron into the conduction band, they are higher charged which increases the scattering probability and cross section (see IIS scattering, section 2.2.10).

However, there has to be an additional reason in order to explain why the mobility is not only a function of the charge carrier concentration but also of the employed Nb concentration. Or in other words: Comparing films with the same free charge carrier concentration one can see that the more Nb they have the lower their mobility is. A quite reasonable explanation arises from figure

\(^9\)The reason for the large importance of the amount of lattice distortion for the electron mobility in TiO$_2$ will be explained in section 7.1.
Chapter 4 DC Electrical Properties of TiO$_{2-x}$

4.8 where the mobility is plotted as a function of the utilized relative O$_{2PP}$. The corresponding resistivities and electron densities are shown in figure 4.6. The 1 at% case was not included in the graph here due to the lack of sample statistics, but it indicates the same behavior as the larger doping levels.

If no Nb is present in the film, the mobility is rising and *saturating* when increasing the amount of oxygen. This can be understood by the fact that a less sub-stoichiometric material contains fewer oxygen vacancies that distort the lattice. A smaller number of such point defects lead to a more ideal TiO$_2$ crystal lattice and thus, the mobility increases. Below a certain limit of the defect density, the vacancies are not limiting the mobility any longer which is why the mobility is saturating.

In the case of additional Nb doping the relationship between mobility and the oxygen content during the sputter process changes dramatically. There, not only the resulting conductivity exhibits a maximum, as it was the case for the undoped films (see e.g. figure 4.5), but also the mobility. Obviously, the beneficial effect of a high oxygen contents is not dominating in Nb doped films but superimposed by an additional effect. Why is in the presence of Nb also the mobility and not only the charge carrier concentration deteriorating with higher oxygen contents? The reason for this could be the strong tendency of Nb to oxidize and to form Nb$_2$O$_5$ as precipitation or at least to bound with oxygen interstitials. DFT calculations support the idea of O$_i$ defects near Nb atoms, which is not present in undoped TiO$_2$ [KTS+09].

This cluster model is supposed to be present in for example In$_2$O$_3$:Sn at high O$_{2PP}$ as well [Bri07]. However, the tendency of Nb forming such clusters seem to be much larger. The enthalpies of formation can be read in table 1.2 which reveal that the reaction from NbO$_2$ to Nb$_2$O$_5$ releases an energy of 155 kJ/mol for every Nb atom. Thus if enough thermal energy is provided to enable diffusion of the Nb atoms and also sufficient oxygen is available, Nb$_2$O$_5$ will form. If, on the other hand, an oxygen poor atmosphere is present one has to compare the enthalpy of formation for every O atom. In this case Nb$_2$O$_5$ is indeed slightly (by $\sim$18 kJ/mol) less favorable than NbO$_2$ allowing a stable process window. Moreover, this scenario of oxidizing NbO$_2$ can explain why the carrier densities for doped films can reach values as low as undoped ones (figure 4.7). The harmful effect of the formation of Nb$_2$O$_5$ upon the mobility can be understood in terms of 3D defects. Such insulating (bandgap $E_G > 4.3$ eV [AR05]) Nb$_2$O$_5$ precipitations break the lattice symmetry and distort additionally the surrounding matrix, which makes them strong scatterers. Fortunately, Nb$_2$O$_5$ is energetically also less favorable, with respect to the oxygen, than TiO$_2$, as otherwise the dopant would reduce the TiO$_{2-x}$ and always form this higher valence oxide.

To shortly summarize; very high conductive TiO$_{2-x}$ films with and without Nb doping have been prepared which exhibit a rather complex behavior and relationship of $\rho$, $n$, and $\mu$ with the O$_{2PP}$. Very high doping efficiencies above 90% could be measured in agreement with theoretical calculations [HKY+08]. An optimal O$_{2PP}$ value during the sputtering has been obtained which is slightly different for every target. For higher Nb concentrations this optimum is around 55%.
Figure 4.9: The temperature dependencies of $\rho$ for an $O_{2PP}$-series of $\sim 250$ nm thick, capped and undoped TiO$_{2-x}$ films on glass. The corresponding Hall-data at room temperature can be seen in figure 4.5. For the sake of clarity some samples in the higher $O_{2PP}$ regime were omitted here. Three different kinds of behavior can be distinguished which are indicated by different line styles. Ideal metallic behavior is represented by a solid line, dashed-dotted line denotes an insulating behavior and the dashed ones a mixed type with a thermally activated mobility. The transitions express themselves not only by a change of their temperature conduct, but also in the strong discontinuities of $k_F\lambda$ with decreasing $O_{2PP}$ which is illustrated by the insert. Within each type, the increase of oxygen vacancies increases $k_F\lambda$ and the conductivity.

### 4.4 Metal Insulator Transition

As it was mentioned in the fundamentals part, this work deals mainly with the behavior of degenerate semiconductors, i.e., a metal-like conductivity. To see that sputtered TiO$_{2-x}$ can show also other and additional effects including a metal insulator transition (MIT), the $\rho$ versus $T$ data of a $O_{2PP}$-series of undoped TiO$_{2-x}$ thin films is plotted in figure 4.9. The solid lines denote metal-like behavior, whereas the black dashed-dotted curve depicts an insulating sample clearly which could only be measured down to 50 K. In between a third group exists with a changed temperature behavior. This groups are separated, furthermore, by strong discontinuities of their $k_F\lambda$ values with decreasing $O_{2PP}$ which is illustrated by the insert. For a deeper understanding of these groups, additional temperature dependent Hall-experiments have been conducted.

In figure 4.10 the exemplary results of such measurements of two different undoped TiO$_{2-x}$ thin films are depicted. Figure 4.10(a) proves the degenerate semiconductor character of even this highest oxidic TiO$_{2-x}$ film. The carrier density stays in principle constant over the entire temperature regime investigated, which corresponds to a constant Fermi-energy. Therefore, the mobility change governs the complete alteration of the resistivity by its strong increase during cooling. From this larger mobility at lower temperatures one can conclude that in these samples grain boundary scattering is not dominant as this would result in an opposite and even stronger mobility versus temperature behavior (see section 2.2.8). In the next sections the exact descriptions of this change and their influencing factors will be explained as this metal-like state is the most important one in the field of high quality TCO materials. It is worth mentioning that even in this state films can
Figure 4.10: The results of two exemplary temperature dependent Hall-data of undoped TiO$_{2-x}$ thin films are shown. Thereby is (a) a 90\% sample, which shows a clear metal-like trend and will be discussed in more detail in the next section. Against it in (b) the insulating trend of a 50\% sample is visualized. In order to do so, logarithmic scales had to be applied in this case and below 50 K it was not measurable any longer, with the setup in use.

have $k_F\lambda < 1$. This indicates a shortcoming of the application of the simple Ioffe-Regel model in the case of TiO$_{2-x}$.

In contrast figure 4.10(b) shows the Hall-data of the insulating 50\% sample. Here, the charge carrier density is decreasing by several orders of magnitude with falling temperature. A standard Arrhenius-law is able to describe the trend of $n$ from room temperature till roughly 150 K with an activation energy of 100 meV. It is striking that it is an insulator, although the carrier concentration at room temperature is higher by two orders of magnitude compared to the metallic 90\% sample. This is in contrast to the idea of a Mott-type MIT (see section 2.2.6) as there a larger carrier concentration (within the same lattice structure) leads a transition from an insulating to a metallic state not vice versa. For this samples also the mobility starts to decrease drastically when lowering the temperature. This indicates a mobility edge which exceeds at some point the falling Fermi-energy. Therefore, the electrons at the Fermi-edge are localized below this temperature. To find the origin for such a mobility edge the structural quality will be investigated in section 6.3.

The value of $1 \times 10^{19}$ cm$^{-3}$ in figure 4.10(a) can be interpreted as a critical charge carrier density for metal-like behavior, which is in agreement with some first rough results in literature [TPS+94]. In figure 4.11 the critical carrier densities and isotropic Bohr radii for a MIT according to Mott are presented for several different materials. In blue the representatives of the TCO class are depicted and the red line visualizes the theory by Mott (equation 2.31).

The typical TCO materials fit quite well to this theory, however, TiO$_{2-x}$ does clearly not fulfill this prediction. For example, anatase single crystals with a carrier density at room temperature of $\sim 1 \times 10^{18}$ cm$^{-3}$ have been demonstrated to be unambiguously non-metallic [FCE+94], although the Mott theory predicts a transition at roughly $1 \times 10^{17}$ cm$^{-3}$. The employed $\epsilon_{st}$ and effective masses for this prediction are listed in table 1.2. Together with the fact that the clearly insulating sample, which has been shown in figure 4.10(b), exhibits even a higher carrier density than the degenerate ones, we can conclude that the metal-to-insulator transition in TiO$_{2-x}$ is not well described by a Mott-transition.
With respect to figure 4.9 it is definite that the sample denoted in black is insulating. Besides the reasons already given, this can be seen by the simple fact that the resistivity increases by several orders of magnitude when reducing the temperature, which is a quite typical behavior for an insulator.

However, there is this intermediate group of $O_{2\text{PP}}$ values marked by the dashed lines in figure 4.9. In their case the question arises, whether they are still degenerate semiconductors, or not. It is worth remembering at this point that $k_F \lambda$ is decreasing abruptly when reducing the $O_{2\text{PP}}$ to the 60 % sample. On the other hand, the carrier concentration is continuously increasing, as described above. Therefore, the mobility has to drop abruptly, indicating a changed transport

![Figure 4.11: The critical carrier concentration for metallic behavior and the respective Bohr radius for several materials including TiO$_2$ and the standard TCO materials. The data was taken from, or calculated with [ES78, EPJ+04, RWW82, BAK+12].](image)

![Figure 4.12: Extrapolation to distinguish metal from insulator behavior of the two lowest conductive TiO$_{2-x}$ samples of the intermediate group. Both diagrams depict the temperature range from 0 K to 10 K, whereas the lowest measured temperature was 2 K. Both extrapolations ($\sigma = a + \beta T^\gamma$, equation 2.29 and 2.28) fit reasonable well, however, lower temperatures would be necessary to decide which model is better suited.](image)
mechanism. To clarify if these samples can still be regarded as being metallic, two typical low-temperature extrapolations are depicted in figure 4.12 which are used to judge the conductivity behavior (section 2.2.6). Only the two lowest conductive samples of this group are shown, but they seem to be still in the metallic state (indicated by the non zero conductivity going to 0 K). However, measurements at even lower temperatures would be necessary, especially, in order to be sure which model is better suited.

In summary, one can conclude the important fact that, in contrast to common TCOs, the MIT in TiO$_2$ is not well explained by the Mott-model. Thus a large charge carrier concentration does not guarantee a metallic behavior.

### 4.5 Intermediate Temperature Range

To understand which different transport mechanism is dominating in these intermediate samples (between the clear metallic and insulating ones), their temperature behavior will be investigated a bit further, before discussing in greater detail the temperature behavior of unambiguously degenerate films.

#### 4.5.1 Hopping

Temperature dependent Hall-measurements of two samples of this changed conductivity mechanism can be seen in figure 4.13. Their behavior differs significantly from the ones depicted in figure 4.10. The carrier concentration is reduced during cooling in contrast to the degenerate case. However, this reduction is smaller than 20\% in contrast to the several orders of magnitude as for clear insulating samples. Even more fascinating is the fact that the carrier density is stable after the drop. This reduction of the free charge carrier density has to be linked to the increasing mobility,
Figure 4.14: Graphs displaying tests of small polaron hopping models, whereby (a) is the adiabatic and (b) is the non-adiabatic case (equation 2.27). They differ from a normal Arrhenius relation by different y-axes. Other models in question, including nearest neighbor hopping and different variable range hopping mechanisms have been tried as well, but these polaron hopping models could represent the largest temperature regime and are the best fit to the experimental data.

Several authors investigated undoped TiO$_{2-x}$ samples with high electrical resistivities and use combinations of different hopping mechanisms including large and (adiabatic and non-adiabatic) small polaron hopping (SPH), nearest neighbor (NN) and variable range hopping (VRH) according to Mott or Efros-Shklovskii [MW09, JVM+12, HWS+04, MMJ+13, YLKM08, YIM10, HCVJ07]. Details about these concepts are written in section 2.2.4 and 2.2.5. In order to describe these intermediate samples the mentioned hopping mechanisms have been tested. Only the SPH models could at least for a reasonable large interval (more than 10 K) describe the curvature of the conductivity function correctly. This would be in agreement with the DFT calculation of Morgan and Watson. They stated that Ti interstitial defects, which could be present due to the larger sub-stoichiometry, would create deep traps resulting in SPH [MW09]. The fit results are depicted in figure 4.14. Interestingly, there seems to be a crossover from the adiabatic SPH ($\ln(\sigma T)$ vs. $1/T$) at "higher" values of O$_{2PP}$ to the non-adiabatic SPC ($\ln(\sigma T^{3/2})$ vs. $1/T$) in the case of even more reduced O$_{2PP}$.

Although the conductivity can be described reasonable well by SPH in this temperature regime, there are some flaws in this explanation. As mentioned in section 2.2.4, SPH is impacting the conductivity by altering the mobility. However, in the temperature range from 200 K to 300 K, where the SPH could be applied, the mobility is not reduced by cooling and the absolute numbers are higher than expected. The conductivity in this regime is also strongly influenced by the...
changing carrier concentration (figure 4.13) which is not governed by the SPH model. Additionally, a rather constant mobility is predicted by this model for the low temperature regime, e.g., below 200 K in [YIM10], which is not in agreement with the measured data. The TiO$_{2-x}$ samples investigated in literature, where the authors ascribe SPH to the conductivity alteration, differ remarkably from the ones investigated here. The room temperature conductivities are several orders of magnitude higher than in those reports. Furthermore, the films investigated in this thesis consist solely of an amorphous and the anatase phase (section 6.3.1). In contrast, the TiO$_{2-x}$ films, where SPH has been attributed to the experimental conductivity data, were made solely or at least partly out of the rutile phase [YLKM08, YIM10, FH63, HWS+04, HCVJ07, AM01, AM95].

In total, none of the mentioned hopping transport mechanisms can describe conclusively the mobility decrease cooling down below 200 K for these samples with an intermediate O$_{2PP}$ value. The question of the correct model or valid combination of several mechanisms is, therefore, still an open one and needs a more intense investigation.

4.5.2 Phonon Scattering

In this and the following sections the results and analyses of clearly degenerate samples will be discussed. As a first example, in figure 4.15 the resistivity vs. temperature data of some undoped TiO$_{2-x}$ films are shown. Some of them were already presented in figure 4.10. All samples presented here are unambiguously in the degenerate state, with a constant charge carrier density as revealed by Hall measurements (not shown here).
Section 4.5 Intermediate Temperature Range

Figure 4.16: Example of the application of the Boch-Grüneisen law on metal films, here, Ag thin films (10 nm to 13 nm) with typically $k_F \lambda = 250$ to 450. They were produced via different sputtering runs on ZnO seed layers including one example of an evaporated film. Details can be read in the dissertation of Patrick Ries [Rie15]. In (a) the absolute specific resistances are depicted and in (b) the residual resistivity $\rho_0$ was subtracted in each case from the fit and the data. This underlines the constancy of the phonon contribution irrespective of the film thickness. Thereby a reduced number of measured values are denoted with points whereas the lines are the theoretical fits.

So far, the ordering scheme of the relative O$_{2PP}$ used during deposition had proven to be very helpful and illustrative. It will hence used frequently in this thesis. Nevertheless, another measured property of a sample will be utilized as an even more precise ranking for the degenerate films, namely $k_F \lambda$. As can be seen in figure 4.15 the resistivity curves are stacked on top of each other with a decreasing value of $k_F \lambda$. The 70% sample is the only exception, which has additionally also a different curve progression. To provide a reason why this sample behaves differently, a close look at the $Q$-factors of the vdP-measurements gives some insight. Although usually this metallic conductive samples exhibit a value of $Q < 1.3$, this one features a value of $Q = 2.5$, despite an equally quadratic shape. Thus, due to some perturbations of the preparation process this sample seems to exhibit a strong inhomogeneity of its properties (e.g., in the microstructure) which alters slightly its characteristics. However, the most remarkable finding in this graph is that with the precise control of the sputtering conditions metallic conductive TiO$_{2-x}$ samples can be produced on unheated glass with only a quite minute degree of sub-stoichiometry. This underlines the findings of Jacimovic et al. who claim that oxygen vacancies form shallow donor levels of about 10 meV [JVM+12]. If otherwise vacancies would form a deep level defect state as some calculations claim, no degenerate behavior could be expected in the case of undoped TiO$_{2-x}$. Before the relationship between temperature and resistivity will be discussed in more detail, there are already some more facts which should be realized and kept in mind. First, the ratios of the resistivities at 300 K, i.e. room temperature, and at 2 K ($\rho_{300K}/\rho_{2K}$) are quite high. Furthermore, these differences between room temperature and 2 K are rather not constant as it is known for ideal metals (see figure 4.16), but increase with the absolute value of the resistivity. A second unusual finding is the low temperature behavior which shows often a small increase of the resistivity during the cool down. This is more or less not known for good metals.
In principle, the temperature behavior of real metals and also degenerate TCOs can be described by the Bloch-Grüneisen (BG) law (see section 2.2.9), with an exponent $n = 5$. To demonstrate this, Ag films of equal thickness were prepared in different sputter runs and a capping against dewetting and a ZnO seed layer to improve the performance, were included. These films were produced by Patrick Ries and the details of the process and a multitude of interesting results regarding structure and electrical performance of silver thin films can be found in his thesis [Rie15]. The results of some temperature dependent measurements and their corresponding fits can be seen in figure 4.16(a). In the appendix an additional study can be seen where films with different thicknesses were produced (figure A.3). The thickness dependent shifting there can be explained in terms of surface scattering (2D defect, see section 2.2.8) which can be diffusively or specular. Quite perfect films are necessary to evaluate such effects, as otherwise, other influences can easily dominate. Therefore, these models are usually applied in the case of metal films or wires [Ang85, Cho65, LB64]. Here, equally thick Ag films are compared which were produced during different runs with varying production details of the seed layer and after deposition treatments. It is easy to see that the data can be described extremely well with the BG model with a mean Debye-temperature of 180 K which is in good agreement with the literature values for silver [TL68, BBR06]. As it has been illustrated in figure 2.5, the $\rho$ vs. $T$ curves approach a linear relationship for $T > \Theta_D$.

Although the samples encompass a relative large range (for silver) of residual resistivities, the magnitude of the phonon contribution for the sputtered films remains between 1.6 $\mu\Omega\text{cm}$ to 1.8 $\mu\Omega\text{cm}$ as one can observe in figure 4.16(b). Even the evaporated film with its much higher resistance, exhibits only a very minute increased phonon contribution to the room temperature resistivity value. This kind of plot, where the residual resistance is subtracted, is very useful to evaluate the fit quality. Otherwise, the shift due to varying amounts of defect scattering can easily obscure the exact shape of the temperature curve.

After we have seen the nearly perfect description by this law in the case of good metals, lets now proceed with a set of degenerate TCO samples. The results given in figure 4.17 demonstrate how well also in these cases the BG law can describe the phonon contribution. The films investigated here were produced quite differently and encompass the common range of resistivities known for medium to high quality TCO films. The ZnO:Al with 1 at% for instance was sputtered from a ceramic target on high temperature substrates including a seed layer by Nicolas Sommer and details can be read in his thesis [Som15] or in [HOW+14]. Gabrielle Jost sputtered hydrogen doped In$_2$O$_3$ to gain high mobile and conductive thin films. Both types were investigated in the context of a cooperation with the IEK-5 of the Forschungszentrum Jülich. The other films were produced in house, whereby the In$_2$O$_3$:Sn layer from a ceramic target and the ZnO:Al reactively from a metal target, similar to the TiO$_2$ ones.

Several trends and differences can already be realized from this small overview, with the resulting fit-parameters given in table 4.2. The deviations of the fit from the measured data, beside the potential resistivity upturn in the case of some low temperature measurements, stays well below 1 $\mu\Omega\text{cm}$. The mean of the squared relative deviations can be used as a measure for evaluating the fit-quality of different approaches.
The most obvious difference between these materials is the amount of the phonon contribution. It is much higher in In$_2$O$_3$ than in ZnO, regardless at which residual resistivity they are compared. This fact is reflected by a higher value of $A$, indicating a stronger electron phonon coupling. The Debye temperature however is slightly higher for ZnO. A value of roughly 900 K for In$_2$O$_3$ is in fairly good agreement with the value of $\sim$1000 K found in literature [LL14, CCL+09, LJZ08, PBRS13, BCP+09], where they range from 700 K to 1100 K. In the case of ZnO a value of 1000 K evolves, which is consistent with literature, too [LLCL12, DOK+07]. However, the authors in the references given till now, determined the Debye temperature also via the electrical resistivity measurements. Heat capacity measurements at In$_2$O$_3$ revealed a value of 420 K [BHR81]. In the case of ZnO different methods like the atomic vibrations derived from anisotropic temperature coefficients or calculating the Debye temperature from the sound velocity, give values in the range of 400 ± 50 K [AAK89, AB69, RE66]. Obviously the Debye temperature which affects the electron-

<table>
<thead>
<tr>
<th>Name</th>
<th>$\rho_0$ [µΩcm]</th>
<th>$A$ [µΩcm]</th>
<th>$T_{Deb}$ [K]</th>
<th>$\varnothing$ deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Al 4.7 at%</td>
<td>781</td>
<td>306</td>
<td>1178</td>
<td>$7 \times 10^{-6}$</td>
</tr>
<tr>
<td>ZnO:Al 4.7 at% 350°C</td>
<td>284</td>
<td>829</td>
<td>962</td>
<td>$6 \times 10^{-7}$</td>
</tr>
<tr>
<td>ZnO:Al 1 at% IEK5</td>
<td>215</td>
<td>874</td>
<td>1008</td>
<td>$3 \times 10^{-7}$</td>
</tr>
<tr>
<td>In$_2$O$_3$:Sn 10 at%</td>
<td>870</td>
<td>1827</td>
<td>865</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>In$_2$O$_3$:H amorph IEK5</td>
<td>303</td>
<td>908</td>
<td>807</td>
<td>$7 \times 10^{-7}$</td>
</tr>
<tr>
<td>In$_2$O$_3$:H cryst. IEK5</td>
<td>194</td>
<td>1962</td>
<td>912</td>
<td>$4 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Table 4.2: List of the parameters according to a least square fit to equation 2.39 of the data presented in figure 4.17. The $\varnothing$ deviation is calculated as the mean of the squared relative residuals. Only the temperature region above a potential resistive upturn was considered.
phonon coupling is severely higher than the classical one describing the thermic vibration. Thus there are different kinds of effective Debye temperatures one for electrical transport and another for heat transport. Nevertheless, the concept of Bloch-Grüneisen scattering is remarkable powerful and widely accepted to describe and explain the behavior of degenerate TCOs.

For example looking at the values of the In$_2$O$_3$ samples, it is interesting to note that for the phonon scattering the dopant is not of great importance. The crystalline, antimony and hydrogen doped samples have practically the same phonon contribution, although the residual resistivity differ a lot. A large part of the reduced residual resistivity in the case of the hydrogen doping is supposed to be caused by the passivation of the grain boundaries [WFMMK15, PJK08] (carrier concentration of both samples is $\sim 1.7 \times 10^{20}$ cm$^{-3}$). In the case of an amorphous In$_2$O$_3$ film, however, the phonon scattering is remarkably reduced which manifests itself in the halved value of $A$. The loss of the crystal structure seems to decrease drastically the electron-phonon coupling. In total, in the case of In$_2$O$_3$ the Matthiesen rule (independence of phonon and defect scattering) can be taken as fulfilled.

In the case of the set of ZnO:Al samples a similar conclusion regarding the dopant concentration can be drawn, comparing the orange and yellow curve. Although the red curve displays also a crystalline ZnO, the quality of the structure seems to be quite poor, as the resistivity is remarkable higher and exhibits a relative strong upturn, which additionally starts at higher temperatures. This bad structural quality is reducing the electron-phonon coupling as had been seen for the amorphous In$_2$O$_3$ film. This strongly reduced value of $A$ can’t be explained by different charge carrier concentrations as the 350 °C sample has even a bit higher electron density ($9.3 \times 10^{20}$ cm$^{-3}$ in contrast to $7.8 \times 10^{20}$ cm$^{-3}$) for the as deposited film. From these results we can conclude that in the case of standard TCOs the resistivity due to phonon-scattering is not only (matrix) material dependent but it is heavily influenced by details of the structure and preparation process, which is not the case for standard metals (compare figure 4.17 and figure 4.16).
Section 4.5 Intermediate Temperature Range

Now we will proceed with TiO$_{2-x}$ and look how the situation is there. But first, the type of the conducting electrons / conduction band has to be taken into consideration. In TiO$_{2-x}$ the conduction band minimum is a d-band, which has a much larger density of states at the Fermi-edge and therefore different electron-phonon interaction mechanisms could take place. Due to the relative high charge carrier density of some, especially doped, films and the large density of states, a dominating direct electron-electron scattering represented by $n = 2$ in the BG formula becomes possible. Also the approach with $n = 3$ has been tested as it accounts for a dominant phonon assisted s-d electron scattering which could be the case as well (see section 2.2.9).

It is important to note that the pure metallic character of all samples which will follow now in the context of phonon scattering, were first proven by temperature dependent Hall-measurements. “Intermediated” samples which exhibit temperature dependent trends like the ones shown in figure 4.13 are not included in the discussion here as in these cases several influencing factors seem to be present and are not fully understood till now.

In figure 4.18 the outcome of two approaches, $n = 5$ like for standard TCOs and $n = 2$, is displayed. Due to the resistive increase approaching low-temperatures, only the values above 60 K were taken into account. It can be seen quite clearly that the ansatz with $n = 2$ is not at all able to fit the progression and curvature of the data. On the other hand the typical approach of $n = 5$ works much better with more than one order of magnitude smaller $\phi$ deviation. It should be noted that for the $n = 5$ case, the residual resistance had to be adjusted by hand slightly. Otherwise, the fits cut the curve above the minimal measured resistance which is physically not meaningful. Thus, when comparing this $n = 5$ fit with the very good agreement the fits could achieve with $n = 3$, the ansatz with $n = 5$ is not convincing in the case of TiO$_{2-x}$ (see figure 4.19).

Also fits with $n = 3$ were tested and a comparative graph of $n = 5$ and $n = 3$ can be seen in 4.19. Here the residuals were subtracted and it can be seen that the representation of the data

\footnote{$n = 5$ represents a direct electron-phonon scattering, typical for s-electrons.}

Figure 4.19: Shown are the BG-fit with (a) $n = 5$ and (b) $n = 3$ for the films, with the data also shown in figure 4.18 of undoped TiO$_{2-x}$. The residual resistivity was subtracted.
could be improved by this model. To further clarify the superiority of the fitting result applying \( n = 3 \), a direct comparison of the three models can be seen in figure 4.20. The fit with \( n = 3 \) is practically perfect and can follow the curve progression much better than the other variants.

For the sake of completeness and to prove the universality of the concept, in figure 4.21 a larger series of undoped TiO\(_{2-x}\) films including a BG-fit with \( n = 3 \) can be seen. Although the samples were prepared during several different sputter runs, they can all be described very well including a successful sorting via their \( k_F \lambda \)-value. The residual resistances encompass 1.5 magnitudes but follow all equally well the BG-formalism. The highest resistive but still metallic conductive sample had thereby a very low \( k_F \lambda \) of only 0.17. This is much lower than the values at which the common TCOs become metallic.

**Figure 4.20:** Example of the fit-quality of the different BG-models for an undoped TiO\(_{2-x}\) film.

**Figure 4.21:** Temperature dependency of \( \rho \) and fit according to BG model using \( n = 3 \) for a series of undoped TiO\(_{2-x}\) films, prepared in several different sputter runs. They show the universal applicability of this model as the residual resistivities encompass more than one order of magnitude. Furthermore, the successful ordering by \( k_F \lambda \) is demonstrated as well.
Section 4.5 Intermediate Temperature Range

Figure 4.22: Resistivity data and fit according to BG-law with \( n = 3 \) for TiO\(_{2-x}\) films with (a) 2.5 at\% Nb and (b) 5 at\% Nb. Only roughly equally thick completely degenerate films were taken into account.

It should also be noted that in the case of using \( n = 3 \) the residual resistance had not to be fixed by hand to prevent any resistivity data to be lower than the fit, but in this case the least square fit fulfilled this necessary condition automatically. In the following mainly the fits and the parameters employing \( n = 3 \) are shown. Nevertheless, also \( n = 5 \) has commonly be tested for comparison and the reduction of the \( \varnothing \) deviation by using \( n = 3 \) is always at least one order of magnitude.\textsuperscript{11}

After discussing undoped TiO\(_{2-x}\) films, now the Nb doped films will be investigated. The results of a selection of 2.5 at\% and 5 at\% Nb doped films can be seen in figure 4.22. Also these films are best described with BG-fit choosing \( n = 3 \), however, the data is not quite as perfectly matched as in the undoped case. It is interesting to note that in the doped case the range of room temperature resistances of metallic conductive samples is much smaller than it was displayed in the undoped case. Some of the doped samples had such a large resistivity increase during the cool down, which set in also at quite high temperatures of 150 K to 200 K that a trustworthy fit could not be obtained there.\textsuperscript{12} Measuring such films up to 400 K revealed that they could at this high temperature regime still fitted well according to the BG-law. However, the low temperature extrapolation is not reliable enough in such cases. In addition, due to the smaller applicable temperature range, the fit parameters would not be of a comparable quality as the ones from the other films. Therefore, these films with a very large resistivity increase are neglected here. The reason for this smaller resistivity window for good metallic conductive films can also be seen in the mobility data shown before in figure 4.8. Samples which can be described nicely with the BG-formula are in the regime of the mobility peak of their respective doping concentration.

In the case of these high quality films the temperature characteristic does not show much of a resistivity increase at low temperatures. Especially data of films, which have also an amorphous seed layer of Si\(_3\)N\(_4\), demonstrate such an ideal curve progression. Despite the challenges mentioned investigating doped samples, the results are quite striking. In figure 4.22 data from samples of three

\textsuperscript{11}For Ag both approaches lead to nearly equivalent results which is due to the low Debye temperature and, therefore, a mainly linear behavior of the resistivity in the greater part of the investigated temperature regime.

\textsuperscript{12}The resistivity increase at low temperatures will be addressed in section 4.7.
different sputter runs are combined and match perfectly. The two samples with an $\kappa F \lambda$ of 5.7 with 5 at% Nb, coincide, although they were not produced together. One can also conclude from this that the $\kappa F \lambda$ scale orders the temperature curves of Nb doped TiO$_{2-x}$ films very nicely, too.

What are the results from these fits? First we investigate the calculated Debye temperatures of these degenerate TiO$_{2-x}$ films. In figure 4.23 the relationship between $T_{\text{Debye}}$, the residual resistivity and the free electron concentration is visualized. Thereby, the residual resistivity is denoted as $\rho_{\text{defects}}$. The determined values of $T_{\text{Debye}}$ are not constant for all the TiO$_{2-x}$ films. However, they are also not directly depending upon the electrical properties of the film, like its charge carrier density or residual resistivity. Therefore, it is unlikely that the observed change is only a fitting artifact. Instead the Nb content is reducing the effective $T_{\text{Debye}}$ from a mean value of 3450 K for the undoped case along 1700 K for 2.5 at% down to 1360 K for 5 at%. Unfortunately until now there are not enough high quality samples with 1 at% or 10 at% available, therefore it is hard to say, how the exact quantitative relationship looks like. To my knowledge, there is no study of the relationship between electrically determined Debye temperature and dopant concentration with a comparable quality for standard TCOs not to mention TiO$_{2-x}$. Thus, the question, whether this demonstrated influence of the doping concentration upon $T_{\text{Debye}}$ is special for TiO$_{2-x}$ or not, can’t be answered at this point of time. The standard TCO films investigated here had charge carrier concentrations in the range of $1 \times 10^{20}$ cm$^{-3}$ to $1 \times 10^{21}$ cm$^{-3}$ and, as was depicted in table 4.2, Debye temperatures of roughly 1000 K. This is lower by at least 500 K than the values presented in figure 4.23(b). Although the fits were done by different values for $n$, the curvature of the resistivity data is already a clear hint that the effective Debye temperature is lower in the standard TCO case. In figure 4.17(b) it can be detected that the slope of the graphs are already more or less linear reaching room temperature, which is not the case for TiO$_{2-x}$ films (figure 4.22). This indicates that TiO$_{2-x}$ is still much farer away from the linear regime, which describes the high temperature limit ($T > T_{\text{Debye}}$).
After discussing the first parameter in the BG-fit, the Debye temperature, now the evaluation of the second one, the prefactor $A$, will follow. Following equation 2.40 the relationship between $A/T_{\text{Debye}}$ and the free electron concentration $n$ is displayed in figure 4.24(a). The data for the TiO$_{2-x}$ thin films lay indeed on a straight line, whereby the undoped ones are a bit higher. Even more interesting the corresponding data for ZnO and In$_2$O$_3$ films, which were produced at the IEK-5 in Jülich and in the institute via different production processes, lay on one line as well. The lines drawn exhibit slopes of -1 as expected in a log-log plot from the formula and represent the experimental data very well. From this we can conclude that the formula for the prefactor is indeed a good description for the influencing factors not only for metals but also for degenerate semiconducting materials.

The electron-phonon coupling constant $\lambda_{\text{ep}}$, which has been calculated on this basis, can be seen in figure 4.24(b). There exists a clear difference between the materials, which is not related to the residual resistance. In the case of standard TCOs the coupling seems to be one order of magnitude lower than in the case of doped TiO$_{2-x}$. A closer inspection reveals that the coupling constant of ZnO is slightly higher than the one of In$_2$O$_3$. In the TiO$_{2-x}$ case the undoped films exhibit somewhat higher values than the doped ones. Besides the Debye temperature, this is another indicator that the presence of Nb in the crystal alters the electron-phonon interaction.

The direct comparison of the electron-phonon coupling constants of TiO$_{2-x}$ and the standard TCOs has of course a shortcoming. The choosing of the exponent in the BG-fit alters not only the curvature but necessarily also somewhat the values of $T_{\text{Debye}}$ and $A$. Although physically it is not meaningful to try to fit the data of ZnO etc. with $n = 3$, it was done to gain in this way a rough estimate of the uncertainty of the mentioned difference between them and TiO$_{2-x}$. It emerged that by doing so the $A/T_{\text{Debye}}$ ratio increases maximumly by a factor of two, which is much smaller than the shown gap between TiO$_{2-x}$ and the standard TCOs.
The discussion of the BG-formula and the resulting fit parameters revealed a couple of fascinating facts of TiO$_2$–x and its differences to metals and other TCOs. However in practice, the key dissimilarity between TiO$_2$–x and the other TCOs can be seen quite easily even without any fitting.

Comparing figure 4.16 with figure 4.17(b) and 4.19, it became obvious that the phonon contribution is not a constant in the case of TCOs as it is the case for simple metal films like Ag. For such degenerate TCOs the phonon contribution of the resistivity seems to be proportional to the residual or defect resistivity. The ratio of these two contributions is shown in figure 4.25. The data displayed proves remarkably well that the phonon contribution varies between the different materials.

The standard TCOs exhibit a phonon contribution of typically 10% to 30% with respect to the resistivity limit at low temperatures. In contrast, the contribution in TiO$_2$–x is by a factor of 2 ± 0.5 even larger than its residual resistivity. With this value the phonon contribution in TiO$_2$–x is roughly one order of magnitude larger than for other TCO materials. Furthermore, within the error margins, this ratio is independent of the doping level. This means in turn that when one can reduce the residual resistivity by preparing less defects etc., the room temperature resistivity will be reduced by a three times larger amount.

### 4.6 Thickness Dependency of $\rho$

In the sections before the TCO layers investigated had comparable and quite high thicknesses of several hundred nanometer, to rule out influences which originate from surface effects. In the following section we will discuss low temperature phenomena, where the dimensionality of the sample is absolutely crucial. Therefore, the thickness dependency of TiO$_2$–x has to be examined.
Section 4.6 Thickness Dependency of $\rho$

Figure 4.26: Measured resistivities as a function of temperature. Two sets of TiO$_{2-x}$ films with varying thicknesses are shown including best fits according to BG-formula with $n = 3$. In (a) undoped samples and in (b) layers with 5 at% Nb are depicted.

In figure 4.26(a) the resistivities of a thickness series of undoped TiO$_{2-x}$ on glass are shown as a function of temperature, including the good fitting result with the BG model with $n = 3$. It is quite intriguing that the specific resistance of the 40 nm film is consistent with the 240 nm one. This implies that the surface scattering is not of a large importance in TiO$_{2-x}$ films of typical thicknesses. In order to investigate this behavior and also the influence of Nb further, samples with varying thicknesses were investigated and one with 5 at% Nb is shown in figure 4.26(b). For coating thicknesses between 100 nm and 1 µm there is again no systematic change, whereas reaching 50 nm the resistivity is increased substantially.

The reason for the nearly thickness independent resistivities can be understood in terms of the mean free path. Calculated by Drude physics with equation 2.8, it was always smaller than 6 nm even at 2 K and below 2 nm at room temperature. This is in contrast to typical metal films like the Ag films shown before, where 35 nm were achieved already at 300 K. The largest mean free path of the standard TCO films investigated in the framework of this thesis reached only 15 nm at room temperature. So at layer thicknesses of several hundred nanometer for usual TCO applications the impact of surfaces scattering upon the measured total resistance is rather limited.

It is interesting to note that comparing the Nb doped and the pure TiO$_{2-x}$ series, the electrical properties of the Nb containing samples deteriorate already at somewhat larger film thicknesses. In a next step the extent of the film is further reduced and a comparison of the electrical parameters as a function of the temperature can be seen in figure 4.27. Although the two samples were sputtered right beside each other and were annealed together, the thinner sample exhibits tremendously different properties. At room temperature the specific resistance of the thicker TiO$_{2-x}$ sample is roughly one order of magnitude lower. By cooling down the 25 nm sample, it indicates a typical degenerate semiconductor behavior with a constant charge carrier concentration and increasing mobility. In contrast, the thinner sample could only be measured down to 100 K reasonably, because the resistivity increased so sharply.
Interestingly, the thin film exhibits only a small decline of the electron density, which can’t explain the huge resistivity increase, although one would expect this from an insulating intrinsic semiconductor. Instead, the mobility declines strongly with cooling and causes the loss of conductivity. A thermally activated mobility could be explained, for example, by charge transport via a hopping mechanism like small polaron hopping (see equation 2.27). Another explanation would be that the film has still an amorphous structure, as in such a case a hopping mechanism would be present as well. Higher annealing temperatures have been tested to see if only the crystallization is impeded in these very thin films.

In figure 4.28(a) the resulting electrical properties at room temperature for Nb doped films with different thicknesses after annealing at 300 °C and 400 °C for 2 h are displayed. A smaller layer thickness results in a somewhat lower mobility which can be understood by an onset of interface scattering. If, however, it is reduced below 50 nm, the mobility and conductivity is tremendously lowered as it has been the case for undoped films as well. Heating not too thin films to 400 °C reveals only slightly improved mobilities and constant electron concentrations. In contrast, the conductivity of the 20 nm films increased by several orders of magnitude and they reached the same charge carrier density as the thicker films. The mobility also increased drastically and nearly up to the values of thick ones. A somewhat smaller mobility for these very thin films is expected due to an intensified surface scattering.

Figure 4.28(b) proves the effectiveness of higher annealing temperatures for TiO$_2$$_{−x}$ films. Here, they were doped with 2.5 at% Nb and annealed at 350 °C instead of the usual 300 °C. As a result, also only 14 nm thick films showed perfect metallic characteristics.\textsuperscript{13} As the interaction volume for such thin films is so small, the crystallinity could not be revealed by XRD. However, the application of a higher annealing temperature leads to a similar tremendous jump of the conductivity as the observed crystallization does for thicker films.

Therefore, we can conclude that the reason for the tremendously lower conductivities of very thin TiO$_2$$_{−x}$ films with and without Nb is that the films stay amorphous after annealing at

\textsuperscript{13}Such metallic conductive and very thin TiO$_2$$_{−x}$ films could only be produced if a Si$_3$N$_4$ layer was utilized not only as a capping layer but also as a diffusion barrier and clean surface under the functional TiO$_2$$_{−x}$ layer.
300 °C. Employing higher temperatures than necessary normally, also the very thin films can reach comparable conductivities with the same temperature characteristics as the thick ones. The reason for the significant increase of the crystallization temperature of TiO$_{2-x}$ films with thicknesses below 50 nm is not completely clear. A possible explanation is that more strain is present in the thinner films impeding the densification upon crystallization. This is because strain releasing mechanisms, like the formation of dislocations and formation of grain boundaries, need a minimal thickness to be energetically favorable. There is also a temperature dependent minimal radius for a nucleus to be stable and to enable grain growth.

Further investigations are necessary to understand this phenomena. For example, it should be tested if the transition or increase of the crystallization temperature is indeed as abrupt as it seems to be in the moment and if a crystalline but insulating TiO$_2$ seed layer enables the crystallization for this very thin films.

### 4.7 Low Temperature Effects

In this chapter the low temperature behavior of degenerate TCO films will be examined. Typically, an increase in resistivity can be seen approaching small temperatures as could be demonstrated already several times in temperature dependent data before. In the following the behavior of typical TCO films will briefly be shown and then the phenomena which can be observed at TiO$_{2-x}$, will be addressed.

The temperature behavior of a set of several hundred nanometer thick metallic conductive TCO samples was investigated and their resistivity data plotted in figure 4.29. The overview in the left graph is to emphasize the very flat temperature dependency and the differences in their conductivity. All four of them exhibit a small conductivity decrease in the low temperature regime. To visualize this in one graph, the relative change with respect to the maximal conductivity is
Figure 4.29: The resistivity as a function of temperature with (a) linear scales as an overview. In contrast to (b), where the relative change from their maximal conductivity for temperatures below 25 K is plotted with a square root temperature scale representing the expected dependency for a 3D weak localization (see equation 2.52). Two of the ZnO:Al films depicted here, were annealed at high temperatures without a capping layer for which reason their conductivity degraded.

displayed in figure 4.29(b). Although it can’t be seen on this scale, but also the electrically best ZnO:Al sample here, with a $k_F\lambda$ value of 20, shows a small decrease of its conductivity of 0.02 %. So it gets obvious that the lower the resistivity of a film is, the smaller is the effect of its increase approaching 0 K. Following equation 2.55 and 2.58 a square root temperature scale, representing $p = 1$, was selected. The black dashed lines prove that indeed the resistivity increase can be described in terms of weak localization (WL) and electron-electron interaction (EEI) in 3D. At least below 10 K the curve progressions fit perfectly well\textsuperscript{14}, whereas above this temperature the onset of the phonon scattering is leading to the deviation.

Now, the behavior of TiO$_{2-x}$ will be presented. In figure 4.30 the resistivity increase is shown for undoped films, which were plotted before in full scale in figure 4.21. The relative increase is inversely proportional to $k_F\lambda$ as in the case for standard TCO materials as depicted in figure 4.29(b). Furthermore, the slope is larger with smaller $k_F\lambda$ values as well. This is in line with the predicted $1/(k_F\lambda)^2$ proportionality factor in equation 2.52. However, there is an important difference between TiO$_{2-x}$ and the other TCO samples, which can be seen in figure 4.30(a). In contrast to ZnO and In$_2$O$_3$:Sn, the rise in resistivity in undoped TiO$_{2-x}$ does not match with the model of a 3D WL or EEI process! None of the samples exhibit a reasonable good fit to a square root behavior as it would be expected. Also a test with instead $p = 3$ in equation 2.55 does not at all fit to the curvature of the data, as it can be seen in figure 4.30(b).

Therefore, another approach for the increase in resistivity has been utilized. A logarithmic temperature scale has been employed accompanied by a linear fit in the low temperature regime. Principally, three models can predict such a behavior, the WL/EEI effects in 2D (equations 2.54 and 2.57) or the Kondo effect described by equation 2.59. To give a better overview the resistivity

\textsuperscript{14}This holds also for the highest conductive ZnO:Al sample, which is not shown here.
Section 4.7 Low Temperature Effects

Figure 4.30: Investigation of the increase of the resistivity at low temperatures for undoped TiO$_{2-x}$ films which have been presented in full scale in figure 4.21. In (a) a square root temperature scale is selected, as it has been done in figure 4.29(b) for standard TCO films. Whereas in (b) the increase is investigated as function of $T^{3/2}$ following equation 2.55 with $p = 3$.

increase is displayed logarithmically as well (see figure 4.31). This approach works perfectly fine for temperatures below $\sim 10$ K.

A 2 D behavior seems to be quite unlikely in a 250 nm thick film. For example, a 3 D to 2 D transition in In$_2$O$_3$:Sn samples was observed, which had mobilities at room temperature of about 20 cm$^2$/Vs, i.e. around the maximum of the mobilities measured for TiO$_{2-x}$ within this thesis. There a 2 D WL behavior was found within a reasonable large temperature interval, if they had a thickness of 13 nm or lower [OOO83]. For larger films the deviation from an ln($T$) behavior increased successively. To ensure that no 2 D mechanism is responsible for the measured temperature characteristic, several undoped samples with varying thicknesses and substrates, sputtered

Figure 4.31: Low temperature resistivity as a function of the logarithmic temperature, as it is predicted by 2 D WL/EEI or also the Kondo-effect. Only for a better overview, the resistivity data and fit results are plotted also logarithmically. The given $T_{\text{min}}$ values are fit parameters according to equation 2.59.
Chapter 4 DC Electrical Properties of TiO$_{2-x}$

Figure 4.32: Low temperature conductivity decrease of a thickness series of undoped TiO$_{2-x}$ films. They have been deposited on varying substrates during different runs, but possess similar values for $k_F\lambda$ of about 1.4 ± 0.2. In (a) a temperature scale of $T^{1/2}$ has been tested, which represents a 3D behavior of WL or EEI, but no good representation of the curvature of the data can be observed. In contrast, in (b) a logarithmic temperature axes is chosen, fitting to a 2D WL/EEI and a Kondo mechanism. However, a 2D effect can be ruled out, as all curves are described similarly well although the thicknesses encompass one order of magnitude.

In four different runs, were collected in figure 4.32. However, they had all quite similar $k_F\lambda$ values of about 1.4 ± 0.2. In figure 4.32(a) a square root temperature scale predicted by a 3D WL or EEI was tested again. No good representation could be achieved and the fit becomes even worse the lower the temperature is. In contrast, in figure 4.32(b) a logarithmic temperature scale has been used and a linear behavior in the low temperature regime $T \leq 10$ K can be observed. This is remarkable, as their thicknesses vary over one order of magnitude, but exhibit comparable electrical characteristics e.g. the mentioned $k_F\lambda$ values. Thus, a 2D effect can’t be the origin for this behavior. However, the origin of the diluted magnetic moments giving rise to the Kondo effect is not clear as these films had no intentionally doping of magnetic elements, but only oxygen vacancies. At this point it should be noted that special care was taken not to touch the measured substrate surface in any way, leave alone with any metallic tweezer etc.

After discussing the behavior of undoped films, now the effect of additional Nb doping will be investigated. In figure 4.22 the resistivity as a function of temperature was plotted for a selection of Nb doped samples. Already at this point it becomes quite obvious that in contrast to the undoped samples, the resistivity approaching zero kelvin is not changing much. In figure 4.33 the temperature regime below 50 K is depicted more closely. The effects are very small and also highly non trivial. To rule out any possible fitting artifacts but still to be able to compare the different samples, the minimal resistivities have been chosen as reference points in this case. In the left picture, i.e. figure 4.33(a), data from films with thicknesses around 250 nm but varying $k_F\lambda$ values are plotted. For the sake of comparison the best conductive undoped sample with a $k_F\lambda = 1.6$ was included here. A close examination reveals that there are indeed samples with a clear resistivity increase, also with Nb incorporated. The amount of the relative loss of conductivity is comparable to the undoped films with the highest $k_F\lambda$ values depicted in figure 4.30(a), although the absolute resistivity rises are much higher. The best undoped sample is close to $k_F\lambda = 2$ of the worst Nb
Figure 4.33: Resistivity change with temperature in relation to the minimal resistivity. In (a) the same samples were plotted, which could be seen in full scale in figure 4.22(a), i.e. approximately 250 nm thick and varying $k_F\lambda$ values. As comparison the best conductive undoped sample from figure 4.30 was included. In contrast (b) depicts samples with roughly equally and high $k_F\lambda$ values but different thicknesses.

doped film shown here. From this it can be concluded that the lower the room temperature $k_F\lambda$ value of film is, the higher the resistivity increase at low temperatures will be.

Increasing the $k_F\lambda$ further reveals a new interesting effect. Going from $k_F\lambda = 2.5$ over 2.9 to 4.2, the resistivity curve starts to change the slope and even the sign below 10 K. Prior to this, i.e. values of $k_F\lambda$ lower than 2.5 (figure 4.30 and 4.33(a)), the monotonic increase during the cooling down is even intensifying at $T \to 0$ K. But above this limit, the increase starts to saturate and even gets compensated. At $k_F\lambda \sim 4$ the resistivity can reach the minimum value it had before at higher temperatures. This trend is continued to the point that the 2K resistivity falls now below the minimum. Fitting such curves according to BG taking only the values above 100 K into account, the resistivity in the complete temperature regime below 50 K is lying slightly below the 'purely' metallic conductivity.\(^{15}\) This is not the case for samples with a smaller value of $k_F\lambda$, doped or undoped. In figure 4.33(b) a set of several samples with such a high value for $k_F\lambda$ and also varying thicknesses are plotted. All samples show an absolute resistivity minimum at 2 K.

This trend is continued, looking at samples which were doped with 5 at% Nb. In figure 4.34(a) some equally thick (∼250 nm) films are shown, which all feature this small resistivity decrease. The corresponding full scale temperature data was presented in figure 4.22(b). The low temperature data of an additional thickness series is also plotted (figure 4.34(b)). All samples exhibit the same feature of a minimal resistivity at the lowest measured temperature. In the case of the 500 nm sample the utilized excitation current was by a factor of five smaller, but still with a quite significant resistivity decrease.

In principle, this resistivity decrease can be described with a linear fit on a logarithmic temperature scale as well (not shown here) which would correspond to a positive exchange interaction of the

\(^{15}\)As mentioned earlier, in the case of the undoped samples, whose $k_F\lambda$ values are typically below 2, the resistivity minima can perfectly be described by a BG-fit. No restrictions about $\rho_0$ had to be installed even if taking only values above 100 K into account, too.
Kondo effect, i.e., positive sign of $J$ in equation 2.59. However, the slopes are typically so small that on a log scale they could be misinterpreted as a linear relationship. Additionally, the still also relevant effect of a resistivity increase, limits automatically the applicable temperature regime to values below 10 K. So up to now no clear judgment of the mechanism of the resistivity decrease can be given. However, it is unambiguous that, additional to the effect of a small resistivity increase, a second phenomena arises at a high enough value of $k_F \lambda$. This second mechanism kicks in at an even lower temperature, but is able to compensate and even outweigh the previous increase. It should be noted that in comparison with the resistivity change of several hundred percent due to phonon scattering, these low temperature effects in the range of about 0.5 % are quite minute.

### 4.7.1 Magnetic Field

To study the low temperature effects more closely, magneto resistance (MR) measurements provide a very powerful tool to distinguish between different effects. In addition, the effective dimensionality of a sample can be investigated via angular dependency with respect to the magnetic field. One major issue in this respect is to disentangle weak localization (WL) and electron-electron interaction (EEI), as both exhibit the same temperature dependencies, but quite different sensitivities for magnetic fields. As pointed out in chapter 2.2.12, WL exhibits a strong negative MR effect whereas EEI is only barely effected by magnetic fields. As before in the case of the temperature dependency, first the behavior of standard TCO films shall be given.

To do so, the MR data of two samples are shown in figure 4.35. They exhibit a relative pronounced conductivity decrease during cool down in the low temperature regime, as one can see in figure 4.29(b). First important thing to note is that at room temperature there is no MR whatsoever measurable.\footnote{The change is less than $1 \times 10^{-5} \, 1/T$, which is within the error margin.} From this fact it can be concluded that the classical magneto resistance effect (see section 2.2.12) can be neglected in this class of materials.
Figure 4.35: The relative change of the resistivity due to an applied magnetic field at several temperatures of two TCO samples which were plotted in figure 4.29. They exhibit comparable $k_F\lambda$ values and resistivity increases. In (a) the data of the 600 °C heated ZnO sample and in (b) the measurement results of the In$_2$O$_3$:Sn sample are depicted.

At low temperatures, where the corrections upon the resistivity are dominant, a pronounced negative MR effect is visible. The effect is larger the lower the temperature is, which is due to the increased dephasing time. Interestingly, the intensity of the effect is quite different for the two samples, although the relative corrections of the resistivity are quite similar. Looking at the resistivity at 2 K and zero field, both films show roughly an increase of 0.6 % compared to their resistivity minimum at somewhat larger temperatures (see figure 4.29(b)).

For the In$_2$O$_3$:Sn film already at 1 T two third of this increase is suppressed and 90 % at 3 T, suggesting that the WL effect is by far dominating the correction to resistivity. ZnO:Al however exhibit a less strong suppression at 1 T. Additionally, the negative slope around zero field is much smaller in this case. Both facts could for example be explained by a larger contribution of EEI to the complete correction. Nevertheless, the negative MR effect is a clear sign of the impact of WL on the resistivity and is in line with literature for standard TCO materials [DKBG11, BTN06, LCLW10, FKK+10, LL14, SMS+07]. It is also important to note that for all degenerate standard TCO films investigated during this thesis no positive MR could be observed. This holds also for fields up to 9 T and for samples with a higher $k_F\lambda$ value where only a very small conductivity decrease is present.

After the case of degenerate standard TCO films, now the MR behavior of TiO$_{2-x}$ films will be discussed in some detail. To begin with, in figure 4.36 the typical temperature dependent MR curves of an undoped and 250 nm thick TiO$_{2-x}$ film are shown. Two things can be noted at first glance. For one, at temperatures above 100 K there is also in this case no measurable MR effect. This was the case for all TiO$_{2-x}$ films investigated in this thesis, regardless of doping, conductivity or thickness. So it is fair to say that the classical MR effect can be neglected here as well. Secondly, the low temperature behavior of the MR is far more complex in the case of TiO$_{2-x}$ than it is for standard TCO films.
Chapter 4 DC Electrical Properties of TiO$_{2-x}$

Figure 4.36: Resistivity as a function of the applied magnetic field up to 9 T at several temperatures ($T \leq 100$ K) for a typical 240 nm thick, degenerate and undoped TiO$_{2-x}$ film. The $\rho$ vs. $T$ data can be seen in figure 4.26(a).

At least two different mechanisms have to be present here, each having another temperature dependency. There is at least one negative magneto resistance (nMR) effect which already kicks in at relative high temperatures of 100 K and which is slightly intensified cooling down further. Comparing dozens of such MR series, a characteristic temperature of about 20 K can be observed at which a positive magneto resistance (pMR) starts to contribute. However, the temperature dependence of the pMR is much severer. Interestingly, not only the temperature is lower at which the pMR is manifesting itself but also the characteristic magnetic field is higher. At small fields the negative slope gets continuously larger throughout the complete temperature regime. The pMR on the other hand gets much stronger than the nMR at higher fields. These qualitative magnetic field and temperature characteristics are kind of universal for TiO$_{2-x}$ and can be seen in the following graphs as well.

Figure 4.37: MR data for fields up to 1 T with a squared magnetic field scale corresponding to the dependency for a 2D WL mechanism (equation 2.60). Thereby is (a) the data of an undoped TiO$_{2-x}$ film with a thickness of 240 nm, whereas (b) was a 25 nm thick layer (the 40 nm film can be seen in the appendix figure A.4(b)). The full-scale $\rho$ vs. $T$ data was depicted in figure 4.26(a) and the resistivity change can be seen in greater detail in the appendix (figure A.4(a)).
Figure 4.38: Examples of the successful fit of the MR data by a combined model for nMR and pMR. In (a) the case of the 40 nm thick undoped sample and in (b) the 25 nm one are plotted. In figure 4.26(a) the resistivity data can be seen. The results of the MR measurements of the 240 nm film illustrated in figure 4.36 could be described equally well.

The mentioned nMR as function of the temperature is visualized, for example, in figure 4.37. There, the MR up to 1 T is plotted with a squared field scale, which would correspond to the proportionality of MR on field strength in the case of 2D WL (equation 2.60). Although the resistivity increase with the logarithm of the temperature could be interpreted with such a model, the magnetic field dependency does not at all support this. The film thickness does also not significantly influence the curvature of the MR data.

Fields of 1 T should be able to suppress a great part of a WL contribution, however the nMR is much weaker ($\ll 1\%$) than the resistivity increase for these samples. If a better comparison than figure 4.26(a) can provide is needed, the $\rho/\rho_{\text{min}}$ data is plotted in the appendix in figure A.4(a).\textsuperscript{17}

In order to be able to describe the MR measurements a least square fit to a combined model of a nMR and a pMR effect was used. The summation of the $s-d$ exchange, or Kondo-effect and the two-band model, i.e. equation 2.62 and 2.63 results in

$$\frac{\Delta \rho_{\text{nMR+pMR}}}{\rho_0} = -a^2 \ln(1 + b^2 B^2) + \frac{c^2 B^2}{1 + d^2 B^2}. \quad (4.1)$$

Indeed, using these four parameter equation, all MR measurements at degenerate TiO$_2-x$ films with and without doping could be described very well. It is worth mentioning that weak antilocalization WAL possesses also a pMR but its characteristics are completely different from the one of the effect which is present here. For instance, the MR effect of WAL is relevant only at even smaller magnetic fields ($\ll 1\,\text{T}$) than the WL, whereas here the pMR needs at least 1 T to start and even 9 T are not enough for a complete saturation.

\textsuperscript{17}A 2D behavior can also be ruled out, because experiments rotating the sample in the magnetic field revealed a maximum difference between the orientations of only 0.3%. Such an isotropic nature of the MR effect is in contrast to a 2D behavior.
Figure 4.39: MR data at 2 K for different undoped TiO$_2$$_{−x}$ series. In (a) measurements are visualized for the samples from different runs, whose low temperature resistivity increase data are depicted in figure 4.30(a) and fitted by a Kondo-model in figure 4.31. In (b) displays similar MR data of a single O$_{2PP}$ series.

The temperature series presented so far revealed that the MR data at 2 K along the full field strength of 9 T represents quite well the complete magnetic field response of a sample. Therefore, the 2 K data of several samples will now be compared to get an idea which are the dominant factors influencing the MR behavior and how large the differences can be.

In figure 4.39 this was done for several undoped TiO$_2$$_{−x}$ films with similar thicknesses. Comparing samples from different runs or also a O$_{2PP}$ series of one run reveals that neither the $k_F\lambda$ value at room temperature nor the one at 2 K is in this case a good benchmark for the trend of the MR curves. For all undoped films prepared and investigated here, also no other electrical parameter like charge carrier density, mobility or the mean free path, showed a definite or clear connection to the MR behavior. Even the thickness series exhibited once a clear decreasing pMR contribution.

Figure 4.40: Results of the MR fits of the undoped O$_{2PP}$ series. In (a) the fitting parameter $b$ as function of the inverse temperature is depicted to prove the validity of the model utilized to describe the nMR. In (b) the calculated ratio of pMR/nMR at 9 T is shown to illustrate the increasing importance of the pMR at low temperatures.
Figure 4.41: Results of MR measurements on Nb doped TiO$_{2-x}$ films with relative high values of $k_F\lambda$. In (a) an example of measured MR data at a film doped with 1 at% Nb including the fits as dashed lines is given. Two samples with higher Nb concentrations are included in the appendix (figure A.5). In (b) the calculated pMR at 9 T and 2 K is shown as function of the $k_F\lambda$ value at this temperature. It visualizes that the almost exclusively positive character of the MR in these films is quite strongly depending on the Nb content, as it can be seen in.

with the thickness, once a raising one. Obviously there are several different effects and transitions which alter the amount and shape of nMR and pMR in undoped TiO$_{2-x}$. Nevertheless, in figure 4.39(b) one effect seems to emerge, the O$_{2PP}$ within one run. The amount of nMR is consistently decreasing with increasing the amount of oxygen in the regime where the other electrical parameters are not changing dramatically and a very high mobility is obtained (see for example figure 4.5 and 4.8). The strong increase in the amount of charge carriers and the beginning deterioration of the mobility resulting in a jump of $k_F\lambda$ marks also a transition in the MR behavior.

In figure 4.40 some results of the MR fits of the O$_{2PP}$ series are depicted. On the right hand side the calculated ratio of pMR and nMR at 9 T is plotted. Thereby, it is illustrated that only below 10 K the pMR increases and starts to dominate. The stacking sequence of the samples following the O$_{2PP}$ can clearly be recognized (except the lowest value of 65 %). The graph on the left side shows the fitting parameter $b$ of equation 4.1 as a function of the inverse temperature. As expected from theory (equation 2.62) the graph visualizes a linear relationship. Thus the nMR data is not only described mathematically quite well by this model, but it is also physically consistent.

Now the alteration of the MR upon Nb doping shall be shortly discussed. Samples with a not to strongly deteriorated mobility, i.e., $k_F\lambda$ values not much lower than the maximum achieved with the respective Nb concentration, have exhibited no increase in the resistivity at small temperatures. Not surprisingly, such samples with no resistivity increase also show nearly no nMR anymore.

A positive MR contribution is absolutely unusual for a degenerate TCO material not to mention an almost exclusive one of several percent. The same two band pMR model can successfully applied, which is shown for a 1 at% Nb sample in figure 4.41(a). Two additional examples of films doped with 2.5 at% and 5 at% Nb are included in the appendix (figure A.5).

In figure 4.41(b) the extracted pMR is plotted against the $k_F\lambda$ both at 2 K. It is easy to see that
the intensity of the pMR is inversely proportional to the Nb concentration. This suggests that one of the two levels necessary for this pMR effect is at least strongly effected by the Nb concentration. Increasing the Nb content would primarily increase the population of this one band. In this way it would weaken the relative intensity of this effect, leading to a smaller relative pMR.

To summarize, in TiO$_2$-$x$ (Nb doped and undoped) effects are present which give rise to negative and positive magneto resistance, whereas only nMR is known typically for standard TCOs without magnetic impurities. It could be shown that the nMR in TiO$_2$-$x$ can be better described by a $s-d$ band exchange, or Kondo-effect than by weak localization as in the case of common TCOs. The additional pMR can be attributed successfully to a two-band interaction model. Increasing the Nb concentration diminishes the nMR contribution but also the maximum relative pMR is reduced significantly, implying that the doping leads to a changed population ratio of the two bands. In other words, the introduced charge carriers are solely in one band and, therefore, the effect based on the two band interaction becomes less important.

### 4.8 Summary, Conclusion and Outlook

In this chapter the DC-electrical properties of reactively sputtered TiO$_2$-$x$ thin films with and without Nb doping have been investigated. Directly at the start, a remarkable difference between TiO$_2$-$x$ and standard TCO materials has been shown. The TiO$_2$-$x$ layers exhibit a very high resistivity in the as deposited state. Upon annealing at temperatures of 250 °C to 300 °C the conductivity increases by several orders of magnitude. In contrast typical TCO materials are difficult to prepare as an amorphous film. However, their conductivity is in comparison only slightly worse than their crystalline counterpart, e.g., In$_2$O$_3$ shown in figure 4.17 and in [HYK96, Ros91]. Like also Hosono pointed out, a great overlap of the orbitals forming the conduction band minimum is required for high mobility. The tremendous drop in resistivity upon crystallization proves a high sensitivity of the overlap to the structural order for TiO$_2$-$x$ films [HYK96].

The necessary crystallization temperature can be controlled by the amount of oxygen deficiency. The less oxygen is provided, or the more Nb is included, the higher the necessary temperature will be. This tendency has been utilized by Hoang et al., whose highly sub-stoichiometric films crystallize at temperatures up to 350 °C. A non-conductive seed layer of stoichiometric TiO$_2$ can reduce it to 300 °C [HYH+08]. However, the films prepared here require even lower temperatures and can refrain from using a seed layer. This result can be explained as the oxygen deficiency is much smaller in these films and as a consequence the crystal structure is not so heavily impeded (see section 6.3). Additionally, capped films prepared with O$_{2PP}$ values below 50 % do not show much of an improvement up to temperatures of at least 500 °C. In section 6.3.1 it will be shown that highly sub-stoichiometric films stay amorphous, as long as they are capped. Thus, films in which too little oxygen is incorporated can not form a crystal of regular TiO$_2$ octahedra. Therefore, I assume that the films of Hoang et al. need some oxygen of the residual atmosphere to diffuse into the film to be able to crystallize, which of course is highly temperature dependent. It has been shown that the Si$_3$N$_4$ capping layer can efficiently prevent any unintended oxidation and
thus conductive films with a higher $O_{2pp}$ value during the sputter deposition can be realized. If not protected, oxygen can diffuse into the film, especially via the grain boundaries, and isolate the polycrystals by creating potential barriers. This was for example also proposed by Rothshild et al. via *in situ* electrical measurements of the annealing in oxygen or vacuum at 350 °C [RKL+03].

<table>
<thead>
<tr>
<th>Nb</th>
<th>$\rho_{RT}$ ($\mu\Omega cm$)</th>
<th>$\mu_{RT}$ (cm$^2$/Vs)</th>
<th>$n_{RT-2K}$ ($10^{19}$ cm$^{-3}$)</th>
<th>$\rho_{2K}$ ($\mu\Omega cm$)</th>
<th>$\mu_{2K}$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>3600</td>
<td>19</td>
<td>9.1</td>
<td>1800</td>
<td>50</td>
</tr>
<tr>
<td>1 at%</td>
<td>1400</td>
<td>15</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.5 at%</td>
<td>720</td>
<td>11</td>
<td>79</td>
<td>280</td>
<td>27</td>
</tr>
<tr>
<td>5 at%</td>
<td>550</td>
<td>8.6</td>
<td>130</td>
<td>200</td>
<td>24</td>
</tr>
</tbody>
</table>

*Table 4.3:* Electrical properties (rounded to two significant digits) of the best conductive TiO$_{2-x}$ films produced in the framework of this thesis. They all have a similar thickness around 250 nm and a Si$_3$N$_4$ capping. Besides the room temperature (RT) values also the resistivities and mobilities at 2 K are given, illustrating the large phonon contribution (charge carriers are practically constant).

In table 4.3 the electrical properties of the best conductive TiO$_{2-x}$ films are listed. In comparison to literature of undoped TiO$_{2-x}$ layers, the films here are exhibiting very low resistivities and have been prepared with techniques much better suited for industrial and practical applications. These much better conductivities have been achieved without using RF-sputtering, pulsed laser deposition, heated or special substrates, post deposition annealing at high temperatures not to mention reducing atmospheres like H$_2$ or vacuum [TPS+94, YIM10, MBC+02, YLKM08]. Even single crystalline samples exhibited more than two orders of magnitude lower conductivities [JVM+12]. In the case of not too large amounts of oxygen vacancies the mobility stays constant in contrast to other reports [JVM+12] and can reach quite high values up to 19 cm$^2$/Vs at room temperature.

Also in case of additional Nb doping the precise selection and control of the $O_{2pp}$ and the usage of a Si$_3$N$_4$ capping layer resulted in superior conductive films compared to literature [JKZ11, HYH+08]. With PLD on glass and annealing at 500 °C in hydrogen some films reached mobilities of 2.6 cm$^2$/Vs [HUF+07] up to 8 cm$^2$/Vs [HUN+07] with the usage of a doping of 6 at%. Using PVD on single crystals of SrTiO$_3$ at 550 °C with a similar amount of Nb like utilized here, only slightly higher mobilities of 10 cm$^2$/Vs instead of 9 cm$^2$/Vs here could be gained [Zha27]. Thus, only in combination with single crystalline substrates and much higher temperatures other authors could prepare with PVD techniques similar or slightly better films than prepared here.

The high quality of the films produced here is, furthermore, supported by comparing them with films which have been prepared via sputtering as well. Yamada *et al.* reported, for example, TiO$_{2-x}$:Nb layers using a RF-sputtering process with annealing at 400 °C in a hydrogen atmosphere and achieved maximally a mobility of 3.6 cm$^2$/Vs with the help of a seed layer [YHJ+09]. The same group achieved 950 $\mu\Omega$cm with a mobility of 3.9 cm$^2$/Vs using DC-sputtering of the same target composition, more than one order of magnitude lower deposition rate and 600 °C with a hydrogen atmosphere as annealing process [YHH+07, YHH+08]. They observed a decrease of the mobility with increasing oxygen content. This is a similar trend like it has been presented before (see figure 4.8), therefore, the generation of Nb$_2$O$_5$ is also in their case a reasonable explanation.
Sato et al. used a slightly reduced TiO$_{2-x}$ target with Nb$_2$O$_5$ pellets placed on top and a post-deposition annealing in vacuum at 400 °C. The films exhibited a much worse resistivity of 1300 µΩcm and with a Nb concentration of 6.4 at% they claim a doping efficiency of only 65% [SAKOS08]. In a next step they varied the Nb concentration up to 9.5 at%, added hydrogen during the sputter process and employed a post-deposition annealing at 500 °C, resulting in a still higher minimal resistivity of 630 µΩcm and an even smaller doping efficiency [SST+10].

Oka et al. employed quite recently in 2014 a feedback loop controlled reactive DC-sputtering technique within the transition regime, like I did as well. With a higher Nb concentration of 7 at% and annealing at 600 °C they reached 720 µΩcm, which is despite the higher concentration and temperature significantly worse. They support the given proposition of a very high importance of a precise control of the O$_{2pp}$ and the non-linear relationship between resistivity and oxygen content [OSJ+14].

The precise control is necessary to provide the very minute degree of sub-stoichiometry, i.e. oxygen deficiency, which results in a degenerate semiconductor behavior. This is because, at low oxygen vacancy concentrations a shallow defect level is formed [JVM+12]. If however, the deficiency is too large, Ti interstitials can form and lead to small polaron hopping with a very low and temperature activated mobility [MW09]. Such a temperature activated mobility could be observed here as well for lower O$_{2pp}$ values, although the exact predictions of the SPH theory have not been realized. With this topic the metal insulator transition of TiO$_{2-x}$ is interrelated. The carrier concentration, above which metallic, i.e. degenerate semiconductor, behavior has been observed is in line with literature, albeit much higher than the Mott-theory predicts (see figure 4.11). Thus, it can be concluded that the MIT in TiO$_{2-x}$ is not solely a Mott-type and the reason for this will be discussed in the last chapter. In contrast, the Mott model works quite well in the case of the standard TCO materials.

Thereafter, another difference between degenerate TiO$_{2-x}$ and the other TCOs has been revealed. TiO$_{2-x}$ exhibits a tremendously, around one order of magnitude, stronger temperature dependency than the standard oxides. The mobility at 2 K can easily be a factor of three higher than at room temperature, reaching values of 50 cm$^2$/Vs for undoped films and 25 cm$^2$/Vs for ones doped with 5 at% Nb. It should be noted that even these comparable high mobilities are up to two orders of magnitude lower than predicted by ionized impurity scattering (IIS) theory at the corresponding charge carrier concentrations (see figure 2.6). Moreover, the mobility is not a direct function of the free electron density. Even when looking at one doping level, the mobility gets reduced with lower carrier concentrations in contrast to the IIS theory. Thus IIS is not the limiting factor in TiO$_{2-x}$ although it is for high quality standard TCOs.

The temperature behavior of the resistivity could very successfully be described by acoustic phonon scattering utilizing the BG-formula for TiO$_{2-x}$ and standard TCOs as well. However, in contrast to them, TiO$_{2-x}$ (with and without Nb) can be represented much better applying $n = 3$ instead of $n = 5$. Thus, the $d$-band character of the conduction band of TiO$_{2-x}$ can be observed through the changed mechanism of the phonon interaction [Cvi11]. The resulting parameters of the fit fulfill very nicely the predicted relationships given in section 2.2.9 and equation 2.40. It could be shown that the prefactor $A/T_{Debye}$ for example is anti proportional to the charge carrier density.

126
of the film in the case of TiO$_{2-x}$ and standard TCOs as well. This doubles the beneficial effect of higher charge carrier densities upon the room temperature resistivity of TiO$_{2-x}$. The calculated electron-phonon coupling constant is indeed more than one order of magnitude larger for TiO$_{2-x}$ than for ZnO etc. as it has been suggested by the larger $\rho_{300K}/\rho_{2K}$ ratio.

The low temperature behavior of the degenerate TiO$_{2-x}$ films reveals some remarkable differences in comparison to the other TCOs. A resistivity increase was detected in case of undoped TiO$_{2-x}$ films, however the data does not match to the predicted relationships of $\rho$ with temperature and magnetic field of weak localization. In typical TCOs the WL effect is strongly present as it has been shown here and also proven by several authors [DKBG11, OMI82, AJG+06, GLL+13, LL14, MRG+02]. In contrast the resistive increase in TiO$_{2-x}$ samples with $k_F\lambda$ values below 4 can be explained in terms of the Kondo effect. For such samples also a nMR contribution is detected and can consistently be described by the prediction of a Kondo or $s-d$ interaction effect. Therefore, nMR behavior is another aspect, besides the $s-d$ phonon scattering, where the $d$-band character of TiO$_{2-x}$ dominates the transport properties. For doped TiO$_{2-x}$ films with $k_F\lambda$ values above 4 an additional till now not known effect reduces the resistivity lowering the temperature below 20 K. So no saturation of $\rho$ is present in these cases and the lowest resistivity is measured at the lowest investigated temperature. However, with a maximal influence below 0.5% it is rather minute. The magnetic field behavior has exhibited a pMR contribution with a high temperature and magnetic field sensitivity in all degenerate TiO$_{2-x}$ films. Samples with no resistivity increase at low temperatures show nearly no nMR but a strong pMR dependency. At 9 T and 2 K this can be 6% large and is clearly reduced by increasing the Nb concentration. The pMR can be described very well with a two-band model suggesting an additional impurity band, affected by the Nb concentration.

In short: In this chapter degenerate TiO$_{2-x}$ samples with and without Nb doping have been presented with outstanding electrical performances for sputtered thin films on glass. The electrical transport in different temperature regimes has been investigated in great detail and large qualitative and quantitative differences in comparison to standard TCOs have been found. Most of these differences have their origin in the $d$-band nature of the conduction band minimum of TiO$_{2-x}$ in contrast to the $s$-band of typical TCOs.

Several further research topics evolve from the achieved results. In order to improve the TCO performance further the better understanding of the annealing behavior is a crucial task. Especially, the usage of a Si$_3$N$_4$ seed and capping layer promises better conductivities and the possibility to utilize the beneficial effects of higher annealing temperatures. The search for a different seed layer which would lead to a c-axis textured anatase TiO$_2$ film is very promising as this would increase the measured lateral mobility due to the anisotropy of the effective masses (cf. table 1.2). Furthermore, the next higher doping regime up to 10 at% should be investigated thoroughly. The conductivities, which are expected to be achievable there, would be really competitive to standard TCOs.

From a fundamental research point of view, the Nb regime up to 1 at% is also of great interest as it could be shown that several characteristics, like the mobility as function of the employed O$_{2PP}$, change drastically compared to undoped films. A more detailed investigation of this lowly
doped regime is expected to give further insight into this transition. Measurements of the electrical characteristics at even lower temperatures\(^ {18}\) should be performed to investigate the observed phenomena of the continuously reducing resistivity below the temperature where the BG law for metals has been saturated.

Similarly precise and detailed studies like performed in this thesis could be performed with Ta instead of Nb as some experiments and calculations suggest a worse, a similar, and some a better performance of Ta doped TiO\(_2\) [CXM\(^ {+11}\), HFU\(^ {+05}\), MGR\(^ {+15}\), HBTP\(^ {12}\)]. Also tungsten is quite promising candidate [CXM\(^ {+10}\)]. Talking about different dopants, the usage of several other elements in combination with the precise O\(_{2PP}\) control during the preparation process and protecting afterwards could be of large interest to investigate if a \(p\)-type conductivity in TiO\(_2\) is possible or not [KE\(^ {11}\), ABJ\(^ {15}\)].

\(^{18}\)For such measurements, the preparation of small structures would be the first challenge which has to be tackled. Van der Pauw samples with sizes of 1 cm \(\times\) 1 cm can not be measured reliably and with a good enough signal-to-noise ratio at temperatures well below 2 K.
AC Electrical Properties of TiO$_2$

In this chapter the results of AC electrical measurements on capacitors will be shown. First, some general remarks concerning the frequency dependencies will be given and afterwards the resulting dielectric functions of undoped TiO$_{2-x}$ films, followed by the effects of varying doping elements. Thereafter, all dielectric constants ($\epsilon_{st}$) will be presented and the possibility of using sputtered TiO$_{2-x}$ films as supercapacitors including the origin of the very high dielectric constants will be discussed.

5.1 Frequency Dependency at Undoped TiO$_{2-x}$

The fabricated capacitative sandwich structures have been investigated by different setups and across a large frequency range. Figure 5.1 depicts an example of the low frequency behavior of an amorphous undoped TiO$_{2-x}$ film measured by the ETO (see section 3.2.3). As the main focus of this setup is the precise resistivity measurement, by applying a lock-in technique, only a very limited number of data points exist. Figure 5.1(a) shows the real part of the resulting impedance of the device. At low frequencies the leakage resistivity dominates the response of the device. By increasing the frequency, the capacitative response becomes increasingly important. Because of

![Figure 5.1: Frequency dependency of the impedance measured by the ETO on undoped TiO$_{2-x}$. In (a) the real part of the impedance is plotted as an example, whereas in (b) the imaginary part as function of the real part is shown, known as Nyquist plot.](image)
the charging and discharging of the capacitor, the measured real part of the resistivity decreases until there is no real part of the resistance. On the other hand, the imaginary part has a maximum (see figure 5.1(b)). The displayed fit proves that the response of the TiO$_{2-x}$ capacitor is well described by the model of an ideal capacitor with a parallel resistor. With the known geometrical dimensions of the devices an $\varepsilon_{st}$ of $\sim 50$ is found for several different undoped TiO$_2$ and as deposited films around the transition point. How different conductivities and dielectric constants alter the frequency characteristic of the impedance has been demonstrated in section 3.3.2.

A close look at the above data reveals that for small frequencies the data does not fit perfectly. Indeed, such deviations from the ideal behavior could often be observed. In principle one frequency would be sufficient to calculate the dielectric constant. However, already at this point it becomes clear that in order to gain reliable results for the dielectric constant, the complete frequency behavior has to be investigated. The extension of the accessible frequency range is thus of high importance to be able to determine a characteristic and trustworthy value for $\varepsilon_{st}$.

Figure 5.2 displays the results of the frequency dependent permittivity measured by HP impedance meter. The values are calculated at every frequency and are not the result of a fit of the real and imaginary part of the impedance as it has been the case in figure 5.1. Therefore, only regions with a roughly frequency independent permittivity should be used to determine the values for $\varepsilon_{st}$. This corresponds to the mid kHz regime of $\omega$ typically.

Several measuring artifacts can lead to a misinterpretation of the data necessitating reliability checks, for instance different sizes of the capacitors or comparisons between two devices on the
same substrate. The mentioned fact that the low frequency regime behaves often non ideally is very prominent to see now. All curves exhibit a slight increase when lowering the measurement frequency. This is especially relevant for the films sputtered within the transition regime of the oxygen hysteresis (see section 3.1.2). The comparison with this sample reveals the origin of this artifact: The ohmic conductivity. Although they all have a comparable high resistivity, the "90 %" sample shows by far the lowest resistivity resulting in a steep increase of the calculated permittivity (see equation 2.71). Thus, another drawback of the ETO is revealed. As the frequency range is limited to 0.5 Hz to 180 Hz and the resistivity has to be low enough in order to effectively and reliably measure a sample (see section 3.3.2), the permittivity can easily be overestimated.

Several other artifacts originating from the setup can be seen as well, e.g., the kink at every sample at $\omega = 300$ Hz and around $4 \times 10^5$ Hz. The most prominent feature of these curves is the strong resonance peak around 10 MHz. However, this is not primarily a measuring artifact but a result of the device characteristic. The origin of this resonance peak is an extrinsic property and not linked to any intrinsic material polarization mechanism which have been described in section 2.3.1. This is proven by comparing different capacitor areas, which result in different absolute values of the capacitor. Taken together with the small inductance $L$ of the electrodes and connection leads, the capacitor constitutes a resonant circuit with a resonance frequency $\omega_0 = 1/\sqrt{LC}$. The proposed shift to lower frequencies using larger areas, which result in a larger capacity $C$, could indeed be observed (e.g. figure A.6).

Regarding the results for the $\epsilon_{st}$ in undoped, as deposited films, samples sputtered at low oxygen contents around the transition region exhibit similar permittivities like they have been measured with the ETO. Values of 45 emerge in the stable frequency regime. Increasing the oxygen flow further into the oxidic regime, $\epsilon_{st}$ increases quite severely up to 80 till 90. These are very high values already and open the possibility to employ TiO$_2$ as a dielectric material in the microchip industry. The structure of sub-stoichiometric TiO$_{2-x}$ films will be investigated in section 6.3. However, the structure of these very oxidic TiO$_2$ samples will be discussed directly in order to understand the high values of $\epsilon_{st}$.

Figure 5.3 depicts the XRD-GI pattern of the same series of undoped TiO$_2$ films before annealing. Samples sputtered at the transition point are completely amorphous, as aforementioned and can be seen, e.g., in figure A.10. However, increasing the oxygen flow, some crystallinity can be detected for these films with thicknesses around 400 nm. The larger the oxygen flow is, the higher the rutile reflex becomes which is accompanied by a smaller anatase contribution at very high O$_2$ fluxes. Although the dielectric constants, known from literature [Par61, LHM94, BG78, CKG+99], scatter severely, they are consistent in terms of that the rutile phase exhibits larger values than the anatase phase.

The reason for the occurrence of the rutile phase can be understood by the investigation by Löbl.
Figure 5.3: XRD-GI pattern of undoped TiO$_2$ films before annealing. The oxygen flow at the transition point was 3.9 sccm. A and R are denoted as the literature positions of the anatase and rutile reflexes, respectively.

et al. regarding the nucleation and growth of TiO$_2$ [LHM94]. Löbl et al. proposed a guideline for the formation of amorphous, anatase, and rutile phases for different energies of the arriving particles and the substrate temperature. It can be condensed in the principal tendency that a higher energy of the arriving particles lead to a higher probability of crystallization in the rutile phase. Exactly this trend is present when increasing the oxygen content due to a larger amount of oxygen ion bombardment. This effect is enhanced by the relative low pressure of 0.4 Pa during the deposition. Additionally, the deposition time has to be increased in order to compensate for the reduced sputter rate at larger oxygen fluxes, which in turn leads to a higher substrate temperature because of the presence of a plasma.

To investigate the dielectric constant of the anatase phase the samples have been annealed at 300 °C for 2 h as it has been done for the conductive TiO$_{2-x}$ samples. The change in the crystalline structure can be seen in figure 5.4 in comparison with figure 5.3. Obviously, the amorphous parts of the samples have been crystallized into the anatase modification. The contribution of the rutile phase has increased marginally and only if there was a rutile portion before the annealing. However,

Figure 5.4: XRD-GI pattern of undoped TiO$_2$ films after annealing at 300 °C. The oxygen flow at the transition point has been 3.9 sccm.
all samples besides the two highest oxygen fluxes show afterwards a by far too low resistivity, especially after subjecting them to a measuring voltage of a few millivolt. Unfortunately, also the results of the two samples with $\rho > 1 \times 10^2 \Omega \text{cm}$ are not beyond any doubt either with values between 100 and 1000.

The mixed phases and the too low resistivities of several devices lead to an inconclusive result for the annealed TiO$_2$. In contrast, the amorphous phase of TiO$_2$ reveals reproducibly a value slightly below 50 which increases with the amount of rutile in the as deposited films.

## 5.2 Effects of Doping

The effects of several different doping elements on the permittivity as function of the frequency have been tested. The combinations have been V, Nb, In$_{90}$Sn$_{10}$ and Nb with In$_{90}$Sn$_{10}$ and they have been prepared by serial co-sputtering in the COSMOS system (see section 3.3.1).

V has been used in order to increase the rutile content which was based on previous studies in the institute [S. 14, L. 14]. The combination of In and Nb was used by some authors to produce TiO$_2$ with **colossal dielectric constants** of several ten thousands. However, they used conventional solid-state reactions involving firing processes at 1400°C for 10 h or expensive preparation techniques like pulsed laser deposition (PLD) on Pt substrates [HLW$^{+13}$, GCW$^{+14}$]. In order to investigate the effects evolving from the usage of sputtering and low temperature annealing and to separate them from the doping effect, the two dopants Nb and In have been tested solely as well. The doping concentrations for all elements have been estimated by energy-dispersive X-ray spectroscopy (EDX) measurements on Cr doped TiO$_2$ conducted by Schmidt 2014 [Sch14]. Therefore, the same sputtering parameters had been used and the power of the secondary cathode adapted according to the relative sputter yields of the doping elements [Nat27].

By increasing the oxygen flow the deposition rate of the main Ti target is reduced, which is why an increasing doping concentration has been detected. Starting at the transition point with $3 \pm 0.3$ at% up to $6.2 \pm 0.2$ at% at the highest used oxygen flow, roughly 6 sccm above the transition. The shifts of the hystereses have been rather minor in comparison to the range of oxygen flows applied in these studies.

Doping with V has not altered significantly the crystal structure prior the annealing (see figure 5.5(a)) in comparison with the undoped case in figure 5.3. Also with V higher oxygen flows exhibit a significant rutile portion with similar intensity ratios and changes with oxygen. On the other hand, the permittivity scatters between 35 and 45 for all samples except the one with the highest O$_2$ flow which has no clear dielectric characteristic with a value of roughly 60. The crystallinity after annealing follows the same tendency as it has done for the undoped case, i.e., a pure anatase film at low oxygen flows and an unaltered rutile contribution (see figure 5.5(b)).

---

$^4$Eventually some reaction with the Al electrodes can lead to a reduction of the TiO$_2$ layer. One monolayer of Al$_2$O$_3$ could introduce oxygen vacancies in the order of $1 \times 10^{19}$ cm$^{-3}$ in a 400 nm thick film. However, Au electrodes have led nearly always to shortcuts often even before the annealing, due to a very large diffusion constant of Au in TiO$_2$. 

RWTH Aachen University

133
The permittivity behavior has changed fundamentally after annealing which can be seen in figure 5.6. First, it should be noted that all capacitors could successfully be measured. Additionally, all devices exhibit high resistivities in the order of $10^5 \Omega \text{cm}$ to $10^4 \Omega \text{cm}$, except the one with the lowest oxygen pressure. The "4.5 sccm" sample is one order of magnitude higher in resistance than the surrounding samples which could be linked with the lower increase of the permittivity at smaller frequencies. Noteworthy, the data of several curves exhibit clearly distinct regions of stable permittivities indicating more than one time constant. This phenomenon will be discussed in more detail in the next section. Films sputtered at the transition point or slightly below exhibit $\varepsilon_{\text{rel}}$ values in the range of 1000 to 2000. Investigating the structure after the annealing it can be observed that higher oxygen flows reduce the crystal quality of the anatase but the rutile contribution is not increased from the as-deposited state (see figure 5.5).

Employing Nb instead of V doping, nearly no quantitative alterations upon the structural or electrical properties of the devices in the as-deposited state can be detected. This includes high resistivities in the order of $10^3 \Omega \text{cm}$ in the anodic regime and $\varepsilon_{\text{rel}}$ values between 40 and 80. Structurally, a clear rutile contribution at increasing oxygen flows can be seen again (see figure A.7(a)). The as-deposited permittivity measurements possess quite a few measurement artifacts, thus, a
Figure 5.7: The permittivity as function of the frequency of Nb doped and annealed TiO$_2$ films. The transition point has been slightly higher in this case at 4.2 sccm. This shift is consistent with the trend of the Nb alloyed Ti targets employed for the TCO samples (see figure 3.5(b)). The reason is a minor sputter yield amplification effect of Nb.

A more detailed description is not feasible. After the annealing, the changes are quite severe with respect to the electrical properties. This includes a large drop of the resistivity for all O$_2$ flows down to the $10^4$ $\Omega$cm range which is at least two orders of magnitude smaller than the comparable values of V doped films.

However, a clear trend with the O$_{2PP}$ can be observed in this case which is exactly opposite to the expectation and the undoped case. In the transition region the resistivities have been larger (roughly $10^3$ $\Omega$cm). So far, there is no clear explanation for this behavior. The crystal structure, for example, follows in principle the usual trend of transforming the amorphous component into anatase and a stable rutile intensity (see figure A.7(b)). The permittivity of the annealed, Nb doped samples can be seen in figure 5.7. Despite the relatively small resistivities all devices could be measured reliably. A clear trend with the O$_{2PP}$ of the permittivity can also be seen, which strengthens the effects raised by the V doped series. The lower the oxygen flow is, the higher $\varepsilon_{st}$ becomes. They are ranging between remarkably large values of 1000 and 3100.

Figure 5.8: Permittivity as function of the frequency for InSn doped TiO$_2$ before the annealing. Low and very high oxygen flows can lead to higher permittivities, however, with different frequency dependencies.
The doping with InSn results in similar crystal structures in the as-deposited condition as the other elements do. They are partially rutile with no anatase contribution as can be seen in the appendix in figure A.8(a). It does not lead to much different permittivities before the annealing in comparison to the undoped and the other doped cases as well which are shown in figure 5.8. Also in this case, the majority of the devices exhibit values around 40. However, this series demonstrates profoundly that already in the as-deposited case of doped films two possibilities exist to gain larger \( \epsilon_{st} \) values. One way is the employing of large oxygen flows which lead to films with a certain rutile contribution. The second way is the sputtering in a slightly oxygen deficient atmosphere.\(^5\) The frequency dependencies, however, are quite different. In the sub-stoichiometric case a large part of the higher permittivity is lost when increasing the frequency. After annealing, the samples possess still high resistivities except from the film with the lowest \( O_{2pp} \) of 80 % which had to be omitted. The resistivities increase successively from \( 3 \times 10^3 \Omega \text{cm} \) at 90 % to \( 3 \times 10^5 \Omega \text{cm} \) at the largest oxygen flow. The maximal permittivity has been 660, whereas at the highest oxygen flow only a minor increase to 90 has taken place. Thus, in comparison with the Nb doped films, the enhancement of the InSn doping is much weaker. Regarding the crystal structure, the anatase phase is, in this case, reduced even more intensely by employing larger oxygen flows. The rutile contribution on the other hand is also nearly not affected by the annealing process.

As the last system, now the combination of InSn and Nb will be investigated as by doping with In-Nb the colossal dielectric constants could be produced in previous experiments by different approaches [GCW\(^{+14}\), HLW\(^{+13}\)]. In figure 5.10, the structure of these films before and after the annealing are shown. In contrast to all other series before, the structures are amorphous after deposition and stay like this even after the heat treatment. Only the largest oxygen flows seem to have a small tendency towards the rutile phase, but this is nothing in comparison to all the other films. As no dopant alone shows such a strong influence compared to the undoped case, the stabilization of the amorphous phase is remarkable. The most straightforward explanation is that the impurity concentration has been simply too high to enable any crystallization. By reducing

---

\(^5\)The DC-resistivities of all used devices have been very high, between \( 10^4 \Omega \text{cm} \) and \( 5 \times 10^6 \Omega \text{cm} \), making a conductivity artifact as reason for the high permittivity very unlikely.
Section 5.3 Eligibility as Supercapacitor and Discussion

The auxiliary power and thereby the doping concentration, this explanation could be tested. The permittivities in the as-deposited state show again frequency stable values of about 40 and high resistivities ranging from $1 \times 10^5 \Omega \text{cm}$ to $7 \times 10^8 \Omega \text{cm}$. This has changed tremendously after the annealing. Several samples have become completely conductive and also the measurement quality of the remaining ones deteriorated sharply. The resulting, questionable values are in the range of few hundreds.

However, no indications of similar high permittivities of few thousands, which are present in the Nb and V series, could be seen, not to mention the several ten thousands proposed by Gai et al. and Hu et al. [GCW+14, HLW+13]. A possible explanation for this discrepancy is that a crystalline structure or at least a long range diffusion is mandatory for this colossal dielectric constant in In-Nb doped TiO$_2$. Employing lower dopant concentrations and higher annealing temperatures are possible ways to realize high permittivities by sputtering also in this system by overcoming the strong crystallization impeding character of the dopants.

5.3 Eligibility as Supercapacitor and Discussion

In this section the results of all series will be combined to elucidate the potential of sputtered TiO$_2$ films as a dielectric for supercapacitors. First, the data of the devices in the as-deposited state are shown in figure 5.11. At low oxygen flows all samples are amorphous and the values scatter between 40 and 50. Thus, in the amorphous and as-deposited phase no doping element effects the permittivity, despite their concentration of about 3 at%. All doping series contain samples with a small rutile contribution which increases with the oxygen flow. Nevertheless, the permittivity stayed typically around 40 in doped TiO$_2$ except the ones with the largest oxygen flows. This is noteworthy, as the undoped films reach higher $\epsilon_{st}$ values in the mid oxygen regime than the doped ones although similar large rutile contributions are present. It can be concluded that the beneficial effect of the rutile phase is weakened by the doping in the as-deposited state.

The changes as a result of the annealing are numerous and very interesting and the $\epsilon_{st}$ values are
Figure 5.11: The $\varepsilon_{\text{at}}$ values determined by impedance spectroscopy for all TiO$_2$ films as function of the respective O$_{2\text{pp}}$ in the \textit{as-deposited} state.

summarized in figure 5.12. Most importantly, films could be prepared by sputter deposition and modest temperatures on glass substrates which reach high permittivities of 1000 to 3000. It is essential to remember that the resistivities of these films with very high dielectric constants are well above $10^2 \Omega \text{cm}$. Therefore, TiO$_2$ films could be prepared by simple reactive sputtering which show great potential as supercapacitors, especially, if not to high frequencies are applied.

This could be achieved with several different doping elements with consistent dependencies upon the O$_{2\text{pp}}$. The V doped films develop their highest permittivities for the lowest oxygen flows, decreasing to a more or less constant value deeper in the oxidic regime. The Nb doped films exhibit more stable maximum values at small oxygen amounts compared to V. This is comparable to the InSn case, but with a smaller deterioration at larger oxygen flows. From these results it can be concluded that a higher rutile content is beneficial for the permittivity only in the as-deposited state.

After the annealing, the permittivities are all the better the less material has been bound to the

Figure 5.12: The $\varepsilon_{\text{at}}$ values determined by impedance spectroscopy for all TiO$_2$ films as function of the respective O$_{2\text{pp}}$ \textit{after} the annealing. Several films with very large permittivity values above 1000 could be produced.
rutile phase during the deposition. In the extreme case of InSn: Nb doping, where no detectable phase transformation took place, the $\varepsilon_{\text{sat}}$ values have kept unaltered and relatively small. This in turn means that electron-pinning is very unlikely to be the relevant mechanism for the films here. This mechanism has been reported to be the effect in In and Nb co-doped amorphous TiO$_2$ layers but which have been deposited by PLD on Pt substrates at room temperature and exhibited permittivities of about 4000 [GCW+14]. A stoichiometry of $(\text{In}_{0.5}\text{Nb}_{0.5})_{x}\text{Ti}_{1-x}\text{O}_2$ ($x = 0.1$) was employed, thus 5 at\% each, which is in the range of the sputtered films here. For this mechanism several dopants of different valence (3+ and 5+ in the case of TiO$_2$ with Ti$^{4+}$) have to be present simultaneously in the material. Therefore, doping with only Nb or V should not lead to an increased permittivity which is in contrast to the presented findings. Also the fact that the films presented here have a very high dielectric constant when they are crystalline but not when they are amorphous contradicts the mechanism of electron-pinning.

To clarify the origin of the high permittivities, figure 5.13 depicts two examples of the relationship of the real and the imaginary part of the permittivity. The behavior of these two devices with very large $\varepsilon_{\text{sat}}$ values can be approximated by a Debye relaxation model (see equation 2.74). Especially, in the case of the V doped sample two clearly distinct relaxation times can be identified. The characteristics of other devices are better described with one stretched relaxation model including the Cole-exponent $\alpha$, ranging between 0 and 1, for the complex dielectric constant [CC41]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_{\text{sat}} - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}.$$  \hfill (5.1)

The other variables have their usual meaning. Such stretched semi-circles could be explained in terms of two time constants like in the V case, whose difference is too small for two distinct semi-circles. In other words, the two semi-circles are merged into a stretched one. Unfortunately, the number of artifacts from the setup, the non-ideal behavior of several samples at low frequencies, and the lack of a large enough amount of data do not allow a systematic study of this exponent and

---

$^6$Remember that the InSn target is mainly indium due to the stoichiometry of 90:10 and dopant concentrations between 3 at\% and 6 at\% have been encompassed.
the relaxation times. Nevertheless, it can clearly be concluded that within the regime of applied frequencies or slightly above, the polarization mechanism causing these very high $\varepsilon_{st}$ values is deactivated. Therefore, atomic and ionic polarization can be ruled out as the origin for this, as frequencies in the 10 MHz range are too low by many orders of magnitude (see figure 2.11). This rules out electron-pinning as well as its relevant frequency is also above this regime [GCW+14]. In contrast, interfacial relaxation processes are typically in the kHz and MHz range. Thus, a Maxwell-Wagner polarization mechanism is proposed to be the origin of the colossal dielectric constants of these sputtered TiO$_2$X films. 

This mechanism relies on two relaxation steps and time constants [PP09, RMR$+11$] as has been observed here. The necessary combination of two different conductive areas is realized by anatase grains and insulating grain boundaries or rutile portions. This is why the very high dielectric constants arise after the annealing/crystallization. Furthermore, it is in accordance with the literature of other doped TiO$_2$ derivatives [RMR$+11$, WC88, LDY$+04$, NA86]. The larger dielectric constants with Nb doping compared to the other elements can be explained in this framework as well, as Nb can enhance the number of charge carriers in the anatase TiO$_2$. The reduction of $\varepsilon_{st}$ with larger oxygen flows is consistent with this picture as the increased amount of rutile crystals are more insulating at room temperature than anatase ones. Thus, a larger rutile contribution after deposition leaves less material over and impedes the crystallization of anatase. The fact that InSn co-doped with Nb has resulted in no significant increase of the permittivity fits to this interpretation as the crystallization has been completely inhibited in this case for this annealing procedure.

The shown high importance of interfaces on the measured permittivity in TiO$_2$ elucidates the enormous variability of the values which can be found in literature. They scatter usually between 24 and 150 [PLG$^+01$, CKG$^+99$, Rob49, YGC$^+96$, BG78, GRA59, GZB97] but even several hundreds till thousand have been reported [Par61, PW60]. Varying electrode materials, deposition techniques, and annealing procedures have a strong impact upon the morphology, crystal orientation, and interfaces and thus upon the overall permittivity.

### 5.4 Summary, Conclusion and Outlook

The permittivity and crystal structure of sputtered TiO$_2$ films have been investigated as function of frequency, doping elements, and post-deposition heat treatment. For amorphous TiO$_2$ films a frequency stable value between 40 and 50 evolves which is independent of the doping and a bit higher than the values of 30 to 38, which are used most often in literature for anatase [Rob49, TPS$+94$, PLG$^+01$, BD05]. Films at increased oxygen flows exhibit rutile contributions which lead to higher $\varepsilon_{st}$ values of approximately 80 to 100. This is comparable to typical values of rutile TiO$_2$ stated in literature [GRA59, CKG$^+99$]. After annealing at 300 °C for 2 h the permittivity of most of the undoped devices could not be investigated because of too low resistivities. With the doping of V, Nb, In$_{90}$Sn$_{10}$, or In$_{90}$Sn$_{10}$ with Nb the films keep their high resistance and are stable through the electrical measurements.
Films with colossal dielectric permittivities up to 3000 have been realized with Nb as dopant showing the best performance. Also with V and In_{0.9}Sn_{0.1} high $\varepsilon_{st}$ values can be achieved. In contrast to the reports which prepared their samples by PLD on Pt and sintering [GCW+14, HLW+13], the combination of In with Nb has not resulted in a very high dielectric constant here. From these results and the frequency dependency of films possessing such colossal dielectric permittivities, it could be concluded that the electron-pinning mechanism is not relevant for these sputtered films. Instead, the Maxwell-Wagner mechanism could be identified as the origin of these very high $\varepsilon_{st}$ values. The implied high importance of interfaces is also the cause for the large scattering of the values found in literature.

These first interesting surveys arose several fields for further research. An important aspect for measuring undoped TiO$_2$ is the test for other electrode materials to find one which is resistant against the necessary heating, does not react with or diffuse into the TiO$_2$, and possesses large and stable resistivities. Such a material or procedure, like capping the complete device after the deposition, is necessary to test higher annealing temperatures in order to be able to produce phase-pure films. In this respect, the change of the sputter parameters (higher gas pressure, lower sputtering power) to produce films at varying oxygen contents but which are completely amorphous after the deposition of several hundred nanometers. Accompanied with an annealing afterwards, values for the permittivity of sputtered TiO$_2$ in the pure amorphous, anatase, and eventually even rutile state could be measured.

A very interesting task is the disentanglement of the effect of an increased oxygen ion bombardment at larger fluxes and the higher dopant concentration which is caused by the reduced deposition rate deeper in the oxidic regime. This could be done by changing the power at the auxiliary cathode within one sequence, or by the deposition of several series at varying powers and their comparison. In the course of such a study, the crystallization impeding effect of InSnNb could be studied in more detail and explained either by a combined effect of these dopants or by a too high impurity concentration. For the InSnNb system it should be investigated if the small Sn amount affects the crystallization and, besides this, what happens at higher annealing temperatures. The investigation of the changes by employing other doping elements, such as Al instead of In (both trivalent), would be very intriguing in order to clarify the relevant parameters and eventually find even higher permittivites.

Measuring of temperature dependence on the permittivity would be of great interest to gain further evidence of the mechanism responsible for these colossal dielectric constants. This includes the freezing out at lower temperatures which have been seen at some very first tests. Moreover, a survey of the high temperature behavior is necessary to further explore its capability as material for supercapacitors [HLW+13].
Chapter 6

EM Waves in TiO$_2$–$x$

In this chapter the interaction of TiO$_2$ with electro magnetic waves of high frequencies will be presented. In the last chapter the high dielectric constant of TiO$_2$ has been measured and the strong influence of surface and interface effects has been shown. Although the absolute value of $\epsilon_{\text{st}}$ of the TiO$_2$ matrix itself is not completely clear it is definitely very high in comparison to other solid materials and typical oxides. Conservatively, a value between 30 and 50 for the anatase and the amorphous phase can be assumed, neglecting effects causing the colossal dielectric constant. In order to see if the intrinsic polarization mechanisms of TiO$_2$, i.e., ionic and atomic polarization, are able to fully account for such high values, FT-IR measurements have been conducted. The following section is dedicated to the optical properties of TiO$_2$–$x$ which are important to understand when applying it as TCO material. In the last section the crystallographic, surface, and morphological properties of Nb doped and undoped TiO$_2$–$x$ films will be discussed. These results are of great significance in order to understand which are the important aspects for producing a high potential TCO.

Figure 6.1: The structure of the anatase primitive cell with the c axis vertical on the left and the three IR active phonon modes. Ti are denoted as small circles, whereas large circles depict O atoms. Equivalent oxygen atoms are labeled with the same number. The (+) shows the position of the inversion center of the $A_{2u}$ mode. Graphic is taken from [GZB97].

Table 6.1: Three IR active TO and LO phonon mode frequencies of anatase TiO$_2$ and the corresponding ones of the rutile phase. These measured values are taken from [GZB97] and [Eag64]. In [SM10] also theoretical values for the modes can be found.
Chapter 6  EM Waves in TiO$_2$–x

### Figure 6.2: FT-IR spectra of amorphous and undoped TiO$_2$ films, sputtered in the oxidic regime to avoid reflectivity due to free charge carriers. In (a) three spectra are shown of films which have been sputtered with different oxygen fluxes in the oxidic regime. In (b) one of them and a fit employing the software toolkit CODE is shown. The by far largest feature at 3500 cm$^{-1}$ can be attributed to a Ti-OH mode at the surface [PY05]. The dips below 1000 cm$^{-1}$ can be attributed to phonon modes of anatase.

### 6.1 Phonons

In the anatase configuration, TiO$_2$ possesses three acoustic and 15 optical phonon modes. Three optical modes are IR active and are depicted in figure 6.1. In table 6.1 the frequencies of the transverse optical (TO) and longitudinal optical (LO) modes of these three types are listed. They were measured at single crystals of anatase [GZB97] and determined by first-principle calculations considering the exchange-correlation [SM10], respectively.

First, the behavior in the mid infrared regime (MIR) will be discussed. In order to be able to excite the phonons of the TiO$_2$, no Debye contribution should be present. Good conductive, TCO-like, samples are highly reflective in the IR regime (see section 2.4.2) due to the plasma frequency of the free carriers. Therefore, the films investigated here are non-conductive, as in the chapter before, and have been sputtered in the oxidic regime down to the transition point. In figure 6.2 the resulting reflectivity data of FT-IR measurements of three as deposited, undoped TiO$_2$ films are presented. The physical principle behind the measurement is discussed in section 2.4.1 and the experimental and fitting details in section 3.4.1.

Figure 6.2(a) shows clearly that within the error margin there is no distinct influence of the oxygen flow on the reflectivity in this MIR regime. With the help of several Tauc-Lorentz oscillators and a constant refractive index the complete curve can be described as it is shown in figure 6.2(b). It should also be noted that the reflectivity is very large. Although a total depth of about 700 nm is irradiated$^1$, nearly 100 % of the light is reflected back, except one major feature around 3500 cm$^{-1}$. Absorbance in this region is commonly attributed to the formation of Ti-OH species at the surface [PY05]. Additionally, around 4000 cm$^{-1}$ a much smoother valley is present which is caused by the thickness dependent interference. At very large wavenumbers the noise increases because of a strongly reduced intensity of the light source.

$^1$An aluminium mirror under the TiO$_2$ layer reflects the light, resulting in an effectively doubled film thickness.
The only relevant features for investigating the phonon contribution are below 1000 cm\(^{-1}\) with very small intensities. Although the damping of the oscillators is very strong due to the amorphous nature of the films, two regions can be differentiated. One around 800 cm\(^{-1}\) and another one even less intense around 450 cm\(^{-1}\). They are in agreement to the literature data of anatase, as a comparison with the values given in table 6.1 reveals. These two regions have been observed in TiO\(_2\) films which were deposited by chemical vapor deposition (CVD) methods as well [BD05].

Doping with Nb does not change the reflectivity in the MIR regime qualitatively. Figure 6.3(a) depicts three Nb doped films in the as deposited state focusing on the relevant wavenumber regime. From the quite reasonable fits, the wavenumber dependencies of the dielectric function of the materials could be calculated as well. One example of the complex permittivity is visualized in figure 6.3(b), calculated from the fit of an undoped film deposited at a high oxygen flow. The graph visualizes that the strong and broad signal at roughly 3500 cm\(^{-1}\) has virtually no effect on the resulting value for the dielectric function or \(\epsilon_{st}\). According to equation 2.81, the influence of an oscillator \(i\) upon the dielectric function and \(\epsilon_{st}\) is proportional to \(1/\omega_{Ti}^2\), the shifted resonance frequency. Thus, the lower the characteristic wavenumber of an oscillator the larger the influence upon the polarizability. This effect can also be seen when comparing the two phonon signals in figure 6.3(a). Although the intensity of the signal around 800 cm\(^{-1}\) is larger than the one at 500 cm\(^{-1}\), the contribution to the permittivity is much smaller, which can be seen in figure 6.3(b). Unfortunately, these wavenumbers are quite close to the lower limit of the setup. Additionally, the signal intensities are very small, about 1 %, which results in a bad signal-to-noise ratio. Nevertheless, one can calculate \(\epsilon_{st}\) values from these data which reveal much lower values than measured by the impedance spectroscopy.
In the mean, they are $\sim 7$ for undoped TiO$_2$ and $\sim 10$ for films doped with 2.5 at% Nb in the as-deposited state, in contrast to the roughly 40 to 50 measured capacitively. This large discrepancy is due to the fact that not all relevant phonons have been measured in the MIR regime. According to table 6.1, phonons are expected at even lower frequencies. Because of this fact and the considerations stated above about the bad signal-to-noise-ratio in the relevant regime, the expansion of the measurement range to the far infrared (FIR) becomes necessary. Such measurements and the analysis have been done by Prof. Ricardo Lobo in the framework of a cooperation with the Laboratoire de Physique et d’Etude des Materiaux (LPEM) in Paris.

For the measurement in the FIR, the transmissivity has been utilized instead of the reflectivity as for the MIR regime. Naturally, no Al mirror has been deposited in these cases and double side polished Si has been used as a substrate material. The resulting FIR data can be seen in figure 6.4. The signals are much more intense in this frequency range and geometry than before in the MIR.

It should be mentioned that the supposed signals above 600 cm$^{-1}$ are the same for all samples regardless of their structure and additionally, can not be linked to known phonon frequencies very well. Because of that, they are regarded as artifacts of the measurement. In contrast, the signals and the distinctions between the samples at lower wavenumbers are well described by their respective structures which are investigated by XRD and shown in figure 6.5.

We first focus on the undoped TiO$_2$ films. After heating them to 300°C, the anatase phase dominates and in the FIR sharp signals at about 260 cm$^{-1}$ and 430 cm$^{-1}$ evolve. This is in perfect agreement with phonon frequencies expected from literature. Annealing the films at 800°C, these two signals become much weaker. The XRD data reveals that at such a temperature most or all of the anatase phase is transformed into the thermodynamically stable rutile one.
Figure 6.5: XRD pattern for the same films which have been measured in the FIR in Paris (see figure 6.4). In (a) the undoped TiO$_2$ films are shown which have been deposited at the transition point and with 7 sccm oxygen. In (b) similar films with Nb doping are depicted. The same square root scale for the y-axis has been chosen for all of them. Moreover, only the 2$	heta$ regime with the most intense reflexes is plotted for a better comparability. The annealing temperature of 800 °C is above the transformation temperature, resulting in a drastic increase of the rutile portion.

The appearance of the rutile phase results in distinct signals at 190 cm$^{-1}$ and, not easy to see, at 500 cm$^{-1}$. From literature, phonon modes are expected in the range of 160 cm$^{-1}$ to 190 cm$^{-1}$ and at 500 cm$^{-1}$ as well [SM10]. The films in the as-deposited state is between these two extremes with weak characteristics of anatase and rutile as well. The Nb doping does not add any new features, but it has a stabilizing effect on the anatase structure. The transformation to rutile at high temperatures is impeded as can be seen by XRD pattern and the FIR spectra consistently. The absence of new signals neither in the FIR nor in the XRD indicates that Nb is substituting Ti in the TiO$_2$ lattice completely.

Calculating from the FIR data, $\epsilon_{st}$ values have been provided by Prof. Ricardo Lobo for these different films as well. They are presented in figure 6.6. To account for the different crystal phase compositions, an estimation for the amount of rutile has been calculated. For every oxygen flow, with and without Nb, a maximal crystallinity has been determined by adding up the XRD intensities of the main anatase and the main rutile reflex in figure 6.5. After that, the observed rutile reflex in a specific measurement has been related to this maximal 'possible' intensity at the chosen thickness, oxygen, etc., in order to find a measure for the ratio of rutile in the film. For example, the undoped film sputtered at 42 mPa, i.e. 7 sccm oxygen, and heated to 800 °C exhibits a nearly pure rutile phase. The comparable sample deposited at a lower oxygen flow has still some anatase contribution and therefore only a rutile portion of about 0.87, although the absolute intensity of the rutile (110) reflex is nearly as high as for the high oxygen partial pressures ($O_{2PP}$) films. Of course, this is only a rough estimate for the volume fraction of the rutile phase in the complete film. However, it can be used successfully, as a measure for the phase composition and for the combined investigation of all films as it has been done in figure 6.6.

The most important result, which can be concluded, is that for amorphous and anatase films,
Figure 6.6: From the FT-IR measurements in the FIR (see figure 6.4) calculated $\varepsilon_{st}$ values in dependency of the estimated rutile contribution. This portion has been calculated by comparing the intensity of the main rutile reflex of a film with the maximum, summed up intensity of anatase and rutile. This maximal possible intensity has been calculated for the two different oxygen flows with and without Nb doping.

i.e. low rutile portions, the undoped TiO$_2$ shows a $\varepsilon_{st}$ of about 50. This is in perfect agreement to the values determined capacitively in the previous chapter. Therefore, the question of the intrinsic/ionic polarizability or permittivity of TiO$_2$ is solved. This is more or less also true for the rutile phase. The ionic mechanism, measured by the phonon contribution, results in an $\varepsilon_{st}$ of more than 80 which is in the regime of values measured electrically in films with a prominent rutile contribution. Besides the anatase stabilizing effect of Nb an additional increase of the phonon contribution of the permittivity can be observed in figure 6.6. Thus, besides the Maxwell-Wagner polarization which is strengthened tremendously by the Nb as it has been revealed before, the ionic polarization is intensified too. A maximum value of 110, although the film is still not completely rutile, is quite remarkable.

To conclude, the large permittivities of TiO$_2$ are indeed an intrinsic feature of the Ti-O bond and the crystal structure. It can be explained in terms of ionic polarization completely, measured by FT-IR in the FIR regime. Additional Nb doping increases the ionicity even further leading to larger dielectric constants.

6.2 Optical Properties

In this section the characteristics at higher frequencies, the visual (VIS) and ultraviolet (UV) regime, will be investigated. This range is obviously essential for any TCO material. Therefore, the analyzed films are conductive and slightly sub-stoichiometric. First, the influence of the usually applied Si$_3$N$_4$ capping layer upon the transmission through such a TiO$_2$–x film will be shown. The transmission through a glass substrate and a Si$_3$N$_4$ capping film alone can be seen in figure 6.14. In figure 6.7 the transmissivities $T$ and reflectivities $R$ as a function of the wavelength for thick, doped with 2.5 at% Nb, and unheated TiO$_2$–x films are plotted. As has been mentioned earlier
Section 6.2 Optical Properties

Figure 6.7: Optical transmissivity $T$ and reflectivity $R$ of ~500 nm thick TiO$_{2-x}$ films doped with 2.5 at% Nb with (solid line) and without (dashed line) a capping. All TiO$_{2-x}$ samples were prepared in one run at different O$_{2}$pp on glass and measured before annealing. For the UV/VIS measurement a clean glass substrate was utilized as a reference.

in chapter 2.4.2 for an undoped film (cf. figure 2.14), the interference effects caused by the very high refractive index of TiO$_{2-x}$ are enormous\(^2\). These fringes can encompass more than 30\% and can result in intensities even slightly above 100\% measured with a glass substrate as reference. A close comparison of the dashed and the solid lines reveals that the application of a Si$_3$N$_4$ capping reduces these fringes significantly.

The influence of the oxygen content on the transmission and absorption will be discussed in detail in the following section. The fundamental absorption of the band gap happening at a wavelength of about 350 nm will be investigated more closely in section 6.2.2. At this point, it is only worth mentioning that the reduction of the interference fringes by the Si$_3$N$_4$ layer works also for high absorbing films, i.e., the "50\%" films. Naturally, the absorption present in films sputtered at low O$_{2}$pp results in drastically reduced intensities of the interferences.

These interference fringes are a much bigger issue in TiO$_2$ than for typical TCOs like ZnO:Al. A comparison of similar O$_{2}$pp series of these two oxides can be seen in figure 6.8(a). It is important to note that the TiO$_2$ films have been capped with a Si$_3$N$_4$ layer. However, the fringes are still much more intense in the case of the capped TiO$_2$ than in the one of ZnO:Al, which can best be seen in the reflectivity data.

From these data, the interference free $T_{\alpha}$ and $R_{\alpha}$ have been determined and presented in figure 6.8(b). The comparison and the sequence of different samples become much clearer by this approach. The transparencies of these TiO$_{2-x}$ films are very high and only slightly lower than

\(^2\)In the dissertation of Rüdiger Schmidt measurements of the refractive index of TiO$_2$ films can be found which had been sputtered in a similar reactive DC-magnetron process. They posses values of 2.46 to 2.48 at 550 nm, which is in perfect agreement to literature [HS11]. These values are remarkably independent of the oxygen flow in the oxidic regime [Sch14].
in the case of the standard TCO ZnO. Comparing the different series, it becomes evident that reducing the O$_{2PP}$ or changing the matrix oxide does not alter the reflectivity within the margin of error much. This large reflectivity is in good agreement with equation 2.86 employing the refractive index of TiO$_2$ and air ($R = 18\%$ with $n_{TiOx} = 2.47$). Additionally, the high reflectivity accounts fully for the loss in transmissivity of the films. In other words, the most transparent films prepared in this work exhibit practically no absorption.

The reduction of these interferences is a crucial issue for employing TiO$_{2-x}$ thin films in any transparent device as they lead to a stained or colorized impression. Such problems can be tackled

**Figure 6.8:** $T$ and $R$ of capped TiO$_{2-x}$:Nb 2.5 at% and uncapped ZnO:Al 4.7 at% films sputtered at different O$_{2PP}$. In (a) the result of the measurements can be seen and in (b) the calculated, interference free $T_\alpha$ and $R_\alpha$.

**Figure 6.9:** Transmissivity of TiO$_{2-x}$ layers as a function of the wavelength with and without an additional Si$_3$N$_4$ seed layer. The films have been heated and are well conductive with $\sim$ 1 m$\Omega$cm for the samples depicted in blue and $\sim$ 30 m$\Omega$cm for the green ones. The two types of films possess also comparable mean transmissivities $T_\alpha$ calculated by the Swanepoel method to remove the interference fringes and envelope the resulting data with the luminosity function (see section 2.4.2).
Figure 6.10: The transmission $T_\alpha$ as function of the wavelength for varying $O_{2PP}$ of 500 nm thick, undoped, and uncapped TiO$_{2-x}$ films before heating. The color code represents different regions of the $O_{2PP}$. Samples which exhibit practically no electrical conductivity after the annealing are depicted in red. The films plotted in blue are conductive even without a capping. The third group in black denotes samples with a drastically decreased mobility which will be discussed in more detail in chapter 6.3.

by the usage of anti-reflex coatings. The easiest mechanism to achieve a reduced reflectivity is to utilize a layer at the interface (here air-TiO$_2$ or TiO$_2$-substrate respectively) with a refractive index in-between the two materials. Si$_3$N$_4$ exhibits a refractive index of 2 [XC95] and can be tailored depending on the deposition procedure [DMH$^+12$]. It is thereby between the $\sim$ 2.5 of TiO$_2$ and the 1 of air. This so called index matching is the reason why the Si$_3$N$_4$ capping slightly reduces the interference fringes. The optical properties of Si$_3$N$_4$ are nowadays of large interest, e.g., for optimized light management and reduced refractive losses in solar cells [DMH$^+12$, IMF$^+15$].

The beneficial effect of Si$_3$N$_4$ for the optical and electrical properties can be enhanced drastically if it is utilized as an additional seed layer. Figure 6.9 demonstrates this very clearly. These films are slightly sub-stoichiometric and highly conductive. Although the two types of layers exhibit similar mean transmissivities the interference fringes are reduced to a great extent. Interestingly, the effect is more pronounced in the regime below 600 nm than above. Fortunately, the human eye is most sensitive in this wavelength regime as well. The investigation of anti reflex coatings and optimized light control is beyond the scope of this thesis. Nevertheless, the encapsulation of TiO$_{2-x}$ in thin Si$_3$N$_4$ layers for reducing the high reflectivity of TiO$_2$ has proven to be very efficient and is a good starting point for further improvement.

### 6.2.1 O$_2$ Content

In the examples shown so far, it became clear that the oxygen partial pressure ($O_{2PP}$) used during the deposition is of crucial importance not only for the electrical performance but also for the optical one. This aspect will now be investigated further.
In figure 6.10 the transparency of an $O_{2PP}$ series of undoped, uncapped but 500 nm thick TiO$_{2-x}$ in the as deposited state is shown. In the upper regime of $O_{2PP}$ up to 75% in this case, the transparency does not change at all. As they possess no capping, these films are completely non conductive after the annealing and are plotted in red. Starting at 70% the transparency is lowered with the $O_{2PP}$, conductivity can be measured afterwards, and the samples are depicted in blue. However, the transparency is not reduced uniformly over the entire wavelength regime but around 800 nm preferably. Further reduction of the $O_{2PP}$ during the sputter deposition leads to a drop of the electrical mobility due to a changed structure. Therefore, they are marked in black. This phenomenon will be discussed later on in chapter 6.3 in greater detail.

In figure 6.11 the changes upon annealing with and without a capping layer are shown. These films are Nb doped, however, no qualitative differences or new features can be seen in comparison with the undoped case in figure 6.10. In the appendix, a comparative plot (fig. A.9) of the raw data of films with different doping levels is shown, which supports this statement. The films with the largest $O_{2PP}$ reach the maximum transmissivity of roughly 85% in the as-deposited state already. Because of that, they do not change due to the heat treatment within the margin of error. On the other hand, the transmissivity of films sputtered at lower $O_{2PP}$ become increased by the annealing process. At first sight, there seems to be no large difference comparing the changes of films without capping in figure 6.11(a) and of the ones with a Si$_3$N$_4$ layer in figure 6.11(b). In both cases the transmissivity is increased by heating the films. However, there is a large difference in the way this increased transmissivity is achieved which can best be seen looking at the films sputtered at 50% $O_{2PP}$. Without a capping layer, the reduction of $T$ around 800 nm mentioned before is removed leading to a wavelength independent $T$ like for films prepared directly at large $O_{2PP}$. This is not the case when a capping prevents any oxygen diffusion from the surface. Thus, I propose a disproportioning reaction in such films, leading to regions with enough oxygen for forming TiO$_2$ and adjacent regions with further reduced stoichiometry.
In the discussion so far, the reduced transmissivity observed in all TiO$_{2-x}$ series due to lower oxygen contents has been attributed to increased absorption by defect states. However, one has to consider the possibility that due to the larger number of free electrons, the plasma frequency has been shifted into the IR regime, resulting in an increased reflectivity at larger wavelengths and a large absorption peak at the plasma frequency. This is typically the case for highly doped TCO films (see figure 2.13). However, the larger (by a factor of $\sim 1.5$) value of $\varepsilon_\infty$ of TiO$_2$ compared to the other TCOs should shift the plasma wavelength to larger values. Additionally, the relatively low charge carrier density of undoped films (up to $1 \times 10^{20}$ cm$^{-3}$ see figure 4.7) makes this interpretation even more unlikely. Another important argument against the Drude mechanism is the shape of transmissivity curves. $T$ is not monotonically decreasing with larger wavelengths - as it is expected for the Drude reflection - but increases again towards 1100 nm (see figure 6.10).

A thickness series of highly doped (5 at% Nb) films is presented in figure 6.12(a). It demonstrates the thickness dependency of the frequency of the interference fringes very nicely. In figure 6.12(b) the calculated interference free transmission has been plotted according to the Beer-Lambert law. The intensities follow this ideal behavior quite closely, especially, the not to strongly absorbing series which has been sputtered at an O$_{2pp}$ of 60 %. The charge carrier densities of the films of this series lie between $3 \times 10^{20}$ cm$^{-3}$ and $5 \times 10^{20}$ cm$^{-3}$. Although this is one order of magnitude higher than the undoped TiO$_{2-x}$ film sputtered at 60 %, which is shown in figure 6.10, the transmission is much higher also in the IR. Therefore, it can be concluded that the decrease of the transmission at larger wavelengths for the TiO$_{2-x}$ films prepared here, is not caused by free electrons in terms of a Drude reflection but by the absorption of defect states caused by oxygen vacancies. If the oxygen deficiency is too large, a broad absorption band occurs at roughly 800 nm.

To conclude this section, the calculated mean transparencies of TiO$_{2-x}$ films with and without Nb doping versus the employed O$_{2pp}$ are depicted in figure 6.13. Till 80 % within the hysteresis, the transparency is independent of the O$_{2pp}$ and of the Nb doping. Below a critical point, the
transmission is reduced linearly with further decreasing oxygen content of the sputter atmosphere. Until this point, the behavior is as expected and typical for reactively sputtered oxides. At this critical point, the density of the oxygen vacancies is increasing strongly, as it has been shown for the undoped case in figure 4.5. The value of the critical $O_{2\text{PP}}$, however, is influenced by the Nb content quite severely. A gradual increase of the critical point with the Nb content could be attributed to the fact that some of the oxygen has the tendency to get bound interstitially to Nb, forming $\text{Nb}_2\text{O}_5$. However, the energy difference between $\text{TiO}_2$ and $\text{Nb}_2\text{O}_5$ is rather minute with respect to the metal ion and also with respect to the oxygen. Moreover, the observed change of the shifting direction is hard to explain. Samples from several runs for every dopant concentration are combined in this graph, so statistical fluctuations can not be the explanation solely. Thus, the dependency of the critical $O_{2\text{PP}}$, in terms of the transmission, seems to be non trivial and further investigations with additional different Nb concentrations are necessary for a better understanding. Eventually, this effect is more related to a specific target than a direct consequence of the stoichiometry chosen.

To summarize, the high refractive index of $\text{TiO}_2$ influences massively the optical appearance of $\text{TiO}_{2-x}$ films and leads to a strong, wavelength dependent reduction of the transmissivity. This is resulting in a colored impression, even when no absorption is present. In order to discuss the intrinsic optical properties of the film, the effect of interference fringes has to be removed. With the help of the Swanepoel method (see figure 2.14 and equation 2.87) this has been done very successfully. The observed reduction of the transparency is caused by absorption at defect states originating from oxygen vacancies. No sign of absorption and reflection by free electron plasma could be seen within the wavelength and charge carrier density regime investigated so far. Below a critical $O_{2\text{PP}}$, which depends on the Nb concentration, the transmission is reduced monotonically as expected for reactively sputtered oxides.
6.2.2 Band Gap

After the optical properties in the IR and VIS regime the frequencies used will be increased further into the UV. In the transmission data, which have been visualized so far, the fundamental absorption below a wavelength of 400 nm could already be seen. However, before the transmission and reflection data can be utilized to determine the optical band gap of a thin film, the characteristics of the substrate and the capping themselves have to be known. In figure 6.14 such an overview is given. The black curve shows the measurement of the pure glass substrate with an empty reference. The transmissivity of this 0.5 mm thick borosilicate glass slides is slightly above 90% in the optical regime and drops sharply to zero below 350 nm. Thus, every transparent film has to have a distinctively smaller band gap as otherwise the absorption of the substrate would inflict the analysis. The TiO$_2$-x films presented in this figure illustrate and encompass the typically observed range. One can see a significant shift between the different TiO$_2$-x films and especially with Nb doping the absorption edge shifts quite closely to the one of the substrate. But so far there is still a significant distance to the glass absorption and the optical band gap can be determined. Before that, the Si$_3$N$_4$ layer should be addressed. Theoretically, Si$_3$N$_4$ exhibits a band gap of above 4 eV, which would be wide enough not to inflict the measurement on TiO$_2$-x. The green curve in figure 6.14 shows that this is also true for the films prepared by sputtering. The relatively thin and amorphous nature of the Si$_3$N$_4$ film leads to a very broad absorption edge which is below the one of glass and cannot be measured by transmission. Furthermore, the comparison between the TiO$_2$-x films without a capping, with a capping, and with an additional seed layer reveals no influence of the Si$_3$N$_4$ film upon the position or shape of the edge.

In section 2.4.2 the theory of the Tauc-method has been presented. In figure 6.15 the calculated absorption (1-R-T) of several undoped and doped TiO$_2$-x films are plotted according to equa-
Figure 6.15: Band gap determination according to the Tauc method (see section 2.4.2) of TiO$_{2-x}$ films with varying O$_\text{2PP}$ and Nb content. In (a) an O$_\text{2PP}$ series of undoped films is plotted and in (b) emphasis is laid upon the Nb content and the measured charge carrier densities. This reveals a strong influence of Nb on the electronic structure of TiO$_2$ besides generating charge carriers.

This finding of a missing or rather weak Burnstein-Moss shift (see equation 2.89) is supported heavily when comparing undoped and Nb doped films in figure 6.15(b). There, the charge carrier densities are listed too and it became quite obvious that a big shift of the band gap is present with adding Nb. However, this is not due to the increased carrier concentration but apparently due to the presence of Nb itself. There is no other explanation for the large shift to 3.5 eV of the film doped with 2.5 at% Nb compared to the undoped film as the charge carrier densities are nearly the same within this two samples.

The lack of a pronounced Burnstein-Moss shift - even though the charge carrier densities are altered by several orders of magnitude between the investigated films - can be explained by the $d$-band nature of the conduction band minimum. The density of states in such a $d$-band is much larger than in, for example, an $s$-band (see table 1.2). As a consequence, all the additionally induced free electrons can occupy new states with nearly the same energies and the optical band gap, from the valence band to the next unoccupied state in the conduction band, is not altered significantly. The incorporation of Nb, on the other side, can change the binding energies and distances between metal and oxygen, thus resulting in a changed electronic structure and a widened band gap.
6.3 Structural Properties

In this section, the structural properties of TiO$_2$$_x$ films will be investigated in order to unravel some important charge transport mechanisms and limiting factors. In section 6.3.1, the crystallinity of the conductive TiO$_2$$_x$ films will be discussed. It should be mentioned that these sub-stoichiometric films are amorphous as deposited regardless of the amount of Nb doping, O$_{2PP}$ value, thickness, or sputtering power (see figure A.10). This is in contrast to the results of chapter 5. There other dopants and especially excess oxygen have been demonstrated to lead to mixed crystallinity (amorph, anatase, and rutile combined) in the as-deposited state. Moreover, the rutile contributions are even thickness dependent under these sputter conditions. However, such films, which are sputtered in the oxidic mode (see section 3.1.1) are highly insulating and in the following I will focus on the structural properties of conductive TiO$_2$$_x$ films. After the crystalline structure in section 6.3.1, the surface topography will be analyzed briefly in 6.3.2.

6.3.1 XRD

With the help of Cu $K_\alpha$ radiation, the structural composition of the TiO$_2$$_x$ films, including several doping levels of Nb, have been investigated. Naturally, the measured intensity depends strongly on the radiated volume of the film. Therefore, the films, which will be compared here have similar thicknesses of about 250 nm if not stated otherwise. In this section, the important influence of the O$_{2PP}$ during the sputtering in the sub-stoichiometric regime and the resulting film quality will be investigated. The reference XRD pattern of powder samples of anatase and rutile can be seen in figure 3.16(b) in more detail. The anatase reference pattern can be seen as a line profile at the back wall of every 3D plot as well.
In figure 6.16 the measured XRD pattern of an O\textsubscript{2PP} series of undoped TiO\textsubscript{2−x} can be seen. All films possess a capping layer and have been heated to 300 °C for two hours. In principle, all interesting features regarding the crystal structure of conductive TiO\textsubscript{2−x} films can already be seen here. All reflexes which evolve from the complete amorphous phase after the deposition (see figure A.10) match to literature position of the anatase structure. Moreover, no theoretically expected reflex is missing and the proportions of the reflexes match the assumed ones roughly.

The most important deviation from the expectation is the occurrence of still amorphous films prepared with low O\textsubscript{2PP} values. At 55 % the films uniformly crystallize in the anatase structure but directly below, at 50 %, no crystallinity can be detected. The same behavior can be observed in figure 6.17(b) for films doped with 1 at% Nb. These films do not even crystallize at slightly higher temperatures. Tests of capped films have been performed at up to 500 °C (cf. figure A.11), without substantial structural or optical modification. Because of the still amorphous structure such films show only rather minute improvements of their electrical properties due to the annealing procedure (see section 4.1).

The reason for this characteristic is that below a critical O\textsubscript{2PP} there is not enough oxygen to form enough stable TiO\textsubscript{6} octahedra. The phase diagram of titanium and oxygen is rather complicated. Nevertheless, it is safe to say that TiO\textsubscript{2} is a stoichiometric compound with nearly no freedom of composition, a so called ’line-phase’ \cite{WE99}. If oxygen supply is insufficient this phase can’t form. For a long range disproportioning reaction even higher temperatures would be necessary to allow large enough diffusion paths. Unfortunately, at 600 °C the substrate starts to soften, which, in addition to the high amount of film stress, leads to cracks and bended samples. In order to further validate this interpretation, one can compare the plots in figure 6.17. Both encompass films which are doped with 1 at% Nb and have been treated identically. The only difference is the fact that the films in figure 6.17(a) are not capped in contrast to the ones in figure 6.17(b). The uncapped films became all crystalline and no clear tendencies can be observed anymore, while the capped ones remained amorphous below 57.5 %. From these results, one can conclude that there is indeed a
critical and very sharp lower border of the amount of $O_{2PP}$ which is necessary to form crystalline $\text{TiO}_{2-x}$. This fact is independent of the amount of Nb doping (see figure 6.18), however, the exact position of this critical point is slightly altered by the employed dopant concentration. Moreover, this proves that if no capping as an efficient oxygen barrier is employed, oxygen can diffuse into the film from the residual oxygen in the Ar atmosphere and alter the properties of the material.

Besides the occurrence of a critical lower $O_{2PP}$ limit for any crystallization to happen, the change of the anatase intensity with increasing $O_{2PP}$ is quite characteristic and the same for all capped series. The maximum intensity and therefore best crystallinity, is not at the highest $O_{2PP}$, as one might expect. Instead, one can observe a clear maximum around 70%. Below this point, the amount of oxygen in the film is reduced, which increases the imperfections and could result in smaller grains. Therefore, the intensity is reduced up to to the critical point. On the other hand, at higher amounts of oxygen in the sputter atmosphere, the intensity is lowered again. However, it is often not continuously lowered, but drops to a value and then stays constant when the oxygen flow is further increased. This can best be seen in figure 6.16 where the four films with the largest $O_{2PP}$ values, ranging from 75% to 90%, exhibit nearly identical intensities. The 5 at% series also shows this behavior very clearly. A possible hypothesis to account for the lowered intensity at higher $O_{2PP}$ is the increased oxygen ion bombardment [AKW10, Köh10]. This destroys the bondings and the TiO$_6$ octahedra in the film leading to a worse microstructure after the crystallization. Such high energy bombardment is known to be harmful for the formation of the anatase structure [AKW10, LHM94].

The idea of an oxygen bombardment is supported by the detailed analysis of the position of the main anatase reflex in figure 6.19(a). Although all values are quite close to the literature position there is a clear ascending tendency towards higher $O_{2PP}$ values. Furthermore, this trend starts to

3A difference in the depth of the race track cannot explain the shift of the critical point. The depth leads mainly to a changed hysteresis for which the $O_{2PP}$, as it is defined, can account for. Secondly, complete new targets have been tested for all doping levels in the course of this thesis, with no clear further trend with respect to the target age.
saturate at large values. The shifting to larger angles is caused by the additional stress in the film which can be linked to the ion bombardment. At least for larger concentrations, the Nb doping leads to a lowering of the reflex angle at all oxygen contents. This is expected as the incorporated Nb ions are larger than the Ti ones, which increase the lattice constant and, because of that, leads to a smaller Bragg reflex angle.

On the other hand, the Nb doping has no influence on the minimum FWHM, as can be seen in figure 6.19(b). Regardless of the doping, a very good FWHM value of 0.25° is typically reached. Films with a very low (101) intensity, which corresponds to low O\textsubscript{2PP} values near or at the critical point, exhibit somewhat larger angles naturally.

To summarize: All films that are sputtered in the sub-stoichiometric regime and heated to temperatures up to 500 °C, show either an amorphous or an anatase polycrystalline structure, i.e., no rutile phase is present.

A lower limit of the amount of oxygen has been identified which is necessary for the film to crystallize during the heat treatment. Below this limit, the films stay amorphous and, therefore, their electrical conductivity also does not improve much (see section 4.1). On the other hand, the maximum crystallinity is not gained at the highest O\textsubscript{2PP} but at around 70 %, slightly varying with the Nb concentration. Above this optimum O\textsubscript{2PP}, the intensity of the anatase reflex drops slightly due to an increased oxygen ion bombardment. The Nb doping alters these trends only marginally, e.g., for high concentrations an increasing lattice constant could be proven.

### 6.3.2 Surface Topography

In the section above, it has been shown that the crystallographic structure of the sub-stoichiometric TiO\textsubscript{2−x} films is either amorphous or anatase with high intensities and a very small FWHM. In this section, the surface topography and grain sizes will be investigated as they represent possible...
scattering mechanisms. A very rough surface, for instance, could lead to reduced mobilities even for ideal crystalline grains.

From the AFM scans depicted in figure 6.20, of a film before and after annealing it became quite obvious that the surfaces of these several hundred nanometers thick films are nearly perfectly flat. A slight crinkling leads to large scale RMS values after the annealing of about 1 nm.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\rho_{\text{fit}}$ (g/cm$^{-3}$)</th>
<th>$\rho_{\text{theo}}$ (g/cm$^{-3}$)</th>
<th>$\sigma$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_{2-x}$</td>
<td>3.84</td>
<td>3.89 [HS11]</td>
<td>1.8</td>
</tr>
<tr>
<td>Si$_3$N$_4$ at 1.2 Pa</td>
<td>2.85</td>
<td>1.8 - 3.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Si$_3$N$_4$ at 0.8 Pa</td>
<td>2.94</td>
<td>1.8 - 3.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Si$_3$N$_4$ at 0.2 Pa</td>
<td>3.03</td>
<td>1.8 - 3.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 6.2: Fit results of XRR measurements on TiO$_{2-x}$ and Si$_3$N$_4$ layers. Typically, the Si$_3$N$_4$ has been sputtered at 1.2 Pa when employing it as capping layer. Lower pressures result in denser and even flatter Si$_3$N$_4$ films. In literature the densities of amorphous Si$_3$N$_4$ films encompass a large range of values [Kro01, Sea98]. This is consistent with the good tunability shown by these experiments.

In figure 6.21 the XRR measurement data and fit results of two TiO$_{2-x}$ layers are visualized, which have been prepared successively, one without a capping layer and the other one with a Si$_3$N$_4$ layer. Such layer stacks can be fitted successfully and reveal consistently the same values for the structural properties of the two films. A summary of the results obtained by several XRR measurements is listed in table 6.2. The annealed TiO$_{2-x}$ layers exhibit electronic densities measured by XRR which are nearly as high as the mass density known in literature. Thus, a
densely packed microstructure can be concluded. The calculated roughnesses are consistent with
the ones determined by AFM and are below 2 nm. Thus, it is safe to say that the scattering at such
smooth surfaces will not play a significant role for the electron transport in these sputtered films.
This statement is supported by the fact that the mean free path of the best TiO$_{2-x}$ films is in the
range of 5 nm at room temperature which is much smaller than the relevant film thicknesses. In
accordance with that, several thickness series have not revealed a clear trend of the conductivity
with the film thickness as is known for standard metals [Ang85].

Such flat surfaces have been expected as the films are prepared by sputtering and, additionally, are
crystallized from the amorphous phase after the deposition. The relatively high kinetic energies
of the arriving atoms (compared to chemical vapor deposition or evaporation) result in a densely
pressed and thus flat morphology. The lack of crystal growth during the deposition removes any
aspects of varying growth velocities of different crystal facets and any possible evolutionary growth
modes. If they would be present, these mechanisms can lead to much larger and strongly thickness
dependent surface roughnesses. Flat surfaces of sputtered TiO$_{2-x}$ are in agreement with literature,
although slightly larger roughness values between 2 nm and 9 nm are known there [MBG+02].

By utilizing AFM and XRR, it could be shown that the film surfaces are nearly perfectly flat
and thus surface scattering can’t impede the electrical transport significantly. In a next step, the
determination of the grain sizes and the comparison with the mean free path is of great importance
in order to be able to estimate the significance of grain boundaries (GB) upon the mobility. With
the help of Roland Sittner, scanning electron microscopy (SEM) investigations have been conducted
to do so and examples of two undoped and uncapped TiO$_{2-x}$ films are shown in figure 6.22.

The interpretation of SEM micrographs is often highly non-trivial as different physical mecha-
nisms influence the secondary electron yield and detection efficiency. A nice review of the SEM
technique and the various sources of contrast has been written by Seiler [Sei83]. The main ori-
Figure 6.22: SEM micrographs of undoped, uncapped, and 500 nm thick TiO$_2$-x films after annealing. The grain size determination has been done within the software by marking dozens of different grains, as it is shown for one example in each picture. The film in (a) has been produced by employing an O$_{2+}$P of 60%, resulting in a mobility of 8.8 cm$^2$/Vs and quite frayed grains of a mean diameter of roughly 700 nm. For comparison in (b) a nearly optimal film is presented, which has been prepared by using an O$_{2+}$P of 70% leading to the best mobility of 18.5 cm$^2$/Vs and shows larger (~1700 nm) and smoother grains. The optical properties of these films are included in figure 6.10 and a much higher transparency for the 70% sample is observed due to the larger oxygen content.

gins of contrast in a SEM are material, topography, voltage, magnetic, and electron channeling or crystallographic orientation. The reactive sputtering from an alloyed target and the relatively low annealing temperatures give no raise for a large scale material inhomogeneity. Energy-dispersive X-ray spectroscopy (EDX) measurements have shown a homogeneous elemental distribution along the complete surface confirming this assumption. Thus, material contrast can be ruled out as origin of the observed patches. Furthermore, topography contrast can be disregarded due to the observed and before proven very flat surfaces. Because of the high conductivity of the film and the Si substrate any charging effects, i.e., a voltage contrast, can be ruled out as well. A magnetic field contrast is also highly unlikely as no hysteresis has been observed during any magneto resistivity measurement and undoped TiO$_2$-x is not expected to be magnetic.

Thus, only the crystallographic contrast remains as a plausible explanation. The idea behind this mechanism is that the probability of primary electrons to get backscattered depends upon the orientation of the crystal plane with respect to the direction of the primary electron beam [GUZIR09]. This means that the varying intensities correspond to different grains with large angle grain boundaries in between. With a backscattered electron detector this mechanism could be exploited optimally. As there is no other source of contrast, it can be seen in the secondary electron detector as well.

Figure 6.23 shows two further examples to visualize the capability of investigating the grain structure of TiO$_2$-x films with SEM. In these cases layers with a high Nb doping have been investigated. One flake is marked with a white and dashed line, illustrating the abrupt contrast change.
In figure 6.23(b) the breaking edge of a capped film is presented in which the different orientations of the crystal planes can be seen quite clearly, including a large angle GB. This micrograph also visualizes the nearly ideal coverage of the amorphous Si₃N₄ capping with the tight sealing of the grain boundaries. As a GB allows a much larger diffusion length than the bulk of a grain, the protecting or passivation of the GB is essential in order to prevent a film from oxidation.

From these arguments one can conclude that indeed the grains of the TiO₂₋ₓ films can be investigated by employing SEM. Quite fascinating differences in the resulting grain structures of TiO₂₋ₓ films can be observed by varying the oxygen content; two examples are shown in figure 6.22. The film prepared at an O₂PP of 60% exhibits much more fragmented and frayed grains than the one sputtered at 70%. The considerably more ideal looking grain structure depicted in figure 6.22(b) coincides with a much larger electron mobility and also optical transmission. Not only the shapes of the grains differ, but also the mean diameter which has been determined by measuring the diameter of about 40 grains of every film. Naturally, these diameters scatter a lot. Nevertheless, significant differences can be detected and the values can be found in table 6.3.

The first and most important aspect is that for all TCO like TiO₂₋ₓ films the large angle grain sizes are remarkable huge. Values of at least several hundred nanometers up to several micrometers have been detected. In comparison, the grain sizes of sputtered ZnO:Al range only between 20 nm and 50 nm determined by XRD using the Scherrer formula and electron microscopy as well [NMY15, EL100, SWU+98]. Also for In₂O₃:Sn films values up to 50 nm can be found typically by XRD [HG86, MSEB00].

---

5 It is worth noticing that the characteristics are concluded by comparing a variety of different samples and investigating several areas on one film.

5 For an investigation of the breaking edge a Si substrate has to be employed. On an insulating and amorphous glass substrate the edges are not precise enough and, more importantly, the picture drifting becomes much to large due to charging.
Table 6.3: Determination of the mean diameter $D$ of large angle grains by SEM analysis of about 40 grains for every film. The calculated standard deviations $\sigma$ reflect the large variety of the grain sizes. The remarkably large distances of large angle GB can hardly be a limiting factor for the charge carriers with their mean free path of 5 nm.

A close inspection with electron microscopy reveals that for In$_2$O$_3$:Sn different kinds of grains can be seen. On the one hand, there are small grains up to 30 nm which are consistent with the out of plane coherence length determined by XRD for textured films. On the other hand, there are large angle grain boundaries which are up to 350 nm apart from each other in highly conductive (200 $\mu$Ωcm) films [SP94].

For TiO$_2$:Nb similar discussions can be found in literature. Even at highly textured, epitaxial films prepared by PLD on LaAlO$_3$ (100), grain sizes of only up to 60 nm have been measured by XRD [YLL+09]. When investigating TiO$_2$:Nb films with a polarized optical microscope, Yamada et al. detected several $\mu$m huge grains in non-textured films sputtered with r.f. on glass. Within these large areas, smaller structures with sizes below 20 nm could also be observed by transmission electron microscopy (TEM) [YHJ+09]. Such a composition seems to be present for the films here as well. The AFM and SEM pictures of the surface and also the lamella-like breaking edge (see figure 6.24 and 6.23(b)) indicate that the very large crystallographic grains are composed of smaller structures. A possible explanation of the origin of the large structures is that a nucleation dominated crystallization is present in such films. The less defects the amorphous film has the smaller is the density of possible nucleation centers. This explains the larger grains for the 70% film. The 60% layer, with its larger oxygen deficiency, exhibits more possible crystallization seeds and local inhomogeneities. This leads to a higher density of grains and larger differences in

![SEM micrography of the sub-grain structure visible on the surface of a TiO$_2$:Nb film within the large grains.](image-url)
the crystallization velocities of different directions which in turn result in the observed frayed and starlike structures. Additional Nb doping has a stabilizing effect on the anatase structure as it has been shown in section 5.2. This gives rise to even larger grains as shown in table 6.3 and which are consistent to the findings in literature [YHJ+09].

The smaller sub-grain structures are a possibility for the material to release strain energy by generating twin boundaries or defects like walls of aligned dislocations. Such defects need much less energy than creating the interfaces of a grain boundary. For metals such a behavior is known and referred as sub-structure or sub-grain [EW72, Hol61] and can, for example, be investigated by comparing TEM and electron backscatter diffraction (EBSD) [Hum01]. Another example of the occurrence of such structures has been found with high resolution transmission electron microscopy on Mg2Si [MPS+13]. Employing special substrates like LaAlO3 with a smaller lattice mismatch to TiO2−x, high deposition temperatures or techniques like PLD results in less stress and microstrain in the film. This is why in such films the sub-grains, which are determined as coherence length by XRD, are larger than for films prepared by sputtering on glass like here.

With respect to the electron transport, the large angle GB is the much more relevant defect. The lattice orientation remains the same across the boundary of two sub-grains. Therefore, in terms of a Bloch wave, this is no efficient scatterer. The angular dependent increase of the electrical resistivity by a GB has been calculated for metals by Nakamichi [Nak96]. In short, he found the following plausible and intuitive relationship; the larger the angle between two grains, the larger the resistivity increase.

Electrical measurements at Cu nanowires and investigations by EBSD could even quantitatively discriminate the impacts of different types of GBs [KZN+10] and confirm the very small resistivity of twin boundaries. As the diameters of the large angle grains are in the micrometer range in these TiO2−x films and the mean free path is below 5 nm, it can be concluded that grain boundary scattering is not of great importance here.6 Furthermore, the fact that the Nb doping leads to even larger grains but smaller mobilities indicates the negligibility of grain boundary scattering as well. In the case of good conductive, degenerated, and dense standard TCO films, GB scattering is also not very important. This is because of the already given argument of larger grains compared to the mean free path and the equality of the mobility determined optically and electrically [CYL00, Ell01, BE14, FKK+10].

To summarize, it is possible to produce very flat films with this production method. Very large grains in the several micrometer range can be prepared in TiO2−x films by sputtering on glass. Due to their huge size in comparison to the mean free path of few nanometers, GB scattering is of not much relevance for these high quality films. Higher defect densities, like oxygen vacancies and stress resulting from a lower O2pp, have two main effects. First, they are reducing the electrical mobility and secondly, they lead to more nucleation centers and thus, to somewhat smaller grains with a more frayed morphology.

---

6This is true as long as no oxidation processes or other degradation mechanisms lead to insulating barriers which would not only increase the resistivity massively but also alter the temperature dependency completely [EM08]. Such processes can be prevented by using a capping layer.
6.4 Summary, Conclusion and Outlook

In this chapter, important insights for understanding the material properties of TiO$_2$ could be gathered. First, the high dielectric constant of undoped TiO$_2$ could be validated capacitively and explained by the mechanism of ionic polarization which has been investigated by the phonon contribution in the FIR regime.

The investigation of the optical properties revealed that a high value of $\varepsilon_{st}$ lowers the plasma frequency. Therefore, higher charge carrier concentrations are possible in TiO$_{2-x}$ compared to, e.g., ZnO:Al without reducing the optical transmission by free electron excitation. All measured absorption of wavelengths between 400 nm and 1100 nm could be proven to be caused oxygen deficiency and not by charge carriers. The large refractive index has been identified as the most important parameter and distinction compared to common TCOs for the optical performance of TiO$_{2-x}$ thin films on glass. The thickness and wavelength dependent interference fringes encompass 30%, creating a colored impression of the film even without any absorption present. The usage of a Si$_3$N$_4$ capping has been identified as an effective procedure for reducing the reflectivity due to the index matching mechanism. This positive effect of reducing the intensities of interference fringes is dramatically increased by employing an additional Si$_3$N$_4$ layer below the TiO$_{2-x}$ film. With this method sub-stoichiometric films with mean transmissivities above 90% could be produced, the interference fringes of which became as small as for standard TCOs like ZnO:Al. An oxygen content during the sputter process below a certain threshold massively increases the absorption of the film. Additional Nb doping does not alter the transmission behavior in the optical regime. However, it could be proven that it widens the band gap significantly but mainly not via the Burnstein-Moss shift of induced free electrons. The small extend of such a blue shift caused by free electrons like in standard TCOs can be understood by the much larger density of states of the conductive d-band in TiO$_2$ compared to the s-bands of the other oxides.

The structure of the sub-stoichiometric TiO$_{2-x}$ films investigated by XRD has been found to be purely amorphous in the as deposited state. With the annealing at 300 °C, they crystallize solely into the anatase phase. A lower limit of the necessary oxygen concentration could be found below which the capped films stay amorphous even at much higher temperatures like 500 °C. Uncapped films, on the other hand, gather the necessary oxygen from the residual gas during the annealing and obliterate thereby the correlation between preparation conditions and film properties. These characteristics are the same with Nb doping and also the FWHM of 0.25° is very small and consistent for all series. The maximum intensity is the same for all series and is developed within the error margin at the same optimum O$_{2pp}$ of about 70%.

AFM and XRR measurements revealed a very flat surface and dense films indicating very good sputter parameters for the TiO$_{2-x}$. Because of this flatness and the material homogeneity, the SEM measurements can make use of the electron channeling contrast. Thus, the crystallographic orientation of the grains becomes visible and the grain sizes can be determined. This reveals sizes in the micrometer regime and a dependence on the used O$_{2pp}$. As this is much larger compared to the mean free path of a few nanometers, it can be concluded that GB scattering is negligible in
TiO$_{2-x}$ as it is for common high quality TCO films as well \cite{CYL00}. Smaller structures of about 20 nm could be observed within the grains which is consistent with literature. They are attributed to stress releasing twin boundaries and conglomeration of dislocations.

As in research Si$_3$N$_4$ layers are deposited by chemical vapor deposition techniques usually and Si$_3$N$_4$ offers a high degree of tunability of its physical properties, it would be quite intriguing to investigate the change of its physical properties like density, roughness, stability, and refractive index by changing the sputter conditions. This would be of high importance in order to improve the optical characteristics like interference fringes and mean transmissivity of capped or encapsulated TiO$_{2-x}$ films.

Although in this work nearly all frequencies have been used in order to understand TiO$_{2-x}$, a small but important regime has been not covered fully. For the purpose of an exact measuring of the plasma frequency of the free carriers, the analyzed frequency regime has to be extended deeper into the IR, closing the gap between the LAMBDA25 UV/VIS and the FT-IR measurements in the MIR and FIR done so far. By doing so, it could be tested how well the prediction of the smaller plasma frequency of TiO$_{2-x}$ compared to standard TCOs is fulfilled. In the course of that, the Drude reflectivity in the IR would give the optical mobility. Comparing it with the electrical ones would further verify that the GB scattering can be neglected in highly conductive TiO$_{2-x}$.

In terms of the structural characteristics, the effect of higher annealing temperatures has been proven to be highly non-trivial. The trends are neither clear nor understood. In this respect some minor indications of a possible beneficial impact of smaller sputtering powers upon the structure have been found and should be examined in greater detail. The impact of higher Nb concentrations on the structural and optical properties should be investigated as well. Doing so, the tendency indicated by comparing undoped and 5 at% Nb doped films could be checked and further insight could be gained in order to explain it.

Of course, a variety of new approaches and characterization tools like EBSD could be tested to improve the analysis and understanding of the crystal structure and its influence on the electrical properties. Especially, finding a procedure or a seed layer, which can be sputtered on glass, to generate c-axes textured TiO$_{2-x}$ would be of very large interest. The much smaller effective masses along the a-axis could be utilized more efficiently which should enhance the mobility of the films drastically. On substrates like single crystalline SrTiO$_3$ \cite{HFU+05, GvD+07b} this beneficial effect can be seen, but they are far too expensive to be of any practical use.
In the last chapters the full frequency spectrum of electrical waves has been used to investigate and understand this fascinating material TiO$_2$. Beginning with DC fields, proceeding with the AC characteristics up to several MHz and finishing with waves whose wavelengths encompassed seven orders of magnitude from 1.5 Å over the ultra violet (UV), visual (VIS), and near infrared (NIR) regime up to the far infrared (FIR) one with about 15 mm. In this final chapter I want to come back to the questions from the beginning and explain, why TiO$_{2-x}$ (in anatase but not in rutile modification) turned out to be a competitive TCO. Then, I will sum up and combine some findings of the previous chapters with respect to most important TCO properties. After that, a compact comparison between TiO$_{2-x}$ and common TCOs will be presented with respect to the factors and influences relevant in a high quality TCO film. To complete this work, some final conclusive remarks and possible further fields of research will be given.

7.1 Why can TiO$_2$ be a TCO

As mentioned in the first chapter it was a big surprise when in the year 2005 Furubayashi et al. presented with TiO$_2$:Nb a 'new transparent metal' as they called it. In this thesis, I prepared films of similar quality by sputtering on glass instead of pulsed laser deposition on SrTiO$_3$. By this technique, even undoped but still metallic conductive films could be prepared. With their high transparency, they belong to this category of transparent metals as well, which has been achieved for the first time.

But why are these findings so surprising and happened so much later than for the other oxides, whose research started in the 50’s and for the latest candidate ZnO in the 70’s? More details can be found in section 1.1, here only as a short reminder: It is the fact that the standard $n$-type TCOs CdO, In$_2$O$_3$, SnO$_2$ and ZnO, including their usual dopants, are located in the same region of the periodic table. Furthermore, the conduction band minima of all these oxides are composed of the emptied, sphere like $s$-orbitals of the metal cations. Only such oxides should be able to form conduction bands with low effective masses due to the high and stable overlap of the

1Tang et al. investigated 1994 undoped TiO$_{2-x}$ in anatase and rutile configuration electrically and optically. He observed an insulator to metal transition very roughly and also a wide enough band gap, but no value for the transmission in the optical regime had been given. Furthermore, their minimal resistivity was one order of magnitude larger than the one I presented here.
adjacent spheres. Surprisingly, density functional theory (DFT) calculations and experiments have consistently proposed effective masses in the range of $0.4 m_e$ for TiO$_2$ as well [HAFD11, HKY+08, KTS+09, HYN+09, FYH+07], which is in the same range as the typical value of $0.3 m_e$ of the other TCOs (see table 1.2). As the conduction band of TiO$_2$ consists of highly oriented $d$-bands this was not to be expected. But that was not enough: The Ti-Ti distances are smaller in the rutile phase than in the anatase one (see table 1.2), which should result in a larger overlap. However, the mentioned low effective mass has been found in anatase, whereas in rutile calculated band masses of $25 m_e$ and even higher ones till $130 m_e$ determined experimentally, can be found. Moreover, the minimal cation-cation distances in standard TCOs are larger than in TiO$_2$. Comparing it with the respective ion radius they are still within the values of the common oxides although the resulting effective masses are quite different. Thus, the cation-cation distance can not explain the observed effective masses and trends when dealing with TiO$_2$.

In order to solve these discrepancies between the expectations and the measurements or, in other words, to gain a qualitative understanding for the results of the DFT calculations, the mass anisotropy of the anatase structure provides a good hint. All calculations and also the measurements on epitaxial films reveal the low value of about $0.4 m_e$ for the $x$ and $y$ (or [100] and [010]) direction only, but a value of roughly $4 m_e$ for the $z$ (or [001]) one [HKY+08, HYN+09]. Such a large anisotropy is not known for standard oxides, therefore, the orientation within the anatase modification deserves a closer inspection.

In figure 7.1 a ball-and-stick model of the anatase octahedron is given together with illustrations of the Ti $d$-orbitals which are hybridized with O $p$ orbitals to form the Ti-O bondings with red endings. These bonding orbitals are, named according to the ligand field theory, $e_g$ ($d_{z^2}$ and $d_{x^2-y^2}$) and two of the three $t_{2g}$ orbitals ($d_{yz}$ and $d_{xz}$) [ATMF00]. The bonding states of these orbitals are occupied and form the upper part of the valence band. Thus, these orbitals can not contribute to the conduction. Calculated by DFT, the lowest unoccupied band and, therefore, also the bottom of the conduction band is primarily composed of the $d_{xy}$ orbital, which lies parallel to the (001) plane.
Section 7.1 Why can TiO$_2$ be a TCO

Figure 7.2: Ball-and-stick models of anatase TiO$_2$. With the help of the software tool MERCURY two important crystal planes are visualized as cuttings through extended anatase crystals. In (a) the (001) plane is shown in transparent blue and in (b) the (100) in green. The atoms which are exactly within the respective planes can be seen in white for Ti and red for O. It is important to note that the (001) plane is solely populated with Ti atoms, which is not the case for the (100) one. The $d_{xy}$ orbitals, which form the bottom of the conduction band, are exactly located within this (001) plane.

In figure 7.2 two important crystal planes of the anatase structure are shown to illustrate the reason for the large anisotropy of the effective masses between these planes. The (001) plane is visualized in translucent blue and the (100) in green. In the (100) plane mainly the bonding orbitals between Ti-O are located, whereas in the (001) the empty $d_{xy}$ orbitals lie without any impeding oxygen. Because of this, the highly oriented $d_{xy}$ orbitals of adjacent octahedra can overlap each other, resulting in a relative low effective mass (an illustrative sketch of this can be seen in figure 7.3). The overlap is large enough to allow a high mobility of at least 50 cm$^2$/Vs for sputtered, undoped TiO$_{2-x}$ at 2 K (see table 4.3).

This scenario can explain the large anisotropy of the effective masses between the $a$ and the $c$ axes of the anatase phase and the mobility increase by three orders of magnitude during the crystallization (see section 4.1). Also, the reduction of the room temperature mobility from roughly 20 cm$^2$/Vs to 9 cm$^2$/Vs by the incorporation of 5 at% Nb$^2$ (see figure 4.7) can be explained by the distortion caused by the larger Nb$^{5+}$ ion compared to the Ti$^{4+}$ one (78 pm and 74.5 pm) [Sha76]. This results in a larger lattice constant as measured by a shift of the (101) reflex position in the X-ray diffraction (see figure 6.19(a)) as also predicted by DFT calculations [KTS+09].

With this model one can also answer the question why the metal-insulator transition (MIT) in TiO$_{2-x}$ does not obey the Mott law in contrast to the standard TCO materials (see figure 4.11). The high importance of disorder can be interpreted as a large Anderson contribution to the MIT (see section 2.2.6).

$^3$The concentration specification 1 at% means that one of hundred Ti cations is substituted by a foreign element.

$^2$With a similar concept Funabiki et al. explains the differences between amorphous and crystalline p-bonded silicon [FKH12].
But how can the distinction to the rutile modification be understood? The smaller distances between the Ti atoms in rutile (3.57 Å and 2.96 Å)\(^4\) than in anatase (3.79 Å and 3.04 Å) should result in a larger overlap and therefore smaller effective mass. With formula 2.17 and 2.18 and the given distances a ratio of the effective masses (\(m^*_{\text{rutile}}/m^*_{\text{anatase}}\)) can be estimated.\(^5\) According to these assumptions, only a small difference would be present. The rutile masses should be 65\% to 83\% of the anatase ones. As indeed the effective mass in rutile is larger than in anatase by a factor of more than 20, one can conclude that the distance between the Ti atoms is not the dominant parameter for the effective mass in TiO\(_2\).

In figure 7.4 two ball-and-stick models of rutile are given to illustrate the key structural difference in comparison to anatase. In anatase the (001) plane is only populated by Ti atoms and no binding orbitals are hindering the overlap of the \(d_{xy}\) orbitals, whereas in rutile, O atoms are situated between adjacent Ti atoms (see figure 7.4(a)). Moreover, the rutile structure does not allow any plane to be existing, where the orbitals forming the conduction band can overlap with their neighbors. This is illustrated in figure 7.4(b) with the (110) plane marked. The oxygen atoms are colored in red as usual, but here the Ti ones are depicted as blue and green spheres indicating the two possible orientations of the octahedra. It can be seen that adjacent octahedra are flipped by 90° and thus there can not be a plane with a low effective mass. The small overlap leads not only to a large effective mass but results in a different charge transport mechanism in rutile.

As pointed out by Tang et al. and others, TiO\(_2\) in the rutile structure does not exhibit a metallic conductivity [TPS\(^6\) 94]. Thus, any charge transport is done via thermally activated hopping mechanisms and, together with the large polaronic effect which increases the effective mass even further and reduces the spatial extend of the electron waves, this leads to small polaron hopping (SPH, see section 2.2.4). In literature SPH has often been ascertained in TiO\(_2\) films.

\(^4\)Two values are given as the octahedra are distorted which result in two different types of adjacent Ti ions.
\(^5\)For this the ratio of the effective lattice constants has to be known which has been approximated by the cube root of the densities. This results in a small correction factor of 0.94 for the effective mass ratio via \(a^2_{\text{anatase}}/a^2_{\text{rutile}}\) of equation 2.18.
Section 7.1 Why can TiO$_2$ be a TCO

Figure 7.4: Ball-and-stick model of the rutile structure created with MERCURY. In (a) the (001) plane is marked in the same way as in the anatase structure in figure 7.2(a). However, in the rutile case oxygen is situated between the Ti atoms in this plane, thus, no large overlap of the conduction band orbitals (also the $d_{xy}$ ones [SS92]) can exist there. For a better illustration of the changed layout in the rutile structure, the (110) plane is marked in (b). For clarity, the Ti atoms are depicted in blue and green to distinguish the two different orientations of the octahedra. The adjacent octahedra are flipped by 90° against each other leading to a denser structure. Because of this, there can’t be any plane with a good overlap of the directed $d$-orbitals forming the conduction band minimum and thus, none with a low effective mass.

[JM+12, HWS+14, MMJ+13, YLKM08, YIM10, HCVJ07]. Although some authors attribute this to the anatase phase as well, they show that their films have rutile contributions as well. This is not the case for the conductive films presented here and also not for all the other TCO related TiO$_2$—based articles. Therefore, I suppose that the resistivity and its temperature behavior is mainly dominated by the rutile portion in the films of these studies, resulting in the SPH characteristics.

To summarize, the relative low effective mass of $n$-type TCO materials is achieved always by a large overlap of the orbitals of adjacent cations, which form the conduction band minimum. In standard TCO materials these are spherical $s$-orbitals, whereby a good overlap is automatically guaranteed. Therefore, the overlap is insensitive against physical disorder and depends only upon the distance between the cations [Rob08]. This explains for example the observed isotropic effective masses in the respective crystal phases and the fact that similar mobilities can be achieved also in the amorphous phase in these cases [Hos07, FKH12].

In TiO$_2$ the necessary high overlap is much harder to obtain due to the highly oriented character of the $d$-orbitals. Nevertheless, this is possible in the anatase structure as all $d_{xy}$ orbitals, which form the conduction band minimum, are laying in the (001) plane. No oxygen atoms with their bonding orbitals are laying in this plane and the Ti atoms are oriented in a way that the $x$-shaped orbitals of all adjacent atoms can overlap with each other. This explains the unexpected low effective mass of TiO$_2$ in the anatase modification as well as its structural anisotropy. Additionally, the difference of the electrical mobility of several orders of magnitude between the amorphous and the crystalline phase can be understood by the high degree of orientational disorder between the TiO$_6$ octahedra in the amorphous phase thus breaking up the overlap between neighboring cations. And last but not least, it elucidates why the rutile structure exhibits much larger masses notwithstanding the smaller cation distance.
Figure 7.5: Conductivity $\sigma$ at room temperature as function of the transparency for a selection of TiO$_{2-x}$:Nb films. It is important to note that only films with a capping but without a seed layer have been included. The observed maximum transparency of 85\% is limited by reflectivity and could already be increased to more than 90\% by some first tests with non-optimized Si$_3$N$_4$ seed layers. In contrast to common TCOs, a clear optimum of conductivity and transparency at $T \sim 70$\% can be observed.

### 7.2 Summary and Relationships of TCO Properties in TiO$_{2-x}$

In the context of this work high quality TiO$_{2-x}$ films could be prepared and in the last chapters their resulting electrical, structural and optical properties have been thoroughly investigated. In this section some of the results, which are especially important for the properties of TiO$_{2-x}$ as a possible TCO, will be summarized and combined.

The lowest resistivities, measured at room temperature, ranged from 3600 $\mu$\Omega cm (with a mobility of 19 cm$^2$/Vs) for undoped films to 550 $\mu$\Omega cm (8.6 cm$^2$/Vs) with 5 at\% Nb doping. In table 4.3 the electrical properties of the most conductive samples can be seen and in section 4.8 a detailed comparison with literature values can be found. It reveals that the films prepared in this thesis exhibit the best conductivities for sputtered TiO$_{2-x}$ films. Furthermore, this is achieved by a much lower annealing temperature (300 °C instead of typically 500 °C and more), lower Nb concentrations, no reducing annealing atmosphere, and no special single crystalline substrates. The reason for these improvements are the exact determination of the hysteresis and precise control of the O$_{2pp}$ during the sputter process. The vital importance of the amount of oxygen deficiency can be seen in every chapter by different means, for example in figure 4.6 and 4.8.

The second main reason is the use of a Si$_3$N$_4$ capping layer: It can effectively hinder oxygen to diffuse into the film during the annealing, which would result in a reduction of the number of oxygen vacancies (electron donors), inactivation of the Nb doping and in the worst case insulating the grains from each other completely.

Naturally, the most important characteristics of a TCO material for any application are conductivity $\sigma$ and transparency $T$ which have been investigated in section 4.3 and 6.2 mainly. In

---

*The residual amount of oxygen in an argon flooded tube furnace or even in a heated vacuum setup is still sufficient for such deteriorating effects (e.g. figure 4.1).*
Section 7.2 Summary and Relationships of TCO Properties in TiO$_{2-x}$

Figure 7.6: Change of $n$ and $T$ as result of the chosen O$_{2P}$ for TiO$_{2-x}$:Nb. Although all doping levels of the capped and equally thick samples have been included into this graph (about 40 data points) a consistent picture arose. As it is typical for TCO materials, low oxygen contents result in high charge carrier densities but also in strongly absorbing films. It is very interesting to note that a very large number of free electrons can be obtained also at highly transparent films at applied O$_{2P}$ values of about 70 % (marked by the dashed ellipse).

The drop of the charge carrier density at the high transparency end is much sharper than for standard TCOs.

Figure 7.5 the room temperature conductivities of TiO$_{2-x}$ films (∼ 250 nm thick and with Si$_3$N$_4$ capping) with varying Nb concentrations as function of their mean transparencies (determined by the Swanepoel method) are depicted. For standard TCOs, transparency and conductivity are clearly opposing functions, thus, the preparation conditions can freely be chosen to balance these two demands [Cas11].

The relationship in TiO$_{2-x}$ on the other hand is highly non trivial. At high oxygen contents the transparency is very large and reaches in such a layer stack (glass, TiO$_{2-x}$, Si$_3$N$_4$) 85 % but because of the high reflectivity not more. This is true even for completely insulating films and the conductivities can encompass several orders of magnitudes with the same transparency within the error margin.

In a short interval below this maximum transparency, there is indeed a monotonic increase of the conductivity as expected in the case of standard TCOs for the full range. Nevertheless, at $T \sim 70 \%$ the conductivity drops nearly as sharp as before at the maximum transparency and afterwards rises again very slowly. So it can be concluded that the best conductivities are accompanied with a high transparency nearly automatically in the case of TiO$_{2-x}$:Nb.

The soft conductivity increases are caused by increasing charge carrier densities which result from a larger oxygen deficiency as it has been shown, for example, in figure 4.6(b). The same mechanism is behind the conductivity and absorption increase in standard TCOs [Ell00, EPJ+04, Hos07]. An illustration of the changes of transparency and carrier density with the O$_{2P}$ during the sputtering of TiO$_{2-x}$ can be seen in figure 7.6. Two things are quite unusual in comparison to other TCOs. First, the free electron density in TiO$_{2-x}$ breaks down very sharply and quite completely when reaching the transparency maximum. This collapse of the charge carrier concentration causes the conductivity drop seen at $T \sim 85 \%$ in figure 7.5. It is even more remarkably as the O$_{2P}$ is
Figure 7.7: Correlation of the electrical mobility $\mu$ and the XRD intensity $I$ of the (110) reflex of anatase with the utilized $O_{2pp}$. In (a) the findings of a target dependent minimum $O_{2pp}$ limit for the crystallization are depicted (see section 6.3.1). Below a specific and very sharp $O_{2pp}$, the crystallization is impeded heavily. Such films stay amorphous even up to annealing temperatures of 500 °C instead of the usual 300 °C. The mobility drops drastically due to the lack of crystallinity as can be seen in (b) (copy of figure 4.8). Above this limit, there is no strong relationship between $I$ and $\mu$. Very interestingly, the mobility stays nearly constant at a high level in the case of undoped films when increasing the oxygen content further. This is not the case for Nb doped films where it vanishes completely although it is declining much more gently.

in some cases still below 100 % of the hysteresis.\footnote{Hysteresis of the $O_{2pp}$ in the chamber when changing the oxygen flow from zero to high and back again in a reactive sputtering process. Details of the definition and examples are given in section 2.1.1 and 3.1.2.} In common oxides, especially doped ones, this is not the case and reasonable conductive samples can be produced even with oxygen contents above the transition point. The reason for this behavior can be seen in the much higher formation enthalpies of TiO \(_2\) and Nb\(_2\)O\(_5\) in comparison to the other oxides, which are presented in table 1.2. A high affinity of oxidation is the consequence and according to the law of mass action this shifts the equilibrium of the reaction far on the oxide side. Actually, this is the main reason why it is such a challenge to produce conductive and transparent TiO\(_{2-x}\). The range of $O_{2pp}$ values in which the films are not already metallic black but still exhibit some free electrons is very small in comparison to other oxides. Employing sputter conditions like in this thesis (several hundred watts of power at an 3 ” target and 1 Pa base pressure), this is less than 5 mPa.

The second interesting fact is that there exists a local optimum of the charge carrier concentration, transparency and $O_{2pp}$ (marked as a dashed ellipse). This is true for every Nb concentration and can be seen in the appendix in figure A.12. However, the intensity of this local maximum is by far not sufficient to fully account for the global maximum conductivity seen in figure 7.5 at $T \sim 70 \%$.

In section 4.3 it has been evinced that the reason for the conductivity breakdown at lower transparencies, i.e., $O_{2pp}$ values, is a dramatic drop of the mobility. A copy of the most important graph can be seen in figure 7.7(b). The reason for this breakdown became clear when investigating the dependency of the structural properties on the utilized $O_{2pp}$ and can be seen in a summarized fashion in figure 7.7(a). A critical $O_{2pp}$ limit can be found below which abruptly no crystalliza-
tion takes place. It has been demonstrated that this is true even for annealing temperatures up to 500 °C, whereas above this $O_{2\text{PP}}$ limit, the necessary minimal crystallization temperature is well below 300 °C. The most likely cause for this behavior is the lack of oxygen to form the TiO$_6$ octahedra. Without a capping layer the crystallization takes place, as the necessary amount of oxygen can diffuse into the film during the annealing.

In section 6.3.1 it has been shown that for every $O_{2\text{PP}}$ series there is a maximum crystallinity which is not at the maximum $O_{2\text{PP}}$ as one would guess. The necessary chemical composition seems to be reached already slightly above the minimal $O_{2\text{PP}}$. Whereas a further increase of the oxygen content is deteriorating the crystal structure slightly. This influence can be understood by an increase of the oxygen ion bombardment on the growing film as it is known for sputtered oxides [AKW10, Köhl10]. Nevertheless, the slight deteriorating effect on the crystallinity cannot explain the tendencies seen for the mobility. The mobility of the undoped case reaches a maximum and stays practically constant within the error margin. Eventually, a small declining effect caused by the bombardment could be present in the mobility as well.

The progression of the mobility of the Nb doped films is completely different and does not at all correspond to the one of the XRD-intensity. Beginning at $O_{2\text{PP}}$ values, which are 10% to 20% above the lower $O_{2\text{PP}}$ limit, a decline of the mobility sets in. This leads to the fascinating effect that approaching the transition point (100%) the mobility for Nb doped films vanishes nearly completely, while in undoped ones it remains high. From this comparison and the high XRD-intensity of the doped films one can conclude that another additional mechanism has to be responsible for this deterioration of the electrical mobility.

The loss of the charge carriers with increasing oxygen content is in absolute numbers much higher for doped films than for undoped ones. This means that not only oxygen vacancies are filled, but also Nb as a dopant becomes inactivated. The reason is a further oxidation of Nb from NbO$_2$ to Nb$_2$O$_5$. No crystalline precipitations have been found by XRD and temperatures are too low for long range diffusion in such a high melting oxide. Therefore, I propose that they are either very small or that the Nb is further oxidized by binding an additional oxygen atom during the sputter process resulting in an oxygen interstitial defect, which is supported by DFT calculations [KTS+09, KY11]. Precise atomprobe measurements comparing samples with different Nb concentrations and sputtered at different oxygen levels could eventually show this proposed higher oxygen concentration in samples with a larger Nb content.

Such Nb$_2$O$_5$ precipitations or bonds to interstitial oxygen atoms represent efficient scatterers due to the local deformations of the lattice. This explains why lower free electron concentrations compared to the maximum value, which is possible at one doping level, is accompanied with a lower mobility (see section 4.3). Furthermore, it resolves why the conductivity as function of the charge carrier density becomes steeper with higher Nb concentrations as it can be seen in figure 7.8.

---

8 Again, all films exhibit similar thicknesses and the small differences have been corrected by a linear factor, which however does not alter the found scattering of $\mu$ and $I$.

9 Here the intensity has been used as a measure of the crystallographic perfection, as the FWHM is very small and for not to low intensities they concentrate at about 0.25°. This means, it is not altered by the $O_{2\text{PP}}$, Nb or higher annealing steps and the intensity for such equally thick films is a more sensitive measure.
TiO$_2$ as a TCO

Figure 7.8: Relationship of the conductivity $\sigma$ and the charge carrier density $n$ at room temperature for 250 nm thick TiO$_{2-x}$:Nb films. The lines are a guide to the eye to illustrate the steeper decline of the conductivity at higher Nb concentrations.

To finish this section, TiO$_{2-x}$ will be included into the classification of conductive materials, as it was done for example in a review of the common TCOs by Edwards et al. [EPJ+04]. In figure 7.9 the charge carrier concentrations and the mobilities of various types of materials are plotted to illustrate the differences of their electric characteristics. Metals gain their high electrical conductivity through their very high electron density and the main difference between various metals lays in their mobility.

Semiconductors on the other side exhibit very high mobilities due to the perfection of their crystal structure and the low effective masses. TCOs lay in between with low enough charge carriers to stay transparent in the optical regime but much larger ones than in typical semiconductors. It can clearly be seen that TiO$_{2-x}$ belongs indeed to the group of TCOs despite all the differences of its electrical, structural and optical properties as they have been worked out in this thesis. Hosono et al. and Funabiki et al. pointed out that materials with electron mobilities larger than 10 cm$^2$/Vs can be accounted as excellent $n$-type materials [HKUK96, FKH12]. In the case of TiO$_{2-x}$ this could now also be achieved by sputtering on glass and low temperature annealing, which increases its potential for an application as TCO quite significantly. Figure 7.9 makes it evident that the mobility of TiO$_{2-x}$ at room temperature is the main reason for not reaching the same conductivity level as the common TCOs.

The two main factors to characterize a TCO film are its transmittance and resistivity and can be combined to find a figure of merit for comparison. For example, Gordon proposed the following ratio of the conductivity $\sigma$ and the absorption coefficient $\alpha$ [Gor00]

$$\frac{\sigma}{\alpha} = - \frac{1}{R_\square \ln(T + R)}, \quad (7.1)$$

with $R_\square$ being the sheet resistivity and $T$ and $R$ the total transmittance and total reflectance.
Section 7.3 Comparing Relevant Factors of TiO$_{2-x}$ and other TCOs

As mentioned before, in this section the main distinctions between TiO$_{2-x}$ and the common TCO materials namely In$_2$O$_3$, ZnO or SnO$_2$ will be illustrated shortly. First, the optical characteristics and afterwards in more detail the electrical parameters, limitations and interesting differences will be presented. The transmission through a TCO device is limited by the reflections at the interfaces and the absorption within the layer and of course the substrate. The absorption is for all oxides negligible, for not to large doping concentrations and increases strongly with the amount of oxygen deficiency.

Figure 7.9: Classification of conductive solids. Overview of correlation of room temperature $n$ and $\mu$ for different classes of materials and dashed lines of constant conductivity. The plotted data points are only an indication of their typical values. Large differences evolve by different preparation techniques and the details of the preparation procedure, especially, in the field of TCOs. The values are taken from [EPJ+04, Min00]. Nowadays, the best TCO films prepared by PLD can reach conductivities slightly above $1 \times 10^4$ S/cm [Cas11, ASM+03]. The best TiO$_{2-x}$ values prepared in the course of this thesis are included, together with one of the best values achieved in literature so far by PLD on SrTiO$_3$ [FHY+05].

respectively. He gave some values for TCO materials with different dopants like ZnO:F, In$_2$O$_3$:Sn or SnO$_2$:Sb, which varied between $0.2 \Omega^{-1}$ and $7 \Omega^{-1}$. Using this formula, the best films produced in this thesis including a Si$_3$N$_4$ seed and capping layer achieved competitive good values between $1 \Omega^{-1}$ and even $6 \Omega^{-1}$. Moreover, it should be noted that standard TCOs are known several decades longer than TiO$_{2-x}$. Also most research has been undertaken with Zn, Al, In and Sn, which is illustrated by the far highest amount of articles regarding this elements comparing different TCOs [Sta12]. A more than one order of magnitude larger number of articles per year compared to TiO$_{2-x}$ is devoted to every of these elements in the time span from 2007 to 2011. Thus, great room for improvement of its performance as a TCO material can be expected. Therefore, the next section will summarize and illustrate the different characteristics and limitations of common TCO materials and TiO$_{2-x}$. This will also highlight the possibilities and challenges of improving its performance.

7.3 Comparing Relevant Factors of TiO$_{2-x}$ and other TCOs
The main difference is the refractive index, which is significantly larger for TiO$_{2-x}$ in comparison to the standard TCOs, which exhibit all the same value roughly (see table 1.2). As a result very intense interference fringes and larger reflectivities can be observed (see section 6.2). This reduces the total transparency and because of the interference fringes causes a thickness dependent color of the layer.

Anti-reflex coatings can be utilized in order to reduce these losses and the colored impression. Si$_3$N$_4$ capping and seed layer have been proven to be quite efficient in this respect. On the other hand, for some applications the large refractive index can be even advantageous.

A very important aspect for the transparency in TCOs is the plasma wavelength or frequency $\omega_p \propto \sqrt{n/(m^*\varepsilon_{\infty})}$ which lead to a reflection of light with smaller frequencies (equation 2.42 and section 2.4.2). This represents an upper limit for the amount of charge carriers, which is applicable in a TCO. Approximately at values in the order of $1 \times 10^{21}$ cm$^{-3}$ the plasma frequency reaches the infrared and higher concentrations have to be chosen carefully not to deteriorate the optical transparency i.e. loose the red part. The larger $\varepsilon_{\infty}$ and the greater effective mass of TiO$_2$ increase this upper doping limit, without loosing intensity of the infrared or red light.

The solubility limit on the other side should not be exceeded as this could lead to light scattering or absorbing precipitations. Fortunately, for TiO$_{2-x}$:Nb this limit (below the anatase to rutile transformation temperature) is expected to be very high due to the very similar ionic radii. Indeed, experiments indicate a solubility of 10 at% up to 20 at% or even more [RDA$^{+04}$, FIHY$^{+05}$, GvD$^{+07}$a, IGY$^{+08}$]. For common TCOs this is much lower, e.g. for Sn in In$_2$O$_3 \sim 7$ at% is expected [FBB$^{+07}$] or < 2.5 at% for Al in ZnO [YLP$^{+02}$].

After the optical behavior, now the influences upon the conductivity and the differences in the charge transport effects will be discussed. There are two separate ways to impact the conductivity, either by changing the free electron concentration and/or their mobility. To generate free charge carriers different doping mechanisms can be utilized. The three most common methods are the same for TiO$_2$ and other TCOs. These are interstitial reducing gases like hydrogen, oxygen vacancies (as they are favorable defects [FKH$^{12}$]) or substitutional dopants. Hydrogen can very efficiently increase the charge carrier density and/or mobility in common TCOs [ZLW$^{+13}$, KZ02, WFMMK15, PJK$^{08}$], whereas for TiO$_2$ it is not quite clear, if it has a positive, negative or no effect.\textsuperscript{10} However, as a reducing or oxidation protection gas during the annealing process it is without a doubt beneficial and often used [YIH$^{+08}$, FIHY$^{+05}$]. Oxygen vacancies are

\textsuperscript{10}Calculation suggest that incorporated hydrogen is trapped at Ti sites and forms small polarons [SBY$^{+14}$], whereas experiments indicate that hydrogen does not become incorporated at all and even enhance the conductivity marginally [HUN$^{+07}$].
for all oxides known to generate carriers and as depicted in figure 7.9, all undoped examples can reach similar charge carrier densities. The major distinction in this respect is that in the case of TiO$_{2-x}$ a much more precise control is needed to prepare well conductive and transparent undoped TiO$_{2-x}$ films. The reason for this is the relative small process window of suitable O$_{2pp}$ values caused by the much higher enthalpy of formation of TiO$_2$ compared to ZnO etc.

The most important charge carrier generation mechanism is the one by doping elements. A minimum requirement to a potential dopant is the possibility of a higher valence state than the host metal cation. Secondly, it has to be able to substitute the metal cation, which limits the possible ionic radii range for an incorporation into the matrix, as a too large difference leads to an insolubility. Of course there are much more requirements and effects, which influence the suitability of an element as dopant in a specific host oxide and much research is done trying different combinations.

To evaluate eligibilities of dopants, their efficiencies$^{11}$ can be calculated and compared. The upper limit of this efficiency is determined by the hybridization probability of the relevant orbitals. It turns out that for many common TCO combinations, the indium free ones especially, these maximum efficiencies are well below 100% often roughly 50% and lower [MSB+79, YYS+00, Szy01]. However, this is not the case for TiO$_{2-x}$:Nb/Ta. Values above 90% are measured for the prepared samples of this work, are supported by the ones of epitaxial films found in literature [HFU+05, FHY+05] and are in agreement with DFT calculations [HKY+08].

This increases the application potential for TiO$_{2-x}$ even more, as such high values are very unique in the field of TCOs [YHH+07, HUN+07, YHH+08]. The combination of a high solubility of Nb in TiO$_2$ and a nearly perfect doping efficiency offers the possibility to generate a huge amount of charge carriers. Common TCOs exhibit a carrier concentration $\leq 1 \times 10^{21}$ cm$^{-3}$ [Gor09, EPJ+04, Cas11, ABJ15], whereas for TiO$_{2-x}$:Nb values above $1 \times 10^{21}$ cm$^{-3}$ have been reached easily in this thesis with Nb concentrations of only 5 at%. In literature even larger values can be found as there Nb levels of 10 at% and more have been used [FHH+11, YHH+07, FHY+05, FYH+07, ABJ15].

After presenting the similarities and distinctions of the effects determining the charge carrier density, now some of the multifaceted mechanisms and phenomenas impacting and limiting the mobility of high quality TCO films will be summarized and compared.

---

$^{11}$Typically calculated as ratio of measured charge carrier density to dopant concentration, which ignores additional sources like oxygen vacancies.
In comparison to good metals like Ag the mobilities in TCOs are massively lower, resulting in much smaller mean free paths compared to their film thicknesses. In section 6.3.2 the surface and morphology of the TiO$_2$$_{x}$ films have been investigated and very flat surfaces have been observed by AFM and XRR. Investigations of thickness series in TiO$_2$$_{x}$, which result in the same specific resistivity have shown that at least above 50 nm surface scattering can be ignored. Thus, surface and interface scattering is of not much importance for TiO$_2$$_{x}$ and also for common TCO materials. The small mean free path in the order of few nanometers but much larger grains is also the main reasons why grain boundary scattering is for degenerate TCOs with large electron densities\textsuperscript{12} usually of not much importance [BE14, FKK+10] (see also section 2.2.8).

On the other hand, scattering at 0 D and 1 D defects is an important issue for all TCOs and the reason, why deposition at elevated temperatures or heating procedures after the deposition increase the mobility significantly compared to unheated or as deposited samples. Different types of defects are present in TCOs of which oxygen vacancies and impurity atoms as dopants exist even in epitaxial, nearly perfect films in order to gain charge carriers. The density of other defects, like stacking faults or dislocations depend heavily on deposition parameters, techniques and misfit to the substrate.

The highly oriented $d$-orbitals are very sensitive to distortions of the lattice, which elucidates the observed mobility break down with decreasing perfection of the crystal structure. The much lower mobilities of films with the same amount of charge carriers but higher doping levels (see figure 4.7) can be understood by the picture of additional deformation of oxygen interstitials. This is consistent with the tendency that the optimal O$_{2pp}$ process window shrinks with increasing Nb concentration.

The distortion effect can also explain the observation that the maximum mobility, which could be achieved at every doping level, is heavily decreasing with the amount of incorporated Nb. In addition to this distortion effect, some DFT calculations suggest an increase of the effective mass of the conduction band from 0.4 to 0.8 (in the $xy$-direction) with 6 at% Nb [HAFD11]. The mobility decrease per defect of such types is much weaker in standard TCOs. In addition, their density is in typical high quality TCO films so low that their contribution of the overall resistivity is quite small.

Regardless of the other scattering mechanism, there is one, which represents the fundamental mobility limit for every highly conductive TCO material, the ionized impurity scattering (IIS) [BPA92].

\textsuperscript{12}Doping levels below $1 \times 10^{19}$ cm$^{-3}$ to $1 \times 10^{20}$ cm$^{-3}$ result in a too low Fermi-energy to overcome the potential barrier at low temperatures and thus, a characteristically falling conductivity during cooling is observed.
The valence state of every active (i.e. generating the necessary free electrons) dopant is at least +1 higher than the matrix cations. The resulting coulomb interaction provides a scattering mechanism which is intrinsic to the doped TCO and exists also in a structurally ideal single crystal. The formulas and detailed descriptions are given in section 2.2.10 and several further reviews denote IIS as the dominant scattering mechanism in common TCO materials [Min00, Gor00, EPJ+04, Cas11].

However, this is not the case for TiO$_{2-x}$ and there are at least three arguments for this statement.

- The clearly best mobility has been achieved for the undoped TiO$_{2-x}$ films, which is in contradiction to the IIS theory as the +2 charged oxygen vacancies should result in half the mobility of dopants in the +1 state, assuming the same charge carrier density.

- The mobilities of TiO$_{2-x}$:Nb films achieved here, which are comparable to the epitaxial ones grown by PLD, are far smaller than for standard TCOs. Thus, they are simply not large enough to become dominated by the IIS.

- The stronger screening effect of the much larger $\epsilon_{st}$ of TiO$_{2-x}$ increases the IIS mobility limit predicted by theory roughly by one order of magnitude to about 1000 cm$^2$/Vs$^{13}$. This is about two orders of magnitude higher than the mobilities measured, or reported in literature, even at 2 K [FHY+05, HUN+07, YHH+08].

Another intrinsic, always present source of increased resistivities is the scattering by phonons. Naturally, this mechanism is temperature dependent, in fact the only one which is listed in this summary.

It has been shown in thesis and is in agreement with literature that in the case of degenerate, standard TCOs, up to 30% of the room temperature resistivity is caused by phonon scattering. However, TiO$_{2-x}$ films exhibit a resistivity at room temperature which is about a factor of 2.5 to 3 higher than at 2 K. Very large mobilities up to 50 cm$^2$/Vs could realized for undoped TiO$_{2-x}$ at 2 K. Thus, phonon scattering is identified as the dominant scattering mechanism in TiO$_{2-x}$ films at room temperature. This relative factor is interestingly independent of the amount of Nb within the regime tested here. As a consequence an increase of the Nb concentration can reduce also the absolute resistivity increase caused by phonon scattering.

For standard TCOs and metals alike the temperature behavior of resistivity can be described with the Bloch-Grüneisen formula for acoustic phonon scattering perfectly. Furthermore, it has been

\[13\text{The maximum mobility depends on the charged dopant density heavily and is here denoted for a degenerate model at high free electron concentrations of } 1 \times 10^{21} \text{ cm}^{-3}. \text{ It can be seen in figure 2.6.} \]
shown that this is also true for the TiO$_2$–$x$ films. A close inspection of the temperature dependency revealed that the electron-phonon interaction is in this case better described by a phonon assisted $s – d$ electron interaction than a direct electron-phonon scattering as it is used for standard TCOs (see section 4.5.2). Measurements of temperature and magnetic field dependency of the resistivity at low-temperatures revealed additional differences between TiO$_2$–$x$ and common TCO materials (see section 4.7). These alterations of the electrical properties are caused by the $d$-band instead of $s$-band nature of the conduction band in TiO$_2$–$x$.

### 7.4 Final Summary and Outlook

In the course of this work transparent and highly conductive, Nb doped and undoped TiO$_2$–$x$ films could be produced on glass by the versatile technique of reactive magnetron sputtering. Thereby, an insulator to metal or degenerate semiconductor transition could be proven and determined precisely. Large deviations from the classical Mott type (correlation type) have been seen in contrast to standard TCO materials indicating a strong Anderson type contribution (disorder type) in TiO$_2$–$x$. This high sensitivity towards disorder is caused by the high directional form of the $d$-orbitals. A qualitative model has been given in order to understand the reasons for the different effective masses in the rutile and anatase phase and the influence of the crystallographic directions.

To achieve highly conductive TiO$_2$–$x$ films, the amount of sub-stoichiometry has been identified as the most important parameter$^{14}$. A very precise control of the O$_{2\text{PP}}$ during deposition and usage of a Si$_3$N$_4$ capping enabled an excellent conductivity and transparency without the need of high temperatures, expensive techniques, substrates or seed layers. The resistivities in the range of $5 \times 10^{-3}$ Ωcm to $5 \times 10^{-4}$ Ωcm of these sputtered TiO$_2$–$x$:Nb films are in the regime of present TCO films [Min00]. With mobilities well above $10 \text{cm}^2/\text{Vs}$ at room temperature they belong to the class of excellent $n$-type semiconductors [FKH12].

The influences on the electrical, optical and structural characteristics by Nb doping have been investigated in considerable detail. It possesses a practically perfect doping efficiency of more than 90 % in contrast to other TCO materials, thus conductivities of 550 µΩcm could be obtained here. A large solubility of Nb in TiO$_2$ and the lack of intrinsic compensating defects enable the access of very high electron concentrations. On the other hand, a heavy impeding of the maximum mobility by doping with Nb has been detected. A clear relationship between the maximum mobility and the Nb concentration has been found and a forecast for the mobility and conductivity for higher concentrations could be given. The mobility decrease is caused by local distortions and the tendency to incorporate interstitial oxygen, which increases with the amount of Nb. Phonon scattering has been identified as the dominant scattering mechanism in TiO$_2$–$x$ in contrast to the ionized impurity scattering (IIS) which limits the mobility in other high quality TCOs. A very high value of about 50 has been measured for the dielectric constant of sputtered TiO$_2$ films which increases drastically$^{14}$

---

$^{14}$A small number of oxygen vacancies is supposed to form a shallow donor level [JVM+12], whereas a too large oxygen deficiency can result not only in opaque and colored films but also in Ti interstitials which give rise to a low-mobility SPH [MW09]
the theoretical IIS mobility limit. Moreover, the plasma frequency is much lower in TiO$_2$ than in common TCOs due to its larger refractive index, allowing a larger free electron concentration, without loosing the optical transparency.

By the usage of dopants like Nb or V in stoichiometric, insulating TiO$_2$ films, dielectric constants up to three thousand could be realized and the Maxwell-Wagner interface polarization has been identified as the mechanism responsible for this colossal dielectric constant. The results of this thesis encourage the great potential of TiO$_{2-x}$ films as a new and highly versatile TCO material and is bringing its application one step closer. Furthermore, it opens the possibility of new fields of usage for sputtered films, namely energy storing supercapacitors.

A series of investigations would be very enlightening and could help to improve the performance and understanding even further. First task would be to investigate more samples in the doping regime between zero and 2.5 at% Nb, as several properties (maximum mobility, magneto resistance behavior, dielectric constant etc.) changed significantly there and more detailed analysis would improve the understanding and the results achieved so far. To further increase the conductivity of these films, higher Nb concentrations and thus electron densities should be tested, keeping in mind the increasing difficulty to obtain the optimal O$_{2pp}$ content. By this, also the question up to which point the relationship between mobility and Nb content found here is valid could be tested. In this respect, more detailed studies of the annealing behavior of TiO$_{2-x}$ films especially with seed and capping layer would be helpful to improve the electrical performance. A very intriguing ansatz to achieve even better mobilities for sputtered films is the usage of a suited seed layer to deposit epitaxial (001) anatase crystals. Achieving this, the plane with the lowest effective mass would be exactly parallel to the applied voltage resulting in a better electrical mobility. Dislocation density and local strain would be lowered distinctively, which are the main causes for the better mobility of the films deposited by PLD on SrTiO$_3$ compared to the sputtered ones of this thesis. Ta could be an even better dopant due to still higher solubility and a smaller theoretical effective mass, which is true for high dopant concentrations and the c-axis especially [HBTP12]. Thus, the adaptation of the preparation and characterization principles, which have been found in this work, to Ta would be very promising.

Further investigations in the field of supercapacitors are also very promising. The large capability of sputtered TiO$_2$ doped with different elements to enable colossal dielectric constants above 6000 have been demonstrated. The results of these stoichiometric and, therefore, electrically highly resistive films are very encouraging and reveal a large potential of further improvement. By employing other dopants like Ta, changed doping concentrations and varied annealing procedures, it should be possible to increase the $\epsilon_{st}$ even more and thus, enabling the next field of application for TiO$_2$.

As there are also some first reports of $p$-type TiO$_{2-x}$ one could think of a complete electronic world based on Ti. TiO$_2$ based dye sensitized solar cells generate energy, which is collected by $n$ and $p$-type transparent and self-cleaning TiO$_{2-x}$ electrodes. They are connected by TiN wires to TiO$_2$ based supercapacitors or water splitting electrodes, with TiO$_2$ as catalyst and protecting layer, to store the energy. Finally, the whole system could be controlled by very fast switching transistors using high-k TiO$_2$ gateoxides.
Appendix

Figure A.1: A 3D profilometer scan of a Hallbar device can be seen, like the one sketched in figure 3.8(a). It was structured via a shadow mask and exhibit a mean layer thickness of approximately 80 nm, although the scan length was in the order of 1 cm. Such scans allow the measurement of the real cross sectional area influenced by a shadowing effect. This area is important for calculating the correct specific resistivity of the material.

Figure A.2: An insulating TiO$_2$-x film is kept at nominal 2 K and its resistivity is measured by different current intensities. Using 100 μA and more, the resistivity drops as the temperature within the film increases. Below 10 μA the resistivity stays constant, as the induced heat can be cooled away by the system completely. However, a lower excitation current reduces the signal-to-noise ration as can be seen in the right half of the diagram.
Figure A.3: Example of the application of the Boch-Grüneisen law on metal films, here Ag with varying thicknesses. Thereby a reduced number of measured values are denoted with points, whereas the line is the theoretical fit. In (a) the absolute specific resistances are depicted and in (b) the residual resistivity $\rho_0$ was subtracted in each case from the fit and the data. This underlines the constancy of the phonon contribution irrespective of the film thickness.

Figure A.4: In (a) the change in the low temperature resistivity of the thickness series of undoped TiO$_{2-x}$ films can be seen (figure 4.26(a)). For the sake of completeness the 1 T MR data of the 40 nm thick TiO$_{2-x}$ film is plotted in (b) with a squared magnetic field scale to prove that the nMR is not due to a 2 D WL effect.
Figure A.5: Example of the temperature dependent MR behavior of TiO$_{2-x}$ films with high $k_F\lambda$ values doped with 2.5 at% in (a) and 5 at% in (b).

Figure A.6: Comparison of the permittivity in the MHz regime of different capacitor areas. The resonance peak, which could be for example seen in figure 5.2 is not an intrinsic material property, but an extrinsic one. The absolute value of the capacity, altered here by the capacitor area, changes the frequency of this peak. This phenomena is caused by a resonator circuit of the capacity of the device and the inductance of the connection leads and electrodes.
Figure A.7: XRD data of the TiO$_2$ series with Nb doping (a) before and (b) after annealing treatment. The phase composition and the trend with the O$_{2PP}$ is quite similar to the undoped and V doped case. Also in this case a rutile portion evolves with increasing the oxygen content above the transition. Interestingly, the anatase portion in the as deposited case at high oxygen flows is significantly larger than for the films, which are undoped or doped with the other elements.

Figure A.8: XRD data of the TiO$_2$ series with In$_{90}$Sn$_{10}$ doping (a) before and (b) after annealing treatment. Also in this case a rutile portion evolves with increasing the oxygen content above the transition. In the case of InSn doping the crystallization into the anatase structure is even more heavily impeded by larger oxygen fluxes.
Figure A.9: Transmissivity as function of the Nb content for TiO$_{2-x}$ films sputtered at O$_{2PP}$ of 90%. The films have been capped and the typical thicknesses of about 250 nm.

Figure A.10: XRD pattern of a selection of TiO$_{2-x}$ films with different amount of Nb and O$_{2PP}$ measured in the as deposited state. All curves are shifted for clarity reasons vertically. Regardless which point in the falling edge of the hysteresis has been chosen no crystalline contributions could be detected. Thicknesses up to 1 µm, sputtering powers between 100 W and 300 W, O$_{2PP}$ values between 40 % and 100 % and Nb concentrations from zero to 5 at% have been tested and resulted always in amorphous films. Of course at too low O$_{2PP}$ values metallic Ti will be deposited, which is crystalline. As the films shown here, are completely amorphous, only diffusively scattered X-rays ("Halo") reach the detector, which result in flat and broad bumps at small 2θ angles.
Figure A.11: XRD pattern of capped TiO$_{2-x}$ films doped with Nb and similar thicknesses annealed at increasing temperatures consecutively. In (a) 2.5 at\% Nb has been incorporated with two different O$_{2\text{PP}}$ values. 40\% is obviously below the critical oxygen concentration, so no crystallization takes place. Higher temperatures reduce the intensity of the reflexes, instead of increasing the crystal order. In (b) examples of 5 at\% Nb are shown. The concept of a critical O$_{2\text{PP}}$ can be seen there as well. Also these relative intense reflexes of above 400 cts are weakened instead of improved by employing higher temperatures. In contrast, the electrical properties improved by these higher temperatures. At this point the mechanisms behind these different trends or if they are perhaps only an measurement artifact is only speculative and further research has to be done. For example, impurities diffusing from the substrate into the film and also the thermal stress induced by the thermal expansion coefficients could influence externally the evolving structural quality which is accessible by XRD.

Figure A.12: The free electron density $n$ of capped TiO$_{2-x}$ films with different amounts of Nb as function of the mean, interference fringes free transparency $T$. The transparency is mainly controlled by the O$_{2\text{PP}}$ during the deposition of these films of similar thicknesses. This graph represents a different point of view of the data shown in figure 7.6. As it is common for TCOs the lower $T$, the higher $n$ becomes. Much more interesting is the very sharp decrease in the case of the highest values of $T$. A close inspection of the trends of the different doping levels reveal the local maximum of $n$ at a high $T$ of 70\%. It can be understood, as reducing the amount of oxygen further still, the films stay amorphous with a larger number of electron trapping defect levels.
**List of Figures**

1.1 History of TCOs .................................................. 3
1.2 Schematic of the different types of orbitals ...................... 4
1.3 Anatase and rutile structure of TiO₂ ............................ 6
1.4 Illustration of the structure of this thesis ........................ 9

2.1 Illustration of Film Formation .................................. 12
2.2 Example for a O₂-Hysteresis ..................................... 15
2.3 Principle of the Berg Model ....................................... 16
2.4 Mott, Anderson Transition ........................................ 27
2.5 Illustration of the limits of the BG function ..................... 32
2.6 Sketch of the mobility of three IIS models ....................... 35
2.7 Principle of the WL and WAL Effect .............................. 36
2.8 Polarization in a capacitor ....................................... 44
2.9 Electronic and Ionic Polarization ................................. 45
2.10 Electron-Pinning and Maxwell-Wagner Polarisation ............... 46
2.11 Frequency dependency of different polarization mechanisms .... 47
2.12 Luminosity Function .............................................. 50
2.13 Example for T,R and A in ZnO ................................... 50
2.14 Visualization of the Swanepoel-Method ........................... 52
2.15 Illustration of the Tauc-method .................................. 53
2.16 Bragg Reflection .................................................. 55

3.1 Sketch of the Sputtering Machine ................................ 59
3.2 Mythic Chamber ................................................... 60
3.3 Sputter Target with Plasma ....................................... 61
3.4 Target Drifting .................................................... 62
3.5 Hysteresis Shift ................................................... 64
3.6 Differences Sputtering Ti:Nb and Zn:Al ......................... 65
3.7 Nickelplated Copper Coffin ....................................... 66
3.8 Hall Bar ........................................................... 67
3.9 Van der Pauw Method .............................................. 68
3.10 Wire Bonding ...................................................... 69
3.11 Not Symmetrized MR, Hall Data ................................ 71
3.12 Equivalent Circuits ............................................... 74
3.13 Capacitor Masks ................................................... 75
3.14 Impedance Simulation ............................................. 77
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.15</td>
<td>Impedance Meter Connection</td>
<td>77</td>
</tr>
<tr>
<td>3.16</td>
<td>XRR example and GI-XRD reference pattern</td>
<td>79</td>
</tr>
<tr>
<td>3.17</td>
<td>Substrate Waviness</td>
<td>81</td>
</tr>
<tr>
<td>4.1</td>
<td>Influence of the Si$_3$N$_4$ capping</td>
<td>84</td>
</tr>
<tr>
<td>4.2</td>
<td>Crystallization temperature</td>
<td>85</td>
</tr>
<tr>
<td>4.3</td>
<td>$\rho$ vs. Higher Annealing Temperatures</td>
<td>87</td>
</tr>
<tr>
<td>4.4</td>
<td>Higher Annealing Temperatures: $n$, $\mu$</td>
<td>88</td>
</tr>
<tr>
<td>4.5</td>
<td>$\rho$, $n$ and $\mu$ for TiO$_{2-x}$</td>
<td>89</td>
</tr>
<tr>
<td>4.6</td>
<td>Influence of O$_{2PP}$ upon $\rho$ and $n$ for Nb doping</td>
<td>90</td>
</tr>
<tr>
<td>4.7</td>
<td>Correlation between $\mu$ and $n$</td>
<td>91</td>
</tr>
<tr>
<td>4.8</td>
<td>Change of $\mu$ upon O$_{2PP}$</td>
<td>93</td>
</tr>
<tr>
<td>4.9</td>
<td>$\rho$ vs. $T$ undoped TiO$_{2-x}$</td>
<td>95</td>
</tr>
<tr>
<td>4.10</td>
<td>Hall-data of insulating and metallic undoped TiO$_{2-x}$</td>
<td>96</td>
</tr>
<tr>
<td>4.11</td>
<td>MIT according to Mott</td>
<td>97</td>
</tr>
<tr>
<td>4.12</td>
<td>MIT of TiO$_{2-x}$</td>
<td>97</td>
</tr>
<tr>
<td>4.13</td>
<td>Hall results Intermediate O$_{2PP}$ Values</td>
<td>98</td>
</tr>
<tr>
<td>4.14</td>
<td>Small Polaron Hopping</td>
<td>99</td>
</tr>
<tr>
<td>4.15</td>
<td>Metallic Conductivity Undoped TiO$_{2-x}$</td>
<td>100</td>
</tr>
<tr>
<td>4.16</td>
<td>Data for different Ag films (fit with $n = 5$)</td>
<td>101</td>
</tr>
<tr>
<td>4.17</td>
<td>Data and BG-fit for standard TCO films with $n = 5$</td>
<td>103</td>
</tr>
<tr>
<td>4.18</td>
<td>Different BG-fit approaches for undoped TiO$_{2-x}$ films</td>
<td>104</td>
</tr>
<tr>
<td>4.19</td>
<td>BG-fit with $n = 3$ and 5 for undoped TiO$_{2-x}$ films</td>
<td>105</td>
</tr>
<tr>
<td>4.20</td>
<td>Comparison of BG-fit quality</td>
<td>106</td>
</tr>
<tr>
<td>4.21</td>
<td>BG-fit with $n = 3$ for series of undoped TiO$_{2-x}$ films</td>
<td>106</td>
</tr>
<tr>
<td>4.22</td>
<td>BG-fit of Nb doped TiO$_{2-x}$</td>
<td>107</td>
</tr>
<tr>
<td>4.23</td>
<td>Debye temperatures of TiO$_{2-x}$ films</td>
<td>108</td>
</tr>
<tr>
<td>4.24</td>
<td>Comparison of electron-phonon coupling of TiO$_{2-x}$ and TCOs</td>
<td>109</td>
</tr>
<tr>
<td>4.25</td>
<td>The phonon versus defect contribution to room temperature resistivity</td>
<td>110</td>
</tr>
<tr>
<td>4.26</td>
<td>Thickness dependent $\rho$ vs. $T$ data of undoped and TiO$_{2-x}$;Nb 5 at%</td>
<td>111</td>
</tr>
<tr>
<td>4.27</td>
<td>Lower thickness limit for metallic TiO$_{2-x}$</td>
<td>112</td>
</tr>
<tr>
<td>4.28</td>
<td>Lower thickness for doped TiO$_{2-x}$ films</td>
<td>113</td>
</tr>
<tr>
<td>4.29</td>
<td>3D WL in standard TCO</td>
<td>114</td>
</tr>
<tr>
<td>4.30</td>
<td>Increase of $\rho$ undoped TiO$_{2-x}$</td>
<td>115</td>
</tr>
<tr>
<td>4.31</td>
<td>Fit of $\rho$ of undoped TCO to Kondo model</td>
<td>115</td>
</tr>
<tr>
<td>4.32</td>
<td>$\rho$ vs. $T$ for TiO$_{2-x}$ thickness series, WL and Kondo test</td>
<td>116</td>
</tr>
<tr>
<td>4.33</td>
<td>Effect of 2.5 at% Nb on the low temperature resistivity</td>
<td>117</td>
</tr>
<tr>
<td>4.34</td>
<td>Low temperature resistivity in the case of 5 at% Nb doping</td>
<td>118</td>
</tr>
<tr>
<td>4.35</td>
<td>MR data of typical TCO</td>
<td>119</td>
</tr>
<tr>
<td>4.36</td>
<td>MR with 9 T of typical undoped TiO$_{2-x}$</td>
<td>120</td>
</tr>
<tr>
<td>4.37</td>
<td>Test of 2 D WL nMR in TiO$_{2-x}$</td>
<td>120</td>
</tr>
<tr>
<td>4.38</td>
<td>Fit of MR data of undoped TiO$_{2-x}$ samples of different thicknesses</td>
<td>121</td>
</tr>
</tbody>
</table>
4.39 MR at 2 K for different undoped TiO$_2$–$x$ films ........................................ 122
4.40 Results of the MR fit of undoped TiO$_2$–$x$ ..................................................... 122
4.41 pMR in Nb doped TiO$_2$–$x$ ........................................................................ 123

5.1 Low frequency impedance on undoped TiO$_2$–$x$ .................................................. 129
5.2 Permittivity as function of the frequency of undoped TiO$_2$ ................................. 130
5.3 XRD pattern of undoped TiO$_2$ sputtered in oxidic regime before annealing ...... 132
5.4 XRD pattern of undoped and oxidic sputtered TiO$_2$ after annealing .......... 132
5.5 XRD pattern of V doped TiO$_2$ ........................................................................ 134
5.6 Permittivity as function of $\omega$ of annealed V doped TiO$_2$ ............................. 134
5.7 Permittivity of annealed Nb doped TiO$_2$ ............................................................ 135
5.8 Permittivity of as-deposited InSn doped TiO$_2$ ..................................................... 135
5.9 Permittivity of annealed InSn doped TiO$_2$ ........................................................... 136
5.10 XRD results for InSn:Nb doped TiO$_2$ ................................................................. 137
5.11 Permittivity of all as-deposited TiO$_2$ films ......................................................... 138
5.12 Permittivity of all TiO$_2$ films after annealing ..................................................... 138
5.13 Cole-Cole diagrams of two supercapacitors ....................................................... 139

6.1 IR active phonon modes in anatase ...................................................................... 143
6.2 FT-IR spectra of amorphous and undoped TiO$_2$ ................................................. 144
6.3 FT-IR reflectivity with Nb doping and calculated $\epsilon(\omega)$ from undoped TiO$_2$ 145
6.4 FT-IR transmission data in the FIR regime ......................................................... 146
6.5 FT-IR results of the FT-IR samples measured in the FIR ................................. 147
6.6 $\epsilon_{st}$ calculated from FT-IR measurements in the FIR ..................................... 148
6.7 Influence of Si$_3$N$_4$ capping on the optical property ......................................... 149
6.8 Comparison of $T$ and $R$ between TiO$_2$–$x$:Nb and ZnO:Al ............................. 150
6.9 Influence of Si$_3$N$_4$ seed and capping layer ....................................................... 150
6.10 Transmission $T_x$ for varying O$_{2PP}$ of undoped TiO$_2$–$x$ ............................... 151
6.11 Influence of the annealing upon $T_x$ ................................................................. 152
6.12 Thickness dependency of the transmissivity ...................................................... 153
6.13 Mean $T_x$ as function of O$_{2PP}$ for varying Nb concentrations ................. 154
6.14 Influence of Si$_3$N$_4$ on the $T$ ......................................................................... 155
6.15 Determination of the width of the band gap of TiO$_2$–$x$ .................................... 156
6.16 XRD pattern for an O$_{2PP}$ series of undoped and capped TiO$_2$–$x$ ............ 157
6.17 XRD pattern of capped and uncapped films with 1 at% Nb ............................ 158
6.18 XRD pattern of films doped with 2.5 at% and 5 at% ........................................ 159
6.19 Analysis of the anatase (101) reflex of several TiO$_2$–$x$ films ....................... 160
6.20 Topography of TiO$_2$–$x$:Nb films scanned by AFM ........................................ 161
6.21 XRR measurements on TiO$_2$–$x$ with and without a capping after annealing 162
6.22 SEM pictures of undoped TiO$_2$–$x$ films, prepared at different O$_{2PP}$ ........ 163
6.23 SEM micrographs of Nb doped TiO$_2$–$x$ ........................................................ 164
6.24 SEM micrography of the sub-grain structure of TiO$_2$–$x$:Nb film ............... 165
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Illustrative sketch of $d$-orbitals in anatase</td>
<td>170</td>
</tr>
<tr>
<td>7.2</td>
<td>Important crystal planes in anatase TiO$_2$</td>
<td>171</td>
</tr>
<tr>
<td>7.3</td>
<td>Illustrative sketch of the role of disorder in anatase (001) plane</td>
<td>172</td>
</tr>
<tr>
<td>7.4</td>
<td>Ball-and-stick models of the rutile structure</td>
<td>173</td>
</tr>
<tr>
<td>7.5</td>
<td>$\sigma$ as function of the transparency for TiO$_2$:Nb</td>
<td>174</td>
</tr>
<tr>
<td>7.6</td>
<td>Change of $n$ and $T$ as result of the chosen O$_2$PP for TiO$_2$:Nb</td>
<td>175</td>
</tr>
<tr>
<td>7.7</td>
<td>Correlation of XRD intensity, electrical mobility, and utilized O$_2$PP</td>
<td>176</td>
</tr>
<tr>
<td>7.8</td>
<td>$\sigma$ as function of $n$</td>
<td>178</td>
</tr>
<tr>
<td>7.9</td>
<td>$n$ and $\mu$ for different materials</td>
<td>179</td>
</tr>
<tr>
<td>A.1</td>
<td>Profilometer 3D Hallbar</td>
<td>I</td>
</tr>
<tr>
<td>A.2</td>
<td>Excitation test on insulating TiO$_2$</td>
<td>I</td>
</tr>
<tr>
<td>A.3</td>
<td>Data and fit of Ag films with different thicknesses</td>
<td>II</td>
</tr>
<tr>
<td>A.4</td>
<td>Low temperature resistivity for undoped TiO$_2$:x and 1 T MR</td>
<td>II</td>
</tr>
<tr>
<td>A.5</td>
<td>MR fits of TiO$_2$:x doped with 2.5 at% and 5 at% Nb</td>
<td>III</td>
</tr>
<tr>
<td>A.6</td>
<td>Comparison of the permittivity in the MHz regime of different capacitor areas</td>
<td>III</td>
</tr>
<tr>
<td>A.7</td>
<td>XRD of Nb doped TiO$_2$</td>
<td>IV</td>
</tr>
<tr>
<td>A.8</td>
<td>XRD of In$<em>{90}$Sn$</em>{10}$ doped TiO$_2$</td>
<td>IV</td>
</tr>
<tr>
<td>A.9</td>
<td>Transmissivity as function of the Nb content</td>
<td>V</td>
</tr>
<tr>
<td>A.10</td>
<td>XRD pattern of TiO$_2$:x with Nb in the as deposited state</td>
<td>V</td>
</tr>
<tr>
<td>A.11</td>
<td>Influence of higher annealing temperatures on the XRD pattern</td>
<td>VI</td>
</tr>
<tr>
<td>A.12</td>
<td>Comparison of the free electron density and the transparency in TiO$_2$:x:Nb</td>
<td>VI</td>
</tr>
</tbody>
</table>
# List of Tables

1.1 List of values for relevant TCO criteria ........................................... 5
1.2 List of physical properties of relevant oxides .................................... 8

2.1 Fröhlich Polaron Constants $\alpha$ ....................................................... 24

3.1 Sputter parameters of $\text{TiO}_2-x$ ..................................................... 62
3.2 Sputter Parameters of $\text{Si}_3\text{N}_4$ ..................................................... 63

4.1 Limits of $n$, $\mu$ ................................................................................. 92
4.2 Fitparameters of figure 4.17 ............................................................... 103
4.3 Electrical properties of the best conductive $\text{TiO}_2-x$ films of this thesis .................................................. 125

6.1 Phonon modes in anatase and rutile $\text{TiO}_2$ ..................................... 143
6.2 XRR results ...................................................................................... 161
6.3 Grain sizes of $\text{TiO}_2-x$ films ......................................................... 165
Bibliography


Bibliography


<table>
<thead>
<tr>
<th>Reference</th>
<th>Description</th>
</tr>
</thead>
</table>


Bibliography

[FYH⁺07] Furubayashi, Yutaka ; Yamada, Naoomi ; Hirose, Yasushi ; Yamamoto, Yukio ; Otani, Makoto ; Hitosugi, Taro ; Shimada, Toshihiro ; Hasegawa, Tetsuya: Transport properties of d-electron-based transparent conducting oxide: Anatase Ti$_{1−x}$Nb$_x$O$_2$. In: Journal of Applied Physics 101 (2007), Nr. 9, S. 093705 Cited on pages 34, 170, and 181.


[GRO⁺03] Ginley, David ; Roy, B. ; Ode, Aiko ; Warm singh, C. ; Yoshida, Y. ; Parilla, Phillip ; Teplin, Charles ; Kaydanov, Tanya ; Miedaner, Alex ; Curtis, Calvin ; Martinson, Alex ; Coutts, Tim ; Readey, Dennis ; Hosono, Hideo ; Perkins, John: Non-vacuum and PLD growth of next generation TCO materials. In: Proceedings of the 3rd International Symposium on Transparent Oxide Thin films for Electronics and Optics 445 (2003), Nr. 2, S. 193–198 Cited on page 12.


[HFU+05] Hitosugi, Taro; Furubayashi, Yutaka; Ueda, Atsuki; Itabashi, Kinnosuke; Inaba, Kazuhiisa; Hirose, Yasushi; Kinoda, Go; Yamamoto, Yukio; Shimada, Toshihiro; Hasegawa, Tetsuya: Ta-doped Anatase TiO2 Epitaxial Film as Transparent Conducting Oxide. In: Japanese Journal of Applied Physics 44 (2005), Nr. 34, S. L1063 Cited on pages 128, 168, and 181.
Bibliography


[HLY+08] Hitosugi, Taro; Kamisaka, Hideyuki; Yamashita, Koichi; Nogawa, Hiroyuki; Furubayashi, Yutaka; Nakao, Shoichiro; Yamada, Naomichi; Chikamatsu, Akira; Kümigashira, Hiroshi; Oshima, Masaharu; Hirose, Yasushi; Shimada, Toshihiro; Hasegawa, Tetsuya: Electronic Band Structure of Transparent Conductor: Nb-Doped Anatase TiO_2. In: *Applied Physics Express* 1 (2008), S. 111203. Cited on pages 8, 94, 170, 180, and 181.


XXII


Bibliography


[LDL+13] Li, Yongfeng; Deng, Rui; Lin, Weinan; Tian, Yufeng; Peng, Haiyang; Yi, Jiabao; Yao, Bin; Wu, Tom: Electrostatic tuning of Kondo effect in a rare-earth-doped wide-band-gap oxide. In: Physical Review B 87 (2013), Nr. 15, S. 155151 Cited on pages 39 and 41.


Bibliography


[SLC10] Shieh, J.; Lin, Y. C.; Chen, C. S.: Influence of phase composition on electrostrains of doped (Bi 0.5 Na 0.5 )TiO 3 –BaTiO 3 –(Bi 0.5 K 0.5 )TiO 3 lead-free ferroelectric ceramics. In: Smart Materials and Structures 19 (2010), Nr. 9, S. 094007 Cited on page 44.


[ZXF+08] Zhang, Jing ; Xu, Qian ; Feng, Zhaochi ; Li, Meijun ; Li, Can: Importance of the Relationship between Surface Phases and Photocatalytic Activity of TiO2. In: Angewandte Chemie 120 (2008), Nr. 9, S. 1790–1793 Cited on page 5.
Danksagung

Am Ende dieser Arbeit möchte ich versuchen all jenen Menschen zu danken, die es mir möglich gemacht haben, diese Arbeit fertig zu stellen.
An erster Stelle gebührt mein Dank Herrn Prof. Dr. Matthias Wuttig, der es mir ermöglicht hat sehr selbständig Grundlagenforschung zu diesem spannenden Thema durchführen zu können. Insbesondere die Vielzahl an verschiedenen Projekten und stets neue Herausforderungen haben meine Zeit am Institut sehr abwechslungsreich und spannend gestaltet.
Außerdem bedanke ich mich bei Herrn Prof. Dr. Dieter Mergel für die Übernahme des Koreferats.


allen die meine Arbeit Korrektur gelesen haben, namentlich Florian Briechle, Hanna Brüning, meinem Stiefvater Karl-Georg Gerspach, Catharina Hermersdorfer, Peter Jost, Sonja Meier und Tobias Schäfter.

meinen Bürokollegen Jennifer Lukas, Tobias Schäfer und Roland Sittner für die sehr freundliche und angenehme Atmosphäre weit über das rein Fachliche hinaus.

allen Mitgliedern des Instituts für die kollegiale Arbeitsatmosphäre.

meinen Eltern für ihren Rückhalt und die Unterstützung gerade auch während der schwierigen Phasen der Promotion und meines gesamten Lebens.
Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit selbständig verfasst und nur die angegebenen Quellen und Hilfsmittel verwendet habe.

Eine Anmeldung der Promotionsabsicht habe ich an keiner anderen Fakultät oder Hochschule beantragt.

Aachen, den 01. Mai 2017