Oxide-Based Resistive Switches: Understanding Fundamentals of Resistive Switching in the Model System SrTiO₃

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Summary

Redox-based metal oxide resistive switching devices were recently proposed as a new class of non-volatile memories due to their superior properties. Through application of bias pulses in the ns-range these devices are able to change non-linearly between low- and high-resistance states in a non-volatile manner. This exciting technology offers new perspectives for computing hardware and is a promising candidate for the replacement of classic transistor-based memories in the near future. Despite these promises of fast non-volatile switching and scalability, the switching mechanism itself and kinetics require attention for oxide materials under high electric fields. To date, studies on resistive switching focus predominantly on oxygen anionic or electronic defects leaving hydroxyl or protonic charge carrier contributions out of the picture. This is surprising, since many of the resistive switching oxides are well-established materials in resistive humidity sensors. In this context, this work fundamentally investigates resistive switching for the model material strontium titanate, SrTiO₃, and presents experimental results on the carrier contributions and their transport kinetics (ionic vs. electronic) towards resistive switching at high electric field strength for memory application.

In the first part of this thesis, an overview on resistive switching is given through the General Introduction. Here, the underlying switching mechanism, typical electrical characterization methods and a brief summary of the physical properties of strontium titanate are discussed.

In the second part of the thesis in Chapters II to IV, the reader is introduced to the experimental and analytical investigation on SrTiO₃ resistive switches. Here in Chapter II this work turns to the role of electric field and frequency dependency for SrTiO₃-based resistive switching devices and analyzes the carrier diffusion processes involved therein. Own-processed Pt|SrTiO₃,δ|Pt resistive switching bits are classically analyzed via cyclic voltammetry under ambient conditions with respect to electrical field strength and time scale. Importantly, these classic experiments are limited to the understanding of equilibrium vs.
Summary

non-equilibrium transport since always a metastable state remains; carrier
diffusion kinetics can hardly be determined. Hence, chronoamperometry
measurements to analyze diffusion kinetics and to understand equilibrium
vs. non-equilibrium transport processes are suggested to the field. The
Memristor-based Cottrell analysis is suggested and used to successfully
determine bias dependent diffusion constant characteristics of SrTiO$_3$ and
to analyze the capacitive and memristive contributions of the resistive
switches. These material characteristics not accessible with state-of-art
methodology allow comparison of materials and improvement of their
materials selection criteria. In addition they directly implicate field
strength requirements to optimize operation of oxide-based resistive
switching devices.

Further in Chapter III, humidification effects on the devices and protonic
contributions towards resistive switching are discussed. In this
experimental study, it is demonstrated that the resistance states, the
current-voltage profile and switching capability are strongly affected by
the moisture exposure level of the resistive switching material strontium
titanate when fabricated as Pt|$\text{SrTiO}_3$|$\delta$|Pt devices. It is shown that the
overall resistance states (low and high) of the switch are strongly
modified by up to four orders of magnitude: The device’s current-voltage
profile shape, number of crossings and switching capability vary with the
moisture exposure level systematically. Cycling between different
humidity exposure levels shows that this process is fully reversible. From
a fundamental perspective, these results demonstrate that moisture and
protonic defects, even though only rarely considered so far, seem to play
an important role in oxide-based resistive switching. Hydroxyl interaction
with the oxide layer seems to be crucial to the basic property of
memristance and even allows to tweak the resistance ratios to engineer
high-performance resistive switching devices.

Motivated by the results and interaction of resistive switching
characteristics of SrTiO$_3$ with humidity, this work focuses in Chapter IV
on these humidification effects in more detail. The role of space charge
regions for the electrode|oxide interface with respect to the relative
humidity applied is experimentally investigated to clarify the protonic
contributions during resistive switching. In these experiments three sets of
samples which differ in their thickness and the free surfaces exposed to the atmosphere are fabricated. Therefore the effect of the total concentration of defects and effective surface to bulk ratio with respect to resistive switching could be investigated. Here, exponential conductivity change is observed as a function of the moisture level for thick samples in contrast to a linear dependency for thinner samples. This study attributes this behavior to the changed Schottky barrier by adsorbed surface water molecules and its interplay with the charge transfer of oxygen anionic-electronic charge carriers in the oxide affecting the memristance itself. Through this approach we are able to demonstrate that the sensitivity upon moisture during resistive switching is highly tunable. Finally the findings of this thesis are discussed towards optimization of materials characteristics for resistive switching devices.
Zusammenfassung


Im ersten Teil dieser Arbeit wird in der General Introduction ein allgemeiner Überblick über resistive Schaltelemente gegeben. Dabei werden die zugrunde liegenden Schaltungsmechanismen resistiver Speicher, typische Charakterisierungsmethoden und die physikalischen Eigenschaften von Strontiumtitanat zusammengefasst.

Im zweiten Teil der Arbeit wird der Leser durch die Kapitel II bis IV in die exerperimentellen und analytischen Untersuchungen an SrTiO₃ basierten Schaltern herangeführt. Kapitel II beschäftigt sich mit der Rolle des elektrischen Feldes und dessen Frequenzabhängigkeit bei SrTiO₃-

anionisch-elektronischen resistiven Schaltern nicht vernachlässigt werden kann. Denn hier ist die Wechselwirkung mit Hydroxylionen aus der Umgebung entscheidend für die memristive Eigenschaft und erlaubt sogar die Schalteigenschaften gezielt zu verändern.


Gegen Ende der Arbeit werden die Forschungsergebnisse dieser Arbeit in Bezug auf die Optimierung von Materialeigenschaften für resistive Schalter diskutiert.
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I General Introduction

1 Resistive Switching Materials, Application and Devices - a Brief Introduction


1.1. Technological Relevance of Resistive Switching Devices

Today we find computers and computing devices everywhere in our daily lives, whereas less than a generation ago computers were still a rare product only for niche applications. This technological progress, also called third industrial revolution or digital revolution, changed most of people’s working tasks and environment and brought us numerous benefits which we take for granted today. Examples are the automatization of industrial production and therefore cheaper products, communication devices like smart phones, new digital products like software and data, new distribution channels like the internet, advances in medical care like computer tomography, and many more.

This digital revolution is strongly linked to the rapid technological development of microprocessors with an exponential growth of the number of transistors per area on integrated circuits as predicted by Gordon Moore in the 1960s. This leads to an increased computing speed and miniaturization. Interestingly today’s computers are still based on transistor technology which dates back to the 1940s and a fascinating progress in material science and fabrication processing of microchips kept the performance growth ongoing. State-of-the-art transistor fabrication processes allow us to fabricate even chips with a feature size, i.e. pitch size, down to 42 nm on industrial scale.
Nevertheless, in the near future the transistor technology development will come to an end and already today several challenges are slowing down the progress in the development to which we got used to in the last decades. The theoretical and physical limits of miniaturization of transistor-based microchips with the nearby end of the ongoing miniaturization is well summarized and discussed by Markov\textsuperscript{5}; For example the heat management during computation prevents that all transistors are operated at full voltage at the same time which is often referred to as dark silicon.\textsuperscript{6} This means that in modern central processing units (CPUs) up to 60\% and on graphics processing units (GPUs) even 98\% of the transistors can only operate at limited speed.\textsuperscript{6} In addition to the end of miniaturization of transistor technology, today’s computing speed in classic computer systems is limited by the capabilities of computer memory which performance improvements could not follow the pace of technological development in recent years.\textsuperscript{7} This limitation is also known as the “von Neumann bottleneck”, which can only be overcome by new computing architectures and technologies.

Because of these limitations we need alternative technologies in computing devices and computer memory to today’s transistors with increased performance at reasonable costs that we can keep on benefitting from the developments in digital technologies as we got used to. Here, different new alternative memory technologies like resistive random access memory (ReRAM), ferroelectric random access memory (FeRAM) and phase change memory (PCM) are competing to replace state-of-the-art transistor-based memories, see Table 1.1.

All of the three alternative memory technologies have the advantage of being non-volatile like flash and have reading and writing times on the ns-range like dynamic random access memory (DRAM). The promise of ReRAM technology, based on the principle of resistive switching devices operating on the control of ionically-driven redox-reaction equilibria, lies in its superior properties of ns-switching speed, high scalability, non-volatility and reduced power consumption for future electronics.\textsuperscript{8} Beyond this, resistive switching devices, often also referred to as memristors\textsuperscript{9}, can even find application in the field of neuromorphic computing. The inherent property of near-continuous resistance tuning of resistive
switching devices combined with the memory effect could allow in the future more than two bit operation going beyond traditional digital computing. In addition different forms of Hebbian learning like spike time dependent plasticity have been shown to exist in memristive devices. These properties can very well mimic the neuronal synapse and its learning ability.\textsuperscript{10}

*Table 1.1: Comparison of performance indicators of promising alternative technologies to state-of-the-art transistor-based memory technologies.\textsuperscript{11-14}*

<table>
<thead>
<tr>
<th></th>
<th>ReRAM</th>
<th>FeRAM</th>
<th>PCM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell Size (F^2)</strong></td>
<td>4</td>
<td>~20-40</td>
<td>~8</td>
</tr>
<tr>
<td><strong>Read Time (ns)</strong></td>
<td>5</td>
<td>20-80</td>
<td>20-50</td>
</tr>
<tr>
<td><strong>Write Time (ns)</strong></td>
<td>0.3-5</td>
<td>50</td>
<td>10/30</td>
</tr>
<tr>
<td><strong>Endurance (# of cycles)</strong></td>
<td>(10^{12})</td>
<td>(10^{12})</td>
<td>(10^{12})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>DRAM</th>
<th>Flash</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>State-of-the-art</strong></td>
<td>6</td>
<td>~4/10</td>
</tr>
<tr>
<td><strong>Cell Size (F^2)</strong></td>
<td>6</td>
<td>~4/10</td>
</tr>
<tr>
<td><strong>Read Time (ns)</strong></td>
<td>10</td>
<td>80/20000</td>
</tr>
<tr>
<td><strong>Write Time (ns)</strong></td>
<td>10</td>
<td>100 μs</td>
</tr>
<tr>
<td><strong>Endurance (# of cycles)</strong></td>
<td>(10^{16})</td>
<td>(10^5/10^6)</td>
</tr>
<tr>
<td><strong>Non-volatility</strong></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>&gt;10 yrs.</td>
<td>&gt;10 yrs.</td>
</tr>
<tr>
<td><strong>Endurance</strong></td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>64 ms</td>
<td>&gt;10 yrs.</td>
</tr>
</tbody>
</table>
century when the physical limits of the scalability of the current transistor technology became imminent,\textsuperscript{5,7,11} research on resistive switching devices came into the focus again; \textit{e.g.} through the work of Watanabe \textit{et al.}\textsuperscript{17} at IBM and Waser \textit{et al.}\textsuperscript{18}. In 2008, Strukov \textit{et al.}\textsuperscript{19} at HP labs made the notable connection of the memristor concept and resistive switching. The memristor (memory + resistor) being a fourth passive circuit element was proposed based on symmetric considerations by Chua in 1971.\textsuperscript{9} It is a hypothetical two-terminal electrical device which is linked by the electric charge and magnetic flux. A memristor’s resistance depends on the current which was flowing through the device in the past. As a passive device it retains this resistance state when no current is flowing making it suitable for non-volatile memory applications. Chua could show that a distinctive property of a memristor amongst others is its pinched hysteretic $I$-$V$ behavior. Later in 1976 Chua extended this concept by proposing a new class of nonlinear dynamical systems called memristive systems based on his memristor considerations.\textsuperscript{20} It is currently still under discussion if resistive switches are real memristors\textsuperscript{9,19}, more general memristive devices\textsuperscript{20} or nothing of the above\textsuperscript{21}. But irrespective of this discussion whether resistive switches are now “real memristors” or not, the superior properties of resistive switching devices and their huge potentials for future applications remain unaffected.
Figure 1.1: Schematic of a resistive switching device including the wiring symbol of a memristor. It consists of a simple nanometer thick metal|oxide|metal structure altering its resistance in a non-volatile and hysteretic current voltage characteristic by applying high electrical fields (as schematically displayed in Figure 1.2).

In principle, one can describe these devices by a simple metal|oxide|metal structure for which the overall electrical conductivity is reversibly altered depending on the devices’ bias and current history by applying high electrical fields (of conventionally $>10^6 \text{ Vm}^{-1}$), see Figure 1.1 and Figure 1.2. The small thickness of the resistive switching oxide in the nanometer range allows the realization of these necessary high electrical fields at moderate applied bias. In cyclic voltammetry experiments this results in characteristic pinched hysteretic current-voltage ($I$-$V$) curves, see Figure 1.2. The high resistance state, HRS (in blue), can then be assigned to one binary memory state, ‘0’, and the low resistance state, LRS (in red), to a second binary memory state, ‘1’. Additionally intermediate resistance states between the low and high resistance state are accessible by a modified sweep rate which then even allows multi-level memory storage within one metal|oxide|metal structure. At low electrical fields these resistive states remain unchanged and the memory state of the resistive switching device can be read out in a non-volatile manner. In other words, such hysteretic $I$-$V$ behavior in cyclic voltammetry experiments shows that at least two non-volatile resistive states can be addressed for such a metal|oxide|metal device by resistive switching.
1.3 The Underlying Mechanism of Resistive Switching

In the last years, scientific reports show that a plethora of materials exhibit resistive switching ranging over all classes of materials like different polymers, chalcogenides, nitrides, simple and complex metal oxides. An excellent overview of switching materials and its performances can be found in “Stanford Memory Trends”. This work focuses on bipolar resistive switching in valence change memories based on metal oxide thin films which promise high stability, endurance and easy integration into standard CMOS fabrication processes. There already exist many reports of devices with different metal|oxide|metal combinations showing resistive switching. These include for example binary metal oxides like TiO$_2$, Ta$_2$O$_5$, CeO$_2$, ZrO$_2$, HfO$_2$, NiO$_x$, etc. but also ternary and complex metal oxides like Pr$_{1-x}$Ca$_x$MnO$_3$, BiFeO$_3$, SrZrO$_3$, SrTiO$_3$, etc. with different electrodes such as Au, Pt, Ti, Al, SrRuO$_3$, ITO, etc. For these devices the phenomena of resistive switching is not restricted to a particular oxide microstructure as it was already observed in devices of single crystals, thin films with epitaxial, polycrystalline or even amorphous microstructure. These also significantly differ in their...
dimensions from several micrometer\textsuperscript{50,61,67} to a few nanometer\textsuperscript{48,56,66} oxide layer thicknesses.

<table>
<thead>
<tr>
<th>Formation of local conductive channels</th>
<th>Change of space charge regions</th>
<th>Redox reactions at the interfaces</th>
<th>Alteration of total charge carrier concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

\textit{LRS} = ‘1’

\textit{HRS} = ‘0’

Figure 1.3: Schematic overview of the fundamental resistive switching mechanisms in valence change memory devices. On top the defect state within the oxide film is schematically shown for the low resistance state (LRS) of the device and on bottom during its high resistance state (HRS).

Independent of these differences, the final performance indicators of such memories are driven by the underlying switching mechanism and the thermodynamics and kinetics of the defects responsible for the resistive switching at high electric fields at room temperature.\textsuperscript{46,68} As for all thin film devices not only the selection of the materials, but also material aspects like defect concentration, morphology and control of the surface/interface chemistry are influencing the thermodynamics and kinetics, and therefore have to be taken into account in the development of resistive switches. The precise switching mechanisms are still under debate and are investigated by many different methods ranging from optical methods\textsuperscript{61,66,69} to chemical analysis\textsuperscript{52,64,70} to theoretical simulations\textsuperscript{36,48}. In the following the atomistic models of mass and charge transfer connected to resistive switching are reviewed and related to the
1.3 The Underlying Mechanism of Resistive Switching

device characteristics. In addition open questions regarding these models are highlighted.

Under discussion are currently filament\textsuperscript{67}, surface\textsuperscript{71} and bulk\textsuperscript{19} effects, or a mixture of them\textsuperscript{72}, as well as cationic migration\textsuperscript{32,73} or incorporated protonic defects\textsuperscript{74} depending on the investigated system, probed time and bias range. The mechanisms are summarized in Figure 1.3:

i) **Formation of local conductive channels;** In filamentary type switching oxides defects are locally accumulated within the oxide by the applied electrical field forming a conductive channel. This results in the low resistance state of the device. These filaments are then partially disrupted by applying a bias of the opposite polarity resulting in a less conductive state.

ii) **Change of space charge regions;** By applying high enough electrical fields the usually at room temperature immobile positively charged oxygen vacancies can accumulate in an oxide close to the vicinity of the electrode. Thereby the effective space charge region at the electrode|oxide interface is altered and the conductivity changes. By applying bias of the opposite polarity the oxygen vacancies are pulled again back to the bulk restoring the initial resistance state and may form a new interface charge at the opposite electrode|oxide interface.

iii) **Redox reactions at the interfaces;** Even though most valence change devices are built out of inert electrode materials like platinum or gold the conductivity can be changed through electrochemical reactions between oxide and the electrode reversibly building up a high resistive interlayer.

iv) **Alteration of total charge carrier concentration;** Top electrodes of the devices studied in the laboratory are often directly exposed to the atmosphere depending on the detailed device structure. By such device architectures the
oxide can directly react with the atmosphere changing for example the overall defect concentration in the film or interacting with other atmospheric species like water.

Resistive switching devices are often categorized depending on the applied bias polarity dependence on switching. In \textit{bipolar} resistive switching devices at one polarity the set process is triggered, during which the device is switched from its high resistance state to its low resistance state, and by applying the opposite polarity the device is reset; switching the resistance state of the device back from low resistance state to high resistance state, see Figure 1.2a. This is in contrast to \textit{unipolar} resistive switching devices in which the set process is triggered at the same polarity as the reset process and only controlled by the compliance current, see Figure 1.2b.

There exist mainly three different ReRAM classes differentiated by the underlying switching mechanism and defect contribution.\(^8\)

i.) Electro Chemical Metallization cells (ECMs), also called conductive bridge resistive access memory (CBRAM). Here, the resistive switching is based on cationic movement like Ag\(^+\) or Cu\(^+\), for which an active metal electrode is employed.

ii.) Valence Change Mechanism cells (VCMs). Valence change memories depend on the migration of anionic defects, namely, oxygen vacancies in an oxide thin film, which alter the overall conductivity of the device.

iii.) Thermochemical mechanism based cells (TCM), here thermochemical redox processes dominate over electrochemical processes. These cells show unipolar switching as the process is based on thermal effects.

A good overview on the different switching mechanisms and classification of resistive switching devices can be found in the reviews of
1.3 The Underlying Mechanism of Resistive Switching

Bruchhaus et al.\textsuperscript{75} and Waser et al.\textsuperscript{18} and for a more detailed discussion see reference\textsuperscript{76}. 
2 Electrochemical Characterization Methods for Resistive Switching – a Short Review

There exists numerous literature on resistive switching devices and reports on their performance indicators. Nevertheless, to date reviews of the methods used for electrochemical characterization in resistive switching are still scarce but may provide helpful guidance for a useful comparison of oxide material characteristics of resistive switching devices. Therefore, in a first attempt, Chapter 2.1 summarizes and discusses the typical electrical characterization methods of resistive switching devices. Next the most important performance indicators of resistive switching devices studied by these methods are discussed in Chapter 2.2. In addition an exemplary literature overview of 41 reports on resistive switching is given in table form in Chapter 2.4: In this literature overview the focus is set on reports on strontium titanate, SrTiO$_3$, as the resistive switching oxide investigated in this study and devices based on doped SrTiO$_3$. Additionally, reports on several binary and complex oxides are added for comparison. Firstly the employed materials and device structures with its dimensions are introduced in Table 2.4.1. Secondly the characterization methods, which were applied in these studies, are presented in Table 2.4.2 together with the underlying switching mechanism reported. Finally the performance indicators of the different devices and their assessment are summarized in Table 2.4.3.

2.1 Electrical Characterization Methods for Resistive Switching

The performance of resistive switching devices is accessed by different electrical characterization methods such as pulsed experiments, cyclic voltammetry, and chronoamperometry. These methods, which are briefly summarized in the following, probe different time scales and equilibria states of the resistive switching device with respect to bias applied.

**Pulsed experiments:** A bias pulse is applied to the device in the time range of picoseconds to microseconds to operate the write and read operation and access the different resistance states.
2.1 Electrical Characterization Methods for Resistive Switching

**Cyclic Voltammetry:** The applied bias to the device is changed with a constant sweep rate in a certain bias range to study the electrical field dependency of the device in a fast way.

**Chronoamperometry:** A constant bias is applied over longer times - minutes to hours - and the current evolution is recorded. Thereby, equilibrated drift/diffusion states of the device and defect kinetics can be studied.

The three electrical characterization methods are listed below in detail for the reader and are summarized in Figure 2.1.

**2.1.1 Pulsed Experiments**
Voltage pulsed experiments, short “VP”, on resistive switching devices come close to the mode of operation of ReRAMs in computers. Thereby, final device parameters can be easily assessed and analyzed through this measurement approach; *i.e.* switching speed, \( R_{\text{OFF}}/R_{\text{ON}} \) ratios, power consumption, read voltage, capability of multi-level resistive switching, *etc.* On the other hand, this method gives only very limited insights into the switching mechanism itself due to the short time scales making this measurement approach unsuitable for detailed material studies to improve the memory and computing performance in a systematic way. Nevertheless, this approach allows a high throughput due to the short measurement times to assess device specifications like endurance, yield, variability, uniformity, *etc.* in a suitable way.

**2.1.2 Cyclic Voltammetry**
This method has its origins in electrochemistry\(^{77}\) to study electrochemical reactions, *e.g.* batteries\(^{78}\). Here the advantage is that not only single electrochemical potentials are studied but a full bias range during a short experimental time. Even though several attempts were made to study the reactions of resistive switching devices in detail through cyclic voltammetry, short “CV”\(^{79,80}\), it is suitable only in a limited way to get insights into the material fundamentals of these devices because the device remains in a metastable state.
Due to the intrinsic character of resistive switching devices, such that the current and bias history define the resistive behavior of the cell, the attained hysteretic behavior in cyclic voltammetry experiments strongly depends on the studied voltage window and the sweep rate applied. Reporting the exact experimental parameters is crucial for understanding and classifying the measured results of a device via cyclic voltammetry. The method has the advantage that it can easily test if the device is showing non-volatile resistive switching at all by attaining a pinched hysteresis.

2.1.3 Chronoamperometry

During chronoamperometry measurements a constant bias is applied and the transient current evolution is recorded over time. Classic examples of the method can be found in the battery field, for details see for example reference\(^\text{81}\). The first chronoamperometry measurements observing an effect in oxide bulk samples similar to resistive switching dates back to the 1960s and 70s\(^\text{82,83}\), but are not yet as popular as cyclic voltammetry experiments to study resistive switching devices.

Applying a constant bias to the device until a constant current is measured allows the device to reach a drift-diffusion equilibrium of the diffusive species for a given electrical field which is not possible in pulsed and cyclic voltammetry measurements. As a consequence, this renders the chronoamperometry measurements as independent of the current and bias history of the device. \textit{Viz.} the set and reset process can be consecutively studied for different field strength allowing to even derive diffusion constants at room temperature with respect to the electrical fields applied to the device.\(^\text{33,46,84}\) Importantly, through the step-wise bias change approach the minimum set/reset voltage can be assessed at which the device starts altering its resistance. These values can differ tremendously from minimum set and reset voltages traditionally analyzed through cyclic voltammetry experiments which are usually estimated too high from the measured data.\(^\text{33}\) In addition, by studying the current decay at zero bias or at opposite bias allows to uncover the respective electronic and chemical relaxation processes like capacitive contributions of the resistive switching device.
Besides all the advantages offered by chronoamperometry measurements, the high electrical stress subjected to the device due to the long measurement times sets some limitations to this method. Here, degradation effects of the devices such as delamination, Joule heating, etc. limit the accessible bias and time range in chronoamperometry measurements. Additionally it is not the first choice of characterization method to study the uniformity or the variance of the devices due to the low throughput. Here, electrochemical methods with faster sampling rates are preferred but it can give valuable insights on the mass and charge transport phenomena involved in the processes.

---

**Pulsed Measurements**

- Final device parameters
- High throughput
- Limited insight into switching mechanism
- Device remains in a metastable state

---

**Cyclic voltammetry**

- Analysis of full bias range at short time
- Validation of resistive switching capability
- Limited insight into switching mechanism
- Device remains in a metastable state

---

**Chronoamperometry**

- Material diffusion constants + kinetics
- Separation of capacitive and memristive contributions
- Independent of bias/current history
- High electrical stress to the device
- Low throughput

---

**Figure 2.1:** Overview of electrical characterization methods being pulsed experiments, cyclic voltammetry and chronoamperometry to analyze resistive switching devices. Here the “ON”- state of the device is marked in red color and the “OFF”-state in blue color.
2.2. **Performance Indicators of Resistive Switching Devices**

The literature overview in Table 2.4.1 summarizes that resistive switching devices based on pure and doped SrTiO$_3$ show resistive switching irrespective of the microstructure and over a wide oxide film thickness range as it is found for single crystals, epitaxial, polycrystalline or amorphous thin films. These resistive switching devices cover a wide range of performance indicator values depending on the investigated material system and the way of assessment, see Table 2.4.2 and 2.4.3. It highlights the great potential of resistive switching devices but also raises the problem of performance comparison of indicator values accessed by different approaches. Therefore the most important performance indicators are introduced and briefly summarized in this chapter. This includes endurance, yield, switching voltage, switching speed, non-volatility and the R$_{OFF}$/R$_{ON}$ ratio. Suitable characterization methods to analyze these various performance metrics are discussed. In addition the critical points assessing and analyzing performance indicators of resistive switching devices are addressed.

**Endurance:** Endurance describes the ability of the memory to withstand multiple data rewrites.\(^{85}\)

**Yield and Switching Uniformity:** Yield describes the amount of functioning switches/bits on a fabricated sample and uniformity of the cycle to cycle and device to device variation.

**Switching Voltage:** Defined by the bias applied when the device is switched to the low (set process) or high (reset process) resistance state. Minimum switching voltage is defined as the voltage by which the set (reset) process is triggered and activated.

**Switching Speed:** Defines how fast the device is switched between low and high resistance states and vice versa.

**Non-Volatility:** It defines the time range for which the low and high resistance states remain unchanged without bias applied.

**R$_{OFF}$/R$_{ON}$ Ratio:** It describes the resistance ratio of the OFF to ON resistance states.
In the following section, these performance indicators are discussed relative to the experimental methods of pulsed experiments, cyclic voltammetry and chronoamperometry introduced in Chapter 2.1.

2.2.1 Endurance
Depending on the targeted application of the resistive switching device this specification might be crucial. As a competitive replacement for fast non-volatile memory, resistive switches stand in competition with flash (>3000 write cycles)\(^8\) and today’s DRAM (>10\(^{15}\) cycles).\(^8\) For the application as a computing unit in the field of neuromorphic computing, the endurance requirements go up to 10\(^{18}\) read/write cycles when compared to today’s CPU (having an expected lifetime of 10 years). This demanding requirement needs a good process control of the fabricated devices. Lee et al. showed endurances up to 10\(^{12}\) for Ta\(_2\)O\(_{5-x}\)/TaO\(_{2-x}\) bilayer structures, see Table 2.4.3 which highlights the already high stability of resistive switching devices today which outperforms the flash memory by 6 orders of magnitude.

In fundamental materials research on resistive switches there are in principle two different approaches to assess the endurance of the devices. On the one hand, in pulsed experiments the device is set and reset through pulses consecutively. After every write/reset step the resistance is then consequently either read out with a low read voltage pulse below the set/reset voltage (abbreviated \(VP\) in \(R_{OFF}/R_{ON}\) methods in Table 2.4.3) or through chronoamperometry by applying a constant low bias below the set/reset voltage (abbreviated \(Cr\) in \(R_{OFF}/R_{ON}\) methods in Table 2.4.3). On the other hand, cyclic voltammetry experiments can be utilized to measure the endurance. Here many voltammetry cycles are measured and their stability is analyzed; e.g. evolution of the set/reset current.

Comparison of the endurance in resistive switching remains difficult, because it strongly depends on the chosen experimental settings such as the bias applied, \(i.e.\) usually a higher bias for reset/set increases the \(R_{OFF}/R_{ON}\) ratio but decreases the endurance. The same holds for the pulse length in pulsed experiments (sweep rate in cyclic voltammetry). The longer the pulses applied (slower sweep rate) the higher the \(R_{OFF}/R_{ON}\) ratio increases, but at the expense of a reduced endurance. Nevertheless
many reports do not consider endurance at all and often only present a single $I$-$V$ curve, which of course makes sense concerning clear presentation of the results. However, it is critical to report any endurance information on the devices measured, otherwise easily accessible information about the quality of the measured device gets unnecessarily lost. Furthermore, the endurance can also shed light on the resistive switching mechanism and long-term degradation mechanism by analyzing the degradation of the high and low resistance states during cycling.  

### 2.2.2 Yield and Switching Performance

The yield is usually not the main focus of fundamental studies on resistive switching. Nevertheless, reporting the yield of the structures together with the switching uniformity of the single performance indicators can give a good hint as to how well the described system is understood and controlled. Because not all parameters influencing resistive switching are known yet, already small deviations in the defect structure, composition within the thin film or on the surface of a sample can have a major impact on the performance of the single devices. The simple structure of resistive switches allows fabricating and analyzing many switches on one sample already in fundamental studies, but unfortunately often important information on yield and switching uniformity gets lost. This additional information would also accelerate the progress in the resistive switching technology.

### 2.2.3 Switching Voltage

For most targeted applications of resistive switches they have to be compatible and linked to transistors in a circuit to unfold their superior properties. Therefore, the switching voltage should be in the operating voltage window of today’s transistor technology, which is of a few volts. The switching voltage in pulsed experiments is the bias applied to the bipolar switching device during the set and reset process. While in cyclic voltammetry experiments the switching voltage is not as clearly defined as in pulsed experiments. Here, it is either the maximum positive ($U_{\text{Set}}$) and minimum negative ($U_{\text{Reset}}$) bias applied to the device during the cyclic voltammetry experiment. Or another popular definition is the bias value during the set and reset process at which a sudden significant jump in current is observed in the $I$-$V$ profile of cyclic voltammetry experiments.
The first two definitions are mainly defined by the chosen experimental settings rather than by the device itself, only the last definition gives insights into the device concerning the switching voltage. In cyclic voltammetry measurements the switching voltage can also depend on the chosen sweep rate\(^9\) making it even more dependent on the chosen experimental settings. To give a definition independent of the experimental settings one can also refer to the minimum switching voltage, \(U_{\text{SET}, \text{min}}\), which can be assessed for example through chronoamperometry.\(^46\)

This parameter defines, together with \(I_{\text{SET}}\), the power consumption. Interestingly even though the thicknesses of measured devices are ranging from a few nanometers\(^{56,67,72}\) to micrometers\(^{17,50,52,67}\) the reported switching voltages are in most reports in the range of 1 V to 5 V and therefore the electric field covers a range of at least three orders of magnitude, see examples of report 1 and 5 in Table 2.4.1 and Table 2.4.3. These results implicate that the field might be decreasing locally within the thin films after electroforming and therefore is mostly independent of the thickness of the devices.

### 2.2.4 Switching Speed

Even though in neuromorphic computing the switching speed can be lower than in traditional computing to reach similar outputs, if memristors should compete in computing speed with today’s transistor technology it has to be in the range of nanoseconds, see Table 1.1. The switching speed of resistive switching devices can only be assessed through pulsed experiments. Here values of \(10^{-7}\) s and even lower are reported\(^{68}\). It remains to be elucidated if the switching mechanisms in these time ranges are the same as for longer time ranges measured during cyclic voltammetry and chronoamperometry experiments.

### 2.2.5 Non-Volatility

This property of ReRAMs is often not assessed or reported in literature, see Table 2.4.3, although this property of resistive switches has a huge potential and sets it apart from volatile DRAM technology which has to be refreshed in the millisecond range.\(^{14}\) Additionally it has an impact on computing applications such as simple subtraction/addition routines going
even towards neuromorphic computing, where the time scales of the non-volatility of the device play a crucial role. Discussing non-volatility depends on the time scale of the non-volatility; one has to distinguish between short-term non-volatility and long-term non-volatility. For computing applications short-term non-volatility in the range of ms to s is sufficient, but for memory application to be competitive with today’s hard disks the non-volatility has to be stable over years. A pinched hysteresis in cyclic voltammetry measurements shows only the non-volatility in the time range of the duration of one $I-V$ cycle. Long term non-volatility and the stability of the resistance states can be assessed through pulsed measurements at elevated temperatures and interpolation to room temperature.

### 2.2.6 $R_{OFF}/R_{ON}$-Ratio

Depending on the targeted application of resistive switches, the stability and fluctuation of the resistance states require an $R_{OFF}/R_{ON}$ ratio of $>10$. For multi resistance state operation within one bit the required $R_{OFF}/R_{ON}$ ratio has to be significantly higher. In literature the range of reported $R_{OFF}/R_{ON}$ ratios goes up to $10^6$. Despite these promising reports it is very difficult to compare this important performance indicator and to draw precise conclusions because of the many different ways the $R_{OFF}/R_{ON}$ ratio is assessed and analyzed.

First differences arise from the characterization method used to measure the $R_{OFF}/R_{ON}$ ratio. For assessment through pulsed measurements at a low read voltage the resistance state is read out after a writing/erasing pulse was applied. This method is the closest compared to the targeted applications. Nevertheless it is difficult to compare these values, because it strongly depends which set/reset voltage was applied, see Chapter 2.2.3. Additionally because of the operation principle of a resistive switch the pulse length of the applied set/reset step can have a huge impact on the ratio making a direct comparison unfeasible. For the read voltage it is important that it is low enough that the system remains in a stable state, not changing the resistance of the device, which can be tested by applying the read pulse for a longer (constant) time. Due to the non-linear $I-V$ behavior of many devices, low or opposite polarity read voltages can strongly affect the assessed resistance states.
In literature resistance ratios are often given from cyclic voltammetry experiments. Here, the opening of the hysteresis is often analyzed to give a resistance ratio. These values cannot be directly compared to values measured through pulsed experiments due to the different time scales. Here one has also to differentiate between two fundamentally different data analysis methods. A linear fit around zero voltage applied for the two branches can give a good estimate of the resistance states accessible in pulsed experiments with low read voltages. A more fuzzy approach, because of the often present non-linearity of the measured resistance branches, is to report the opening of the $I$-$V$ hysteresis at a freely chosen bias. Here not only the non-linearity of the device, but also volatile drift/electronic effects and overall resistive switching through ionic movement make a comparison of experimental results difficult. The $R_{OFF}/R_{ON}$ ratio measured in cyclic voltammetry also often depends on the sweep rate applied and the voltage window probed.\textsuperscript{46,72} Therefore it is essential to give the sweep rate and the exact analysis method of every $R_{OFF}/R_{ON}$ ratio reported that was assessed with cyclic voltammetry.

A third approach of assessing the resistance ratio is through chronoamperometry.\textsuperscript{40,46,54} It has to be noted that these resistance states are measured in the drift/diffusion equilibrium and all possible relaxation processes changing the resistance state at zero bias cannot be accessed. Therefore the resistance ratio can be overestimated at higher voltages. Nevertheless, this approach makes the resistance ratio independent of the pulse length or sweep rate during the experiment making a device to device comparison easily possible.

2.3. **Conclusion on Electrical Characterization of Switching Devices**

This overview on the main three electrical characterization methods demonstrates the complexity of the analysis of resistive switching devices and their performance metrics. All three methods are complementary in their probing time and voltage scales and are strong tools to characterize and study resistive switching phenomena. Even though resistive switching devices have a simple structure and electrical measurement data is easily collected, the analysis of such data has to be carried out precisely and the
limitations of each method has to be taken into account. Otherwise reports on fabricated devices and their switching performance data can only lead to poor interpretation. This makes direct comparison of different structures difficult and might slow down the development of this technology.
2.4. Exemplary Literature Overview of Resistive Switching Devices

2.4.1 Exemplary overview of oxide resistive switching device designs from literature

<table>
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<tr>
<th>No</th>
<th>Oxide</th>
<th>Top Electrode</th>
<th>Bottom Electrode</th>
<th>Microstructure</th>
<th>d / nm</th>
<th>A / μm²</th>
<th>Main Carrier</th>
<th>Ref.</th>
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<td>01</td>
<td>SrTiO₃</td>
<td>Au</td>
<td>Au?</td>
<td></td>
<td>30</td>
<td>10⁶</td>
<td>n-type</td>
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<tr>
<td>02</td>
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<td>Pt</td>
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<td>50 μm</td>
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<td></td>
<td>740</td>
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<td>10⁵</td>
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<td></td>
<td>n-type</td>
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<td>2.5×10⁵</td>
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<td>n-type</td>
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<td>3×10⁶</td>
<td>n-type</td>
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<td>Pt</td>
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<td>TiN</td>
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<td>Pt/Ti</td>
<td></td>
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<td>3.6×10\textsuperscript{3}</td>
<td>p,n-type</td>
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<td>Au</td>
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<td>5-20 μm</td>
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<td>Pt/Ti</td>
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<td>SrRuO\textsubscript{3}</td>
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<td>0.1×0.1</td>
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<td>Pr\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} (x&lt;0.8)</td>
<td>Au/Ti</td>
<td>SrRuO\textsubscript{3}, Nb:STO</td>
<td>epitaxial</td>
<td>30-50</td>
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<tr>
<td>41</td>
<td>Mn:BiFeO\textsubscript{3}</td>
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<td>Pt/Ti</td>
<td></td>
<td>350</td>
<td>7×10\textsuperscript{4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(d\): oxide thickness  \(A\): top electrode area

\[\text{SrTiO}_3, \text{Doped SrTiO}_3, \text{TiO}_x, \text{other binary and complex oxides}\]
### 2.4.2 Exemplary literature overview of experimental methods and switching models from literature

<table>
<thead>
<tr>
<th>El. Methods</th>
<th>Additional Methods</th>
<th>Switching Model</th>
<th>Ref.</th>
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</thead>
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<td>Formation of vacancy clusters at the interface</td>
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<td>Interface vacancy accumulation, Schottky barrier, vacancy incorporation during</td>
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<td>Interface vacancy accumulation, Schottky barrier</td>
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<td></td>
<td></td>
<td>and oxygen vacancy migration</td>
<td></td>
</tr>
<tr>
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<td>optical microsc.</td>
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<td>Change of vac. under electrode / Schottky barrier interface</td>
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<tr>
<td>12 CV</td>
<td></td>
<td>Local inhomogeneous Schottky barrier at interface causes trapping/detrapping</td>
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<tr>
<td></td>
<td></td>
<td>electrons trapped</td>
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<tr>
<td>13 CV, AC, Cr.</td>
<td>Hall</td>
<td>Change of interface states changing Schottky barrier height or charge trapping</td>
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<td></td>
<td></td>
<td>in interface states</td>
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<tr>
<td>14 CV, Cr.</td>
<td>SIMS, EELS</td>
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<td>16 CV</td>
<td>STM</td>
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<td>TEM, EELS, Hall, XRD, Opt.</td>
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<tr>
<td>18 cAFM</td>
<td>XRD, XPS, AFM, TEM</td>
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<td>Schottky barrier height</td>
<td>17</td>
</tr>
<tr>
<td>20 CV, Cr.</td>
<td>XRD, XPS, SEM, EDS, AFM</td>
<td>Migration of vacancy forming filaments, electron trapping</td>
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</tr>
<tr>
<td>No.</td>
<td>Method</td>
<td>Details</td>
<td>Page</td>
</tr>
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<td>Hall</td>
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<td>CV</td>
<td>Hall, AFM, optical microsc.</td>
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<td>XRD, Raman, Band Gap, RBS, Hall, SIMS, HFS</td>
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<td>optical microsc.</td>
<td>Displacement of ionic species through the bulk</td>
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<td>Arrhenius meas.</td>
<td>Metallic Ni filaments</td>
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<td>26</td>
<td>CV, VP</td>
<td>TEM, AES, XPS</td>
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<td>27</td>
<td>CV</td>
<td>XPS, TEM, XRD</td>
<td>Ni filaments and vac. filaments</td>
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<td>Filament</td>
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<td>CV, Cr., VP</td>
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<td>Thermally activated, dominated by charge hopping through defects of vacancies (filaments)</td>
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<td>XRD, HRTEM, EDS, XPS</td>
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<td>Local mechanism</td>
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<td>Electrochemical migration of vac., interface effect</td>
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<td>XPS, SEM, XRD</td>
<td>Neutralization/ionization of vac. filament-related nonpolar resistive switching</td>
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Electrochemical Methods (El. Methods): Pulsed experiments (VP), cyclic voltammetry (CV), impedance measurement (Imp.)

Abbreviations for additional experiments see nomenclature on p. 181
<table>
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<tr>
<th>Ref.</th>
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<td>BRS ⊙</td>
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<tr>
<td>37</td>
<td>BRS</td>
</tr>
<tr>
<td>38</td>
<td>BRS</td>
</tr>
</tbody>
</table>

* BRS: bipolar resistive switching  
URS: unipolar resistive switching  
Switching directions: Clockwise Anti-clockwise Both directions  
$R_{\text{OFF}}/R_{\text{ON}}$: ratio of resistance in high and low resistance state.  
** Resistance ratios measurement methods: Chronoamperometry (cr.), pulsed experiments (VP), cyclic voltammetry (CV)
3 Strontium Titanate – A Model Oxide Material to Study Resistive Switching

This chapter gives an overview of the resistive switching oxide material employed in this study, namely strontium titanate, SrTiO$_3$.

Table 3.1: Physical properties of strontium titanate, SrTiO$_3$.$^{97-100}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (RT), $a$</td>
<td>0.3905 nm</td>
</tr>
<tr>
<td>Density, $\rho$</td>
<td>5.12 g cm$^{-3}$</td>
</tr>
<tr>
<td>Dielectric permittivity, $\epsilon$</td>
<td>300</td>
</tr>
<tr>
<td>Melting point</td>
<td>2353 K</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.2 eV</td>
</tr>
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</table>

3.1. Crystallographic Structure and Chemistry of SrTiO$_3$

Strontium titanate is a metal oxide which has a simple cubic ABO$_3$ perovskite crystal structure at room temperature with a lattice parameter of 0.3905 nm and a density of 5.12 g cm$^{-3}$, see Figure 3.1.$^{97}$ Here the Ti$^{4+}$-atoms are six fold coordinated by O$^2$-atoms and each Sr$^{2+}$-atom is surrounded by eight TiO$_6$ octahedra. This structure is stable over a wide temperature range between 108 K up to the melting point of strontium titanate, which lies at 2353 K.$^{98,99}$ and over a wide oxygen non-stoichiometry down to SrTiO$_{2.5}$. This can result for example from reducing conditions ($<$0.1 mbar) at elevated temperatures ($>$500 °C).$^{100}$ Therefore phase changes induced by the electrical field due to Joule heating during resistive switching at ambient conditions are not expected.

At lower temperatures (as well as by extrinsic doping to solid solution) the structure undergoes phase transitions to lower symmetries. In the range of 108 K to 65 K it undergoes a phase transition turning into a tetragonal structure, between 55 K to 35 K into an orthorhombic structure and possibly below 10 K into a rhombohedral structure.$^{101-103}$

Pure SrTiO$_3$ single crystals are transparent in the visible range and up to wavelengths of 5 μm into the infrared.$^{101,104}$ Upon reduction and increased
oxygen non-stoichiometry a broad absorption appears into the infrared and single crystals appear intermediate to dark blue in color.\textsuperscript{104,105}

![Figure 3.1: Sketch of cubic perovskite structure of strontium titanate, SrTiO$_3$, at room temperature with oxygen atoms in blue, strontium atoms in red and titanium atom in green.]

3.2. Defect Chemistry and Electronic Structure of SrTiO$_3$

Stoichiometric SrTiO$_3$ exhibits, in single crystals and ambient conditions, a chemical oxygen diffusion coefficient\textsuperscript{106} of $\sim10^{-17}$ m$^2$s$^{-1}$ and a rather low cation mobility.\textsuperscript{107-109} Therefore the cations Sr and Ti can be considered in a first approximation immobile, which applies also to resistive switching at typical conditions used for SrTiO$_3$ switches. For stoichiometric SrTiO$_3$, the oxide can be considered as a good insulator with a 3.2 eV band gap (at T = 0 K) separating the valence from the conduction band.\textsuperscript{105,110}

Excitingly, SrTiO$_3$ reveals most of its interesting properties when its structure becomes imperfect due to defects such as oxygen non-stoichiometry or by extrinsic doping. Computational studies confirm that the formation of Schottky defects are energetically more favorable than Frenkel defects for SrTiO$_3$.\textsuperscript{107,111} The most common defects in SrTiO$_3$ are oxygen vacancies due to the relatively weak oxygen bonds.\textsuperscript{109} The extent
3.2 Defect Chemistry and Electronic Structure of SrTiO₃

of the non-stoichiometry strongly depends on the oxygen partial pressure due to the oxygen exchange reaction:\textsuperscript{109,112}

\[ V_{o^{\cdot\cdot}} + \frac{1}{2} O_2(g) \rightleftharpoons O_o^{x} + 2h^{\cdot} \] \hspace{2cm} \text{Equation 3.1}

\[ \frac{\Delta\delta}{2} O_2(g) + \text{SrTiO}_{3-\delta} \rightleftharpoons \text{SrTiO}_{3-\delta+\Delta\delta} \] \hspace{2cm} \text{Equation 3.2}

Here, the Kröger-Vink notation is used and \( g \) is referred to the gas phase and \( \delta \) to the oxygen non-stoichiometry.

The exact \( \delta \) non-stoichiometry has a strong impact on the electrical conductivity\textsuperscript{110,113-115} and therefore, dependent on environmental or processing conditions (oxidizing/reducing atmospheres) \( \text{SrTiO}_{3-\delta} \) exhibits either a predominant oxygen ionic conduction \textit{via} vacancies in the lattice\textsuperscript{116} or an electronic conduction \textit{via} holes (p-type) or electrons (n-type) at high and low oxygen pressures in accordance to its Brouwer diagram\textsuperscript{117-120}, see Rothschild\textsuperscript{121} for details.

Additionally, the non-stoichiometry can be tuned by extrinsically doping \( \text{SrTiO}_3 \), \textit{i.e.} by acceptor dopants like iron, \( \text{Sr(Fe}_{x}\text{Ti}_{1-x})\text{O}_{3-\delta} \), or by donor dopants like niobium, \( \text{Sr}_{1-x/2}\text{Nb}_{x}\text{Ti}_{1-x}\text{O}_3 \), to promote either the p-type or n-type conduction, respectively.\textsuperscript{109,116,122} This makes \( \text{SrTiO}_3 \) an interesting model oxide for a mixed conductor as one can adapt the defect chemistry over the whole range from being n-type to p-type electronic or a predominant oxygen ion conductor by the choice of partial pressure, temperature or extrinsic doping.

The rather high \( \text{SrTiO}_3 \) oxygen mobility is highly temperature dependent. Activation energies of \(~1.5\) eV along grain boundaries and \(~1\) eV in the oxide bulk are reported.\textsuperscript{123-125} It was further confirmed by impedance spectroscopy analysis that electronic conduction along grain boundaries is predominant in polycrystalline samples.\textsuperscript{124,125} Gregori, Maier and co-workers\textsuperscript{123,125,126} discussed the role of space charge for changes in the grain to grain boundary ratio of \( \text{SrTiO}_3 \). Here reducing the grain size to the nanoscopic range for \( \text{SrTiO}_3 \) pellets were equivalent to a change of oxygen partial pressure of up to 12 orders of magnitude for classic macro
crystalline pellets. As a result the electronic conduction changed from predominant n-type conduction to p-type conduction within the oxide as an increased grain boundary volume, and hence, space charge influence prevailed for the nano-grained SrTiO$_3$ samples studied.

Additionally, strain can affect the transport properties changing the local bond strength in doped and undoped SrTiO$_{3-\delta}$ films. Waser, Guo and co-workers$^{128}$ revealed that the Brouwer diagram changes dependent on the variation of space charge volume relative to film thickness and strain state of a SrTiO$_{3-\delta}$ thin film. De Souza highlighted the role of grain boundaries on extended defects in SrTiO$_{3-\delta}$ in theory and experiments.$^{106,129,130}$ Very recently, first theoretical reports have discussed changes in the local dislocation concentrations that alter oxygen diffusion coefficients under high fields during switching. This has a direct implication on electronic carrier diffusion.$^{131,132}$

Despite oxygen vacancies being the most important defects concerning the transport in SrTiO$_3$, also hydroxyl ions can be incorporated through the reaction of oxygen deficient SrTiO$_{3-\delta}$ interacting with anionic, electronic and protonic carriers by moisture, see references$^{109,133,134}$ for details. Here, water molecules from the gas phase are first adsorbed at the surface and can subsequently be incorporated into an oxide’s bulk via the following hydration reaction:$^{109,133,134}$

$$\text{H}_2\text{O} + \text{O}^\bullet + \text{V}^{**} \rightleftharpoons 2\text{OH}^\bullet$$

Equation 3.3

, where the Kröger-Vink notation is used. Rather than bulk protonic conduction, in oxides, often surface, interface or grain boundary conduction of protons are relevant for conductivity changes of SrTiO$_3$ at elevated water concentrations.$^{135,136}$ It is important to note that conductivity changes by moisture depend strongly on temperature condition and microstructural features such as porosity of the metal oxide.$^{135,137}$ Further, the reaction towards hydroxyl species can also be influenced by reactions to other ambient gases at the interface, e.g. side reactions towards CO or CO$_2$.$^{137}$
3.3 Application of SrTiO3 and its Solid Solutions

Review on the defect chemistry and conduction models for the material SrTiO$_{3-\delta}$ are given in detail by the excellent studies of Merkle and Maier$^{109,138}$, and Waser$^8$.

3.3. Application of SrTiO$_3$ and its Solid Solutions

Strontium titanate finds use in many different applications, especially in microelectronics due to its good insulating properties, excellent tunability of the conduction character via doping, high charge storage capacity, optical transparency in the visible region and chemical stability.$^{122,139,140}$

Due to the lattice parameter match, SrTiO$_3$ is largely employed as a substrate for epitaxial growth of high temperature superconducting films.$^{110,139}$ The tunable conductivity of SrTiO$_3$ is used in the development of fuel cells anodes.$^{122,141}$ The low microwave losses of SrTiO$_3$ make it an attractive material for tunable microwave electronics devices such as: phase shifters, filters, delay lines, tunable oscillators, etc.$^{142}$ The high resistive sensitivity of SrTiO$_3$ makes it suitable to be applied in sensors, for example to sense oxygen$^{143}$, hydrocarbons$^{144}$ or humidity$^{137}$. SrTiO$_3$ also finds application as biocompatible nano-tube arrays in medicine for osteoporotic bone implants.$^{145}$

The ability to control the conductivity in SrTiO$_3$ is additionally exploited in the design of capacitors$^{146}$, thermistors, varistors, electrodes and metal oxide semiconductor field effect transistors (MOSFET’s) in the microelectronic industry.$^{115,147}$ In the case of MOSFET’s SrTiO$_3$ is becoming one of the preferred high-$\kappa$ dielectric alternatives to replace SiO$_2$ as gate oxide.$^{148}$

3.4. SrTiO$_3$ as Resistive Switching Oxide

The well-understood defect chemistry, tunable electrical properties and industrial experience make it very interesting to exploit strontium titanate as resistive switching oxide.

Several groups demonstrated resistive switching for SrTiO$_{3-\delta}$ with Pt, Ti, Ni, Pd, Au, Nb:SrTiO$_3$ or SrRuO$_3$ electrodes at local electric field strengths of $10^5$-$10^9$ Vm$^{-1}$. $^{45,49,51,53,63,68,91}$ SrTiO$_{3-\delta}$ shows promising non-
volatile oxygen anionic-type controlled resistive switching at electric field strengths of more than $10^6 \text{ Vm}^{-1}$ with ratios of high and low resistance states, $R_{\text{OFF}}/R_{\text{ON}}$, of up to $10^3$, switching speeds of $<100 \text{ ns}$, retention $>10$ years, endurance of $>10^6$ cycles, see also Table 2.4.3. The wealth of experience in working with SrTiO$_{3.8}$ as a transistor gate oxide on a chip makes its integration into future ReRAM devices highly feasible.

Despite the many reports on resistive switching of SrTiO$_3$ the detailed resistive switching mechanism remains under debate. For example, the role of the Schottky barrier at the metal|oxide interfaces was highlighted by Sawa, whereas e.g. Waser and coworkers emphasized the formation and rupture of conductive filaments as responsible for the bipolar resistive switching in SrTiO$_{3.8}$. A common view is that positively charged oxygen vacancies are accumulating in locally defined sites through the external electrical field applied forming conductive filaments and lowering the overall resistance of the device. By applying the opposite polarity to the device these filaments get partially dissolved resetting the device back to a high resistance state.

Nevertheless these filaments do not give a complete picture of the defect chemistry involved in these devices. Hence, depending on the applied bias amplitude a second counteracting mechanism involving the interplay of oxygen vacancies in the oxide with the whole electrode area has to be considered. This gives an $I$-$V$ hysteresis with opposite switching direction than the filament switching. This second mechanism found by Muenstermann et al. in SrTiO$_3$ and by Shibuya et al. in Sr$_2$TiO$_4$ is triggered by applying higher electrical fields in cyclic voltammetry experiments than necessary for the formation of filaments. Additionally, Kubicek et al. demonstrated on SrTiO$_3$ devices by impedance spectroscopy that this second mechanism has slower kinetics when compared to the first filamentary type. Here, either the filament or the second mechanism is dominant dependent on the sweep rate selected in cyclic voltammetry operation of the resistive switching device for the same bias range. Here, one could observe an $I$-$V$ hysteresis of opposite bipolar resistive switching direction or even in a mixed regime with $I$-$V$ curves showing complicated multi crossings.
In summary SrTiO$_3$ exhibits very promising switching characteristics and is a good model material for oxide-based valence change memories. From a fundamental point of view it is essential to get a better understanding of the defect chemistry of SrTiO$_3$ under bias, especially the single defect contributions and its kinetics at the rather unusual conditions for charge transport in oxides present during resistive switching, namely at ambient and high electrical fields.
4 Aim of this Work

The aim of this work is to gain a better understanding of the fundamental resistive switching mechanisms in valence change memories with the focus on the kinetics of the defect chemistry and charge transport involved during the resistive switching based on the oxide SrTiO$_3$. In order to succeed new analytical tools are tested like chronoamperometry to probe the kinetics of the switches.

Here new aspects to the field of resistive switching and electrochemical analysis techniques based on SrTiO$_3$ are contributing on the following:

(i.) In Chapter II, the main challenge is to fundamentally understand the defect kinetics of oxygen vacancies in oxide-based resistive switching devices in dependence of high electrical fields at ambient conditions for the mixed conducting oxide SrTiO$_3$. Therefore the “Memristor-based Cottrell Analysis” is proposed and experimentally applied on SrTiO$_3$.

(ii.) In Chapter III, the so far mostly neglected protonic contributions during resistive switching in valence change memories and the sensitivity to change in relative humidity is for the first time studied in a model experiment for SrTiO$_3$.

(iii.) In Chapter IV, the influence of surface to bulk ratio and free exposure of oxide surface towards the atmosphere is studied in dependence of electrical field and the relative humidity exposed for SrTiO$_3$.

This work has the objective to provide a connection between material and defect properties of the resistive switching oxide, being here SrTiO$_3$, to its switching performance. Hence, is not aimed to have the best performing resistive switch necessarily, rather to contribute to the fundamental understanding on the chemistry and physics behind resistive switching. In addition the thesis aims to contribute with new tools to the analysis of diffusion processes under high electric fields in oxides, which may further allow to compare materials in switching. The role of the charge carriers, ranging from electronic, ionic to protonic, is in focus of the thesis.
II Defect Kinetics in Resistive Switching Devices

This thesis chapter was published as “Memristor Kinetics and Diffusion Characteristics for Mixed Anionic-Electronic SrTiO$_{3-\delta}$: The Memristor-based Cottrell Analysis Connecting Material to Device Performance”, F. Messerschmitt, M. Kubicek, S. Schweiger, J.L.M. Rupp

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Abstract

Memristors based on mixed anionic-electronic conducting oxides are promising devices for future information storage applications such as non-volatile memory or neuromorphic computing. Unlike transistors solely operating on electronic carriers, these memristors rely, in their switch characteristics, on defect kinetics of both oxygen vacancies and electronic carriers through a valence change mechanism. Here, we fabricated Pt|SrTiO$_{3-\delta}$|Pt structures as model material in terms of its mixed defects which show stable resistive switching. To date, experimental proof for memristance is characterized in hysteretic current-voltage profiles; however, the mixed anionic-electronic defect kinetics that can describe the material characteristics in the dynamic resistive switching are still missing. We show that chronoamperometry and bias-dependent resistive measurements are powerful methods to gain complementary insights into material-dependent diffusion characteristics of memristors. E.g. capacitive, memristive and limiting currents towards the equilibrium state can successfully be separated. The Memristor-based Cottrell analysis is first time proposed to study diffusion kinetics for mixed conducting memristor materials: We found fast oxygen diffusion coefficients of $3\times10^{-15}$ m$^2$s$^{-1}$ for bias increase up to 3.8 V for SrTiO$_{3-\delta}$ memristors. These newly accessible diffusion characteristics allow improving materials and implicate field strength requirements to optimize
operation towards enhanced performance metrics for valence change memristors.

5 Introduction

Today’s memory technologies, e.g. Dynamic Random Access Memory (DRAM) and flash memory, rely heavily on the miniaturization of transistors to maintain the projected performance growth. However the physical limitations of this approach are nearing which emphasizes the need for new technologies to be developed. In recent years, resistive switches deployed as Resistive Random Access Memories (ReRAMs), which are a non-volatile type of memory, received extensive interest as a promising candidate for the replacement of current transistor technology. In 2008, Strukov and Williams reported a connection between the mathematical memristor concept developed by Chua. In general, a resistive switch can attain different resistance states which are controlled by the polarity or magnitude of an applied bias resulting in pinched hysteretic \( I-V \) profiles. In the last years, resistive switching has been reported for various classes of materials ranging from sulfides (e.g. Cu\(_2\)S, Ag\(_2\)S) to binary oxides (e.g. TiO\(_2\), SiO\(_2\), CuO, NiO, CoO, Fe\(_2\)O\(_3\), MoO, VO\(_2\)) over to complex oxides (e.g. SrTiO\(_3\)-\(\delta\), (La,Sr)MnO\(_3\), (Pr,Ca)MnO\(_3\), BaTiO\(_3\), (La,Sr)(Co,Fe)O\(_3\), CeCu\(_3\)Ti\(_4\)O\(_{12}\)). Among those the most extensively studied switching oxides are already processed in today’s semiconductor industry as gate oxides like SrTiO\(_3\)-\(\delta\), SiO\(_2\), TiO\(_2\)-\(\delta\), Ta\(_2\)O\(_5\)-\(\delta\), or HfO\(_2\)-\(\delta\). For oxide-based memristive systems one has to distinguish between switches whose mechanism relies on mobile metal cations and those relying on mobile oxygen anions: Electrochemical metallization switches relying on cations consist of an active electrode material, e.g. Ag or Cu, from which the cations migrate at high electric fields through an electrolyte forming a metal filament towards a second inactive electrode, e.g. Pt. In contrast, valence change resistive switches rely on oxygen anion migration over structural defects (oxygen vacancies) in the oxide under high electric fields. Here, oxygen ionic defects govern the resistive switches’ device characteristics relative to the field strength and charge carrier flux history. Although anionic resistive switches are highly promising as novel memory devices their
Defect kinetics at different electric field strengths and the implication on the memristive device are largely unexamined.

To date, studies on anionic-memristive systems focus primarily on reports of hysteretic and memristive I-V profiles of metal|oxide|metal combinations and their processing. Classically, the memristance of anionic switch devices is only measured by either cyclic voltammetry or the analysis of low and high resistance states addressed by short pulses. Both methods do not directly correlate the oxide’s bulk and interface non-equilibrium carrier kinetics or defect thermodynamics to the measurable memristive device performance. Therefore, to establish engineering guidelines for the material selection, the development of new methodology is required to connect the materials’ defect kinetics to memristive device performance with respect to switching speed, scalability, endurance, high to low resistance ratio, and power consumption.

Through this work, we focus on strontium titanate, SrTiO$_{3-\delta}$, a well-established mixed conducting memristive oxide to fabricate own memristive cross-bar bit devices. We investigate and apply new methodology to discuss the role of carrier diffusivities on memristive device performance. For this, we introduce the selected oxide material and discuss its defect chemistry and performance with respect to memristors. Additionally, the state-of-the-art methodology in the field for probing memristive devices in view of carrier contributions is carefully examined.

5.1. What is the Role of Defects and Carrier Contributions for Memristive Devices based on SrTiO$_{3-\delta}$?

The perovskite SrTiO$_{3-\delta}$ is a mixed anionic-electronic conducting model material for which classic defect chemistry models are well established and reports of memristive switching devices already exist.

*Defect chemical consideration:* SrTiO$_{3-\delta}$ reveals a simple cubic perovskite structure with intertwined sublattices of TiO$_2$ and SrO. In this structure, the overlap of the oxygen 2p and cationic Ti 3d-orbitals is rather small$^{157}$
with a wide electronic band gap of about $E_{\text{Gap}} = 3.2 \, \text{eV}$.$^{8,157}$ As a consequence, the electrical conductivity is rather low for the undoped state and the equilibrium point defect concentrations determine the overall electrical conduction. The defect concentration dependency on temperature, atmosphere, processing or bias can be leveraged. For example, dependent on environmental conditions $\text{SrTiO}_3-\delta$ exhibits either predominant oxygen ionic conduction $via$ vacancies in the lattice or electronic conduction $via$ holes (p-type) or electrons (n-type) in accordance to its Brouwer diagram, see Rothschild$^{121}$ for details. For the targeted application of $\text{SrTiO}_3-\delta$ as an active oxide component in valence change ReRAMs it has to be noted that these typically operate in air at moderate temperatures, $i.e.$ room temperature up to 80 °C. Extrapolation of typically high temperature derived conductivities and diffusion data studied on bulk undoped $\text{SrTiO}_3-\delta$ ceramic pellets to these conditions suggest a predominant p-type$^{112}$ (hole) conduction mechanism with a low chemical oxygen diffusion coefficient of $\sim 10^{-17} \, \text{m}^2\text{s}^{-1}$ in single crystals for ambient conditions.$^{106}$ However, it remains unclear whether this hypothesis on the dominating carrier contribution kinetics holds due to the following arguments for memristive devices:

First, extrapolation of high temperature defect models (>500 °C) to room temperature is precarious and one may carefully examine the validity for this rather new room temperature application as memristors. Further review on the high temperature-defect chemistry and conduction models for the material $\text{SrTiO}_3-\delta$ are given in the excellent studies of Merkle and Maier$^{109}$, and Waser$^8$.

Second, operation of memristive oxides requires high local electric field strength on the oxide film, typically $>10^7 \, \text{Vm}^{-1}$, influencing the defect chemistry and charge transfer characteristics. To date, charge transfer, in terms of the dominant carrier types and according activation energies are predominantly investigated close to 0 V bias and purely discussed with respect to temperature, atmosphere, or microstructure for oxides. This differs to oxide-based memristive devices operating at high electric field strength and ambient conditions.
Third, most models are derived for bulk ceramic pellets and single crystals. The role of thin film-processing related characteristics is rarely discussed for the memristive oxides, i.e. lattice strain, microstrain or simply the grain boundary density may vary and requires debate. In thin films those properties are likely to affect the defect thermodynamics and resulting carrier transport properties or the non-stoichiometry. For example, strain can affect the transport properties changing the local bond strength in doped and undoped SrTiO$_3$-$\delta$ films.\textsuperscript{127} Gregori, Maier and co-workers\textsuperscript{123,125,126} discussed the role of space charges for size-effect changes in the grain to grain boundary ratio of thin films. Waser, Guo and co-workers\textsuperscript{128} revealed that the Brouwer diagram changes dependent on the variation of space charge volume relative to film thickness and strain state of a SrTiO$_3$-$\delta$ thin film. De Souza highlighted the role of grain boundaries on extended defects in SrTiO$_3$-$\delta$ in theory and experiments.\textsuperscript{106,129,130} In addition, amorphous residuals or overall crystalline to amorphous phase content changes can affect the transport kinetics by near order structural changes of such oxide thin films.\textsuperscript{158-160} Review contributions of Yildiz\textsuperscript{161} and Rupp\textsuperscript{162} revealed that lattice strain for thin film processing of oxides can be used as an engineering tool to tune their defect chemistry, transport and non-stoichiometry. Recently, we showed that strain engineering in new types of oxide multilayer micro-dot devices can control anionic conductivity contributions beyond classical doping.\textsuperscript{163} Here, first chip-based micro-contacting strategies were presented to tune real anionic strain effects for potential moderate temperature applications like resistive switching devices.\textsuperscript{163,164}

Therefore, current defect models derived for high temperature bulk pellet ceramics and single crystals need to be carefully tested in their applicability to establish atomistic models for memristive switching in mixed conducting anionic-electronic oxide thin films operated at room-temperature under high electric field strength; as are the prevailing conditions in memristive metal|SrTiO$_3$-$\delta$|metal devices.

Memristive Devices: Several groups demonstrated resistive switching for SrTiO$_3$-$\delta$ with Pt, Ti, Ni, Pd, Au, Nb:SrTiO$_3$ or SrRuO$_3$ electrodes at local electric field strengths of $10^5$-$10^9$ Vm$^{-1}$.\textsuperscript{45,49,51,53,63,68,91} In these studies
SrTiO$_{3-\delta}$ single crystals or thin films deposited via pulsed laser deposition were examined. A promising endurance of $10^6$ cycles, retention of $10^5$ s and $R_{\text{off}}/R_{\text{on}}$ ratio of 100 could be demonstrated for SrTiO$_{3-\delta}$-based memristive switches. The wealth of experience in working with SrTiO$_{3-\delta}$ as a transistor gate oxide on a chip make its integration into future ReRAM devices highly feasible. For further information about integration and specifications of ReRAMs see references$^{8,165,166}$. Different mechanisms for resistive switching and memristance on the atomistic scale were proposed for SrTiO$_{3-\delta}$ in literature and are still under debate: Sawa$^71$ emphasized the role of the Schottky barrier and of changes along metal|oxide interfaces. Waser and co-workers$^{68}$ argue that oxygen vacancy filaments in SrTiO$_{3-\delta}$ are responsible for the resistive switching. Depending on the applied bias amplitude the mechanism could even be changed between filament and homogenous interface type switching on SrTiO$_{3-\delta}$ samples.$^{91}$ However, independent of the mechanism the thermodynamics of the anionic diffusive species at the high electric fields involved during resistive switching determine the required SET/RESET voltages, read voltages and the range of accessible resistance states for the memristive device. On the other hand, it is the drift and diffusion kinetics which define performance specifications of a memristive device such as switching speed and endurance. Therefore, we need new methods to access these fundamental carrier transport parameters for memristive anionic-carrier systems.

5.2. How to Probe Electric Contributions of Charge Carriers and their Atomistic Role to Memristance?

Today, most electrical measurements in ReRAM research are done either by pulse experiments or by cyclic voltammetry measurements. Pulse experiments during which the bias pulse is applied for few nano- to micro-seconds are close to later application conditions in computers. Although, this method allows directly extracting important specification parameters, it gives only very limited insights into the switching mechanism and in particular into the carrier kinetics.

On the other hand, classic cyclic voltammetry measurements during which the bias is constantly changed with a certain sweep rate are carried
Defect Kinetics in Resistive Switching Devices - Introduction

out. We can identify in the literature on SrTiO$_{3-\delta}$, that this is the established method to characterize memristive behavior, however, the electric carrier kinetic and thermodynamic parameters involved are not experimentally accessible. This is surprising since their diffusivities and concentrations are the basis of the device characteristics. Several ex-situ analyses such as x-ray absorption near edge structure analysis (XANES)$^{167}$, x-ray fluorescence$^{167}$, conducting atomic force microscopy (cAFM)$^{62,67,91}$, impedance spectroscopy$^{62}$, atom probe microscopy$^{168}$ and x-ray photoelectron spectroscopy (XPS)$^{52}$ of oxide film microstructures and their defects were reported to reveal the memristive mechanism. Nevertheless, those measurements are rather a snapshot of the defect state and do not allow to develop models depending on the charge carrier flux. Computational work by the groups of Riess$^{169-171}$ and Strukov$^{19}$ have successfully demonstrated that the shape, magnitude, and number of resistance states in memristive $I-V$ profiles can be related to carrier diffusivities and flux for mixed conducting oxides.

It is important to note that very recently the experimental methodology to connect carrier transport kinetics to memristance was extended for cationic-switches by Waser and co-workers.$^{156}$ The authors described the switching kinetics from cyclic voltammetry measurements by applying the Randles-Sevcik$^{172}$ equation for a Pt|$\text{Cu}|\text{SiO}_2|$Pt device operating on Cu-filament formation. However, in mixed anionic-electronic memristive oxide systems, such as for the SrTiO$_{3-\delta}$ system, the dominant electronic carriers always superpose the anionic currents of the switching species, making the system inapplicable for Randles-Sevcik analysis$^{81}$ (ionic transference number $\ll 1$). The major challenge is to identify additional methodology to probe the carrier kinetics that drive the anionic resistive switching devices beyond the classic methods of pulse experiments and cyclic voltammetry. Direct comparison of these parameters allows studying materials compositions and tuning of material constituents to fit the purpose and to establish engineering guidelines for material selection for memristor devices.

To this end, we develop 2-terminal Pt|$\text{SrTiO}_ {3-\delta}$|$\text{Pt}$-based multi-bit memristive cross-bar device structures. These can be used to systematically investigate resistive switching characteristics and kinetics.
for a model mixed anionic-electronic conducting oxide. In standard memristive device tests of mixed electronic-anionic conducting oxides it is difficult if not impossible to distinguish between the dominant charge carrier type and its diffusion kinetics with respect to the device’s field strength and bias history. We discuss the potential and limitations in terms of carrier kinetic evaluation for classic cyclic voltammetry of mixed conducting, SrTiO$_{3-\delta}$ memristive bits and extend the classic electrochemical methods by two new approaches being bias-dependent activation energy measurements and chronoamperometry for memristors. Through this new methodology, dominant carrier types, time constants and diffusion coefficients can be determined with respect to applied bias as driving force for the memristive devices: First, we investigate the dependency of the electrical conductivity activation energy on high electric fields and polarity of bias, to get a more complete picture of the dominating carrier transport mechanism involved in resistive switching. Second, we develop the analysis method for chronoamperometry measurements for mixed conducting memristive oxide devices to study the defect kinetics and thermodynamics as transients to bias applied. Here, we demonstrate that three regimes can be ascribed being dominated either by a capacitive-like or memristive current or a limiting current close to thermodynamic defect equilibrium with respect to bias and polarity operated. This work presents the first description of a Memristor-based Cottrell equation and gives the basis for analysis of material-dependent carrier diffusion coefficients in mixed conducting anionic-electronic memristors. Through smart choice of mixed conducting oxide materials based on now accessible kinetic characteristics under bias one can directly implicate future electric circuit device designs and tune the memristive bit operation in terms of their time constants, threshold voltage for switching and equilibrated resistance states e.g. tune their low to high resistance state ratio, read/write voltages, power consumption and endurance.
6 Experimental Section

Two-terminal cross-bar contacted Resistive Random Access Memory (ReRAM) switches were processed based on SrTiO₃ redox building block elements. The basic single device ReRAM elements were always composed of two platinum metal lines sandwiching a SrTiO₃ oxide element.

6.1 Thin Film Preparation of the ReRAM Device

The oxide-based ReRAM constituent SrTiO₃ was deposited on a randomly oriented single crystalline sapphire substrate with pre-structured Pt-bottom electrodes via pulsed laser deposition. For the pulsed laser deposition, own SrTiO₃ ceramic targets were synthesized by uniaxially and isostatically (88 MPa for 2 min) pressing and sintering of powder (Aldrich Chemistry, USA, ≥99.5%). Sintering conditions were an isothermal hold for 24 h at 1650 °C for a heating rate of 5 °Cmin⁻¹ and cooling rate of 25 °Cmin⁻¹, respectively. The SrTiO₃ thin films were then deposited on round, randomly orientated, double side polished sapphire substrates (Stettler company, Switzerland, Ø35 mm) by pulsed laser deposition (PLD, Surface Advanced PLD Technology, Germany; KrF excimer laser, 248 nm). A round metal mask with a 20 mm diameter hole was used to maintain access to the bottom electrodes. The deposition was carried out at 48 mJ per pulse at a repetition rate of 10 Hz with a substrate-to-target distance of 8.5 cm and under a constant oxygen flow with a background pressure of 0.0267 mbar at 700 °C. After reaching a background pressure of 4×10⁻⁶ mbar the substrate was heated up to the deposition temperature with a rate of 10 °Cmin⁻¹. 48000 and 29000 laser pulses were employed resulting in a film thickness of 620 nm and 740 nm analyzed via profilometer measurements Dektak XT Advanced profilometer (Bruker, Germany). Cubic phase of the thin film was confirmed by X-Ray Diffraction (Bruker D8, CuKα), see Supporting Information Figure 21.1.
6.2. ReRAM Device Fabrication

In the following we describe the device microfabrication route to shape the thin film constituents to single side- and cross-bar memristive ReRAM elements on the sapphire substrates. All steps of the device fabrication were carried out in an ISO class 4 cleanroom. Prior to the photolithography of the bottom electrodes the sapphire substrates were thoroughly cleaned for 3 minutes in an ultrasonic bath in acetone, isopropanol and water bath consecutively and then dried for 5 minutes on a hotplate at 110 °C. For micro patterning the bottom metal electrodes AZ nLOF 2070 (1:0.4) negative photoresist (Microchemicals, Germany) was used. The samples were spun at a speed of 4750 RPM for 45 seconds, then soft baked at 110 °C for 180 seconds and afterwards rehydrated for at least 10 minutes. The samples were then aligned (Karl-Suss MJ3B mask aligner) and exposed through a custom made photolithography foil mask (Selba, Switzerland) to broadband ultraviolet light with a dose of 210 mJcm⁻² and subsequently a post bake at 110 °C for 90 seconds was carried out. Finally the bottom electrode pattern was developed with MIF 726 developer for 90 seconds and rinsed in water. In a next step the samples were cleaned in an O₂ plasma Asher (Technics Plasma TePla 100 Asher system) for two minutes.

The thin film deposition of the ReRAM metal electrode elements was carried out by electron beam evaporation (Plassys MEB 550, France). The bottom metal electrodes consist of Ti 25 nm (adhesion layer) and Pt 100 nm. The remaining photoresist was then stripped off successively in DMSO, acetone and water. The top electrodes were fabricated alike after the pulsed laser deposition of the SrTiO₃ without adhesion layer.

6.3. Electrical Characterization of ReRAM Device Elements

All electrical measurements were carried out in a custom made closed high-vacuum microprobe station with a heating stage enabling a temperature range of RT-650 °C (Everbeing Taiwan and Electrochemical Materials ETH Zurich Switzerland) with Solatron impedance analyzer (SI 1287 Electrochemical Interface, SI 1260 Impedance Phase Analyzer). For contacting the microelectrodes tungsten and platinum tips were
positioned via micro positioners employing a stereo light microscope (Nikon SMZ 1500).

In this study basically three types of electrical characterization were pursued as strategy: First, \textit{bias dependent conductivity measurements via} temperature to study the Arrhenius like behavior of transport and defects involved. Rather unusual is that we applied a variation of positive and negative bias stress for activation energy measurements to correlate these findings later on to the ReRAM characteristics. Second, classic ReRAM \textit{cyclic voltammetry} device measurements with respect to sweep rate for room temperature were undertaken. Third, the ReRAM elements were subjected to \textit{chronoamperometry measurements}. In these titration experiments a constant bias stimulus is applied to a single ReRAM device element and the current response is studied over time.

For the first type of measurement namely the \textit{bias dependent conductivity measurements} the samples were heated in the temperature range of 300–525 °C in 25 °C steps. After a minimum equilibration time of 10 minutes an averaged conductivity over 5 minutes was measured. The temperature was measured with a micro positioned K-type thermocouple positioned on top of the sample close to the measured top-electrode. The bias stimulus was varied from +100 mV to ±3 V for the Arrhenius measurements. Data analysis and fitting was undertaken with MATLAB.

The ReRAM \textit{cyclic voltammetry} device measurements were carried out for a bias range of ±1 V to ±12 V to define reasonable SET and RESET voltages with ±4 V for sweep rates of 5–50 mVs\(^{-1}\) to prevent electrical breakdown. All bits were at least cycled 10 times as an initial electroforming step to set the bit in a stable state before any further electrical characterization was carried out analogue as reported in literature.\textsuperscript{49,90,167,173} For testing reproducibility behavior always a minimum of 10 consequent cycles were measured up to 200 cycles.

For the \textit{chronoamperometry} measurements first ten subsequent cycles with a SET and RESET voltage of ±4 V with a constant sweep rate of 50 mVs\(^{-1}\) were applied to equilibrate the system. Thereafter a first SET voltage with a positive polarity to the top electrode was applied for
120 minutes and the current measured before the sample was set into its low resistance state again by applying the RESET voltage for an hour. The SET and RESET voltages were either increased or decreased by 0.1 V steps in a bias range of 1.0 V to 4.0 V.

6.4. Chemical and Structural Characterization
After the electrical characterization one sample was cleaved and 5 nm platinum was sputtered to record top- and cross-view scanning electron microscope images (SEM, LEO 1530, Zeiss). All thin film samples and PLD targets were characterized by X-Ray Diffraction (Bruker D8) at a Cu K\textalpha{} wavelength.
7 Results & Discussion

7.1. Two-terminal Pt|SrTiO$_{3.8}$|Pt Memristive Device Fabrication for an Addressable Cross-bar Array

For the experiments, we micro fabricated Pt|SrTiO$_{3.8}$|Pt memristive elements in a cross-bar array electrode structure. A photograph of a prepared sample with up to 25 addressable memristive Pt|SrTiO$_{3.8}$|Pt "bits" is shown in Figure

7.1a. Here, different 2-terminal micro electrode geometries are demonstrated that were processed for in-plane and cross-plane electrical measurements of single Pt|SrTiO$_{3.8}$|Pt bits down to a feature size of 25 µm. The SrTiO$_{3.8}$ metal oxide components of the memristive device structures were fabricated by pulsed laser deposition (PLD) with a targeted film thickness of 600 nm and Pt electrodes via electron beam physical vapor deposition (EBPVD) with 80-150 nm in thickness. A light microscopy image and magnification of a cross-bar array device structure of 25 separately addressable bits are shown in Figure

7.1b. The cross-bar array suited as a possible high packaging density circuit design for 2-terminal ReRAMs$^{174,175}$ is schematically shown in Figure

7.1c. One bit consists of two platinum electrodes and a SrTiO$_{3.8}$ thin film in-between as active anionic-switching material for a cross-plane configuration as shown in Figure

7.1d. X-ray diffraction (XRD) confirms the cubic SrTiO$_{3.8}$ phase for the metal oxides in the memristive bits in accordance with reference$^{176}$, see Supporting Information Figure 21.1. The cross-plane scanning electron microscope (SEM) image displays a dense microstructure and typical columnar grain growth for the SrTiO$_{3.8}$ thin film elements of targeted thickness (also confirmed by profilometer), Figure

7.1e-f. This is in agreement with earlier studies on PLD growth of perovskite thin films.$^{127,177}$
Figure 7.1: a) Photograph of a multi bit Pt|$\text{SrTiO}_{3-\delta}$|Pt memristive device structure with in- and cross-plane 2-terminal electrode geometries. b) High magnification of cross-bar array showing 5 memristive Pt|$\text{SrTiO}_{3-\delta}$|Pt bits. c) Schematic cross plane view of addressable multi-bit memristor structures for cross-bar array and for d) single bit with equivalent circuit symbol. e) SEM cross-sectional image showing dense columnar polycrystalline growth of oxide $\text{SrTiO}_{3-\delta}$ film via PLD with 620 nm in thickness. f) SEM top-view image of platinum electrode and $\text{SrTiO}_{3-\delta}$ film.
7.2. Measuring Memristance of Pt|SrTiO$_{3-\delta}$|Pt Bits in a Cross-bar Array Device via Classic Cyclic Voltammetry

The current-voltage ($I$-$V$) profile of a single Pt|SrTiO$_{3-\delta}$|Pt bit element addressed in a cross-bar array is shown for 30 consecutive cyclic voltammetry measurements in *Figure 7.2a*. A hysteretic $I$-$V$ characteristic is observed depending on the applied SET and RESET voltages and current direction (polarity) for the memristive bit element at a constant sweep rate of 50 mV$s^{-1}$. Applying an increasing positive bias up to a SET voltage of +4 V to the top electrode of the structure strongly increases the current and switches the bit from its high resistance state, *HRS*, (OFF state) to its low resistance state, *LRS*, (ON state). Reversing the polarity of the bias switches the resistance state back from low (ON) to high (OFF) at a RESET voltage of -4 V for a bit. Based on the analyzed hysteretic $I$-$V$ profiles, a *bipolar memristive* characteristic can be assigned for the single Pt|SrTiO$_{3-\delta}$|Pt bits which is in accordance to earlier reports of references$^{68,167}$; viz. a *non-volatile memristive behavior* is confirmed by the pinched hysteretic profile. A bias of ±4 V and the corresponding switching current are clearly low enough to prevent the bit from unipolar switching as reported in reference$^{68}$. We calculated the electric field strength at switching as $6.5 \times 10^6$ Vm$^{-1}$, which is comparable to that of thin film devices based on SrTiO$_{3-\delta}$ in the field.$^{45,49,51,53,63,68,91}$ The switching endurance was confirmed for more than 200 consecutive cycles in the cyclic voltammetry measurements, see *Supporting Information Figure 21.2*. It is worth mentioning that the stable resistance states of a SrTiO$_{3-\delta}$ switch depend not only on the history but also on the atmosphere, especially the humidity; similar dependencies were also recently reported for cation-based switches.$^{80}$
Bipolar memristive switching SrTiO$_{3-δ}$ oxide elements rely on a redox-valence change mechanism altering electrical carrier contribution via defect movement upon bias and current flux history. We analyzed the time-dependence of the memristance by variation of the sweep rate for fixed SET and RESET voltages of ±4 V for a single Pt|$\text{SrTiO}_{3-δ}$|Pt bit, Figure 7.2b. The SET current, $I_{\text{SET}}$, defining the ON resistance state systematically increases by a factor of 4.8 when decreasing the sweep rate by one order of magnitude from 50 to 5 mVs$^{-1}$ (+4 V). As expected, the ON resistance drops from 33.1 MΩ (13.3 MΩm) to 7.8 MΩ (3.1 MΩm) and the memristive hysteretic $I$-$V$ loop is enlarged; viz. the involved local charge carrier concentration profiles are in a metastable time-dependent
state for similar electric field strength. We summarize the decreasing SET current and the respective current density for the increase in sweep rate in Figure 7.2c. Comparison to literature reveals that this time dependent behavior is typical for resistive switching and reflects the metastable defect state of the memristive Pt|SrTiO$_{3-\delta}$|Pt bits presented.$^{178}$ To attain a precise kinetically equilibrated resistance state, even lower sweep rates than 5 mV$s^{-1}$ would be required for SrTiO$_{3-\delta}$-based switches. This is in accordance with simulations on perovskite memristive switches$^{68}$ and experiments on SrTiO$_{3-\delta}$ and Cr: SrZrO$_3$.$^{68,90}$

We conclude from these findings that this anionic-electronic conducting memristive system remains in a metastable state during cyclic voltammetry measurements. Obviously, at significantly shorter times as commonly used in pulsed experiments such a stable state cannot be reached either. With these standard methods it is challenging if not impossible to come to a conclusion on the underlying resistive switching mechanism and defect kinetics for a memristive anionic-electronic bit. However, in order to predict the materials switching behavior on writing and erasing bias pulses in ReRAMs and voltage-to-time operation schemes it is highly important to define the kinetics of involved carrier processes. In the following, we therefore suggest two new methodology approaches based on bias-dependent activation energy measurements and chronoamperometry to investigate the anionic and electronic defects and their charge carrier diffusivities as complementary tools in the memristor field. We discuss the involved defects and carriers with respect to the programming voltage (SET), field strength, and operation parameters to determine their impact on memristance of Pt|SrTiO$_{3-\delta}$|Pt bits.

7.3. Bias-dependent Carrier Kinetics and their Activation Energies in Memristive Pt|SrTiO$_{3-\delta}$|Pt Bits

We investigated the electric conductivity and their activation energies for single Pt|SrTiO$_{3-\delta}$|Pt bits for a rather unusually wide bias range of 0.1 V to 3 V with respect to carrier flux direction (polarity), Figure 7.3. This corresponds to an electric field strength of up to 5x10$^6$ Vm$^{-1}$ for the given device geometry. The effect of an external bias stimulus on a memristive Pt|SrTiO$_{3-\delta}$|Pt bit can alter both its metal-oxide interfacial and bulk oxide
transport, see schematic Figure 7.3a: For instance, by applying an electric field the Schottky barrier height at the metal-oxide interfaces and their metal-oxide band bending can be altered. On the other hand the oxide can exchange oxygen in a reaction with the gas phase whereby its oxide non-stoichiometry can be modified. In the following, we examine the Arrhenius-type dependence of electric conductivity with respect to the applied bias and polarity for a Pt|SrTiO$_{3-\delta}$|Pt bit, Figure 7.3b-d:

First, we measure the temperature dependence of conductivity by applying a small bias of +0.1 V, Figure 7.3b: The activation energy of conductivity was calculated as equal to 1.40±0.07 eV. This is in good agreement with literature data of pellets for SrTiO$_{3-\delta}$ for which 1.45 eV$^{125}$ and 1.52$^{124}$ eV were reported for similar small bias and temperatures. The authors further confirmed by impedance spectroscopy analysis that electronic conduction along grain boundaries is predominant.$^{124,125}$ In accordance, it is reasonable to ascribe a predominant p-type conduction mechanism for the memristive bits tested at 0.1 V bias stimulus in air in this study.

Second, for positive bias (top-electrode positive) up to 3 V, Figure 3b: A clear drop in activation energy by Δ0.24 eV to 1.16±0.07 eV is measurable for increasing bias strength from 0.1 to 3 V. In consistency, the overall conductivity is also observed to increase for larger bias.

Third, for negative bias (top-electrode negative) up to -3 V, Figure 7.3c: Switching the polarity to negative bias reduces similarly the activation energy to 1.24±0.16 eV for -3 V. All measured electrodes on both samples show a similar temperature-dependent electrical conductivity independent on the heating and cooling cycle. Therefore, it can be concluded that all fabricated switches have comparable chemistry and a good adhesion of the platinum electrodes before, during and after electric testing under bias and temperature. To the best of our knowledge these bias-dependent activation energy conduction measurements are new to the field and can consequently not be compared to literature of anionic-oxide based memristors.
Figure 7.3: a) Schematic showing the bias-dependent Schottky barrier height of one single interface and the alteration of the oxygen vacancy depletion zone for a Pt|SrTiO$_{3-\delta}$|Pt memristor bit. b) Arrhenius plot of electric conductivity for positive bias (top electrode) during heating (open symbols) and cooling (filled symbols). c) Arrhenius plot of electric conductivity for negative bias (top electrode). d) Calculated activation energies with respect to bias as driving force for a Pt|SrTiO$_{3-\delta}$|Pt memristor bit including reference data from literature$^{124,125}$ for 0.1 V.

We observe that both, the increase of positive as well as negative bias, lower the activation energy. The following changes in ionic or electronic defects under bias may account for the experimental finding: i. the Schottky barrier height ($\Phi_b$) at one metal|oxide interface is systematically lowered. ii. The concentrations and mobilities of the vacancy defects are increased under bias. Comparing with values from literature for a p-type electronic conduction along grain boundaries, we would expect an activation energy of 1.5 eV and for the oxide bulk an activation energy of $\sim$1 eV.$^{123}$ Therefore, a pronounced conduction of the bulk could be
possible at higher electric fields. iii. Joule heating within the oxide bulk might take place and has to be taken into account responsible for an increased conductivity at lower temperatures for higher electric fields as shown in simulations resulting in a falsely too low activation energy.\textsuperscript{68} We can exclude Joule heating as dominant factor in our experiments as we will show later in the discussion of the diffusion coefficients.

Interestingly, we observe an overall asymmetry in the decay of the activation energy for increasing bias magnitude with respect to the applied polarity to the device, see Figure 7.3d. We further report bipolar current-voltages profiles, which are asymmetric with respect to polarity in the cyclic voltammetry characteristics, Figure 7.2a. Taking both experimental evidences into account, this essential asymmetry for bipolar resistive switching exists despite the symmetric Pt|SrTiO$_{3-\delta}$|Pt electrode-oxide design and methodology applied. On the one hand, variations in the oxygen surface adsorption reaction may exist, since the Pt electrodes and their exposure to air is not symmetric. The top electrode is exposed with the whole surface to air and the oxide, and the bottom electrode is located between the substrate and oxide, Figure 7.1e. On the other hand, a different PLD film growth close to and further away from the substrate may result in an asymmetric thin film microstructure.\textsuperscript{179} Another possible origin of the observed asymmetry could also be caused by the first cycle in a pristine bit depending on the bias polarity applied first to the electrodes similar as described in literature for electroforming, see reference\textsuperscript{168}. We can clearly exclude the electroforming to account for the asymmetry in presented Pt|SrTiO$_{3-\delta}$|Pt bits as the same hysteresis direction was observed independent on the firstly applied bias direction (polarity). Therefore, we conclude that either the variations in oxygen surface adsorption of the electrode-gas interface or the anisotropy of typical PLD-processed thin film microstructures may be accounted for the observed asymmetry in the bias-dependent activation energies for the Pt|SrTiO$_{3-\delta}$|Pt bit conductivities.
Figure 7.4: Results of chronoamperometry experiments measured on different bits for increasing bias voltage (solid lines and symbols) and decreasing bias voltage (dashed lines, open symbols): a) Evolvement of current over time with respect to constant bias measured for a Pt|SrTiO$_3$-$\delta$|Pt-bit structure via chronoamperometry. For a SET bias range three regimes can be identified: I. Decay of current with respect to time indicating the capacitive regime. II. Increasing conductivity is measured with respect to time for a specific minimum SET threshold voltage of $V_{SET,min} = 1.2$ V indicating the memristive nature and switching of the device. III. Stable limiting current, $I_{lim}$, is reached. The circuit elements are indicated in accordance to the regime. b) Exemplary chronoamperometry data for a RESET bias range of -1.0 V to -2.5 V until an equilibrated high resistance state is reached, HRS$_{eq}$. c) Equilibrated high and low resistance states (HRS$_{eq}$ and LRS$_{eq}$) with respect to applied bias showing the accessible resistance states for a given bias.
7.4. Chronoamperometry to Investigate Material-dependent Diffusion Characteristics for Memristive Pt|SrTiO$_{3-d}$|Pt Bits

In the following, we investigate the method of chronoamperometry to probe anionic diffusion contributions for memristive Pt|SrTiO$_{3-d}$|Pt bits. In this method, the current evolution is followed over time with respect to a constant applied bias. Classic examples of the method can be studied in the battery field for details see e.g. reference$^{81}$. We newly apply and test the method for memristive bits whereby well-defined equilibrium states can be studied in contrast to classic cyclic voltammetry experiments.

Figure 7.4 displays the chronoamperometry characteristics of a Pt|SrTiO$_{3-d}$|Pt bit in the cross-bar array structure for which the current evolution over time is studied for constant bias in the range of 1.0 to 4.0 V. Figure 7.4a shows the chronoamperometry characteristics for a positive constant bias applied to the top electrode (SET voltage) for 2 hours. Between every bias step the according negative bias (RESET voltage) is applied for at least an hour to completely reset the device and set it into its equilibrated OFF state again, see Figure 7.4b. The time interval is chosen so that the electric current is measured until a stable equilibrated limiting current, $I_{\text{lim}}$, is reached, Figure 7.4c. The reproducibility of the data is proven by two independent Pt|SrTiO$_{3-d}$|Pt bits, where the SET/RESET voltage is increased in $\Delta 0.1$ V steps (full lines & solid symbols) and decreased on a different bit (dashed lines & open symbols). Therefore, we can conclude the current evolution over time is independent of the bias step direction and the SET/RESET process is fully reversible. Although the method of chronoamperometry was already used on similar perovskite oxides in the 60s and 70s$^{82,83}$, the time and bias dependency of the current was so far neither discussed in detail nor put into relation for application and description of memristors. We exemplify on the SET states of a Pt|SrTiO$_{3-d}$|Pt bit that the current over time characteristics at constant bias can be categorized into three regimes, denoted as I-III in Figure 7.4a:

Regime I \( \left( \frac{dl}{dt} < 0 \right) \): The current drops during the first seconds for a constant bias stimulus applied. This current drop points strongly towards
capacitive processes being responsible for \( \frac{dI}{dt} < 0 \) as denoted in the circuit model of Figure 7.4a, although a slightly flatter and no purely exponential decay of the current is observed. This regime gets less pronounced at higher voltages until it vanishes completely for SET voltages > 2.8 V.

**Regime II \( \left( \frac{dI}{dt} > 0 \right) \):** In this regime the current increases over time until a stable limiting current is reached. For an applied bias range < 1.2 V, however, this regime is not visible. This means that the voltage as external stimulus is too low to activate the processes responsible for memristive behavior resulting in increased conductivity. Thus, at low bias voltages the resistive portion stays unchanged in its high resistance state, \( R(t) = HRS_{eq} \) (OFF), see Figure 7.3a. Only the capacitive current decay of regime I is visible until a stable current is reached as depicted in the circuit model analogy for regime I. At a critical threshold voltage of 1.2 V, however, the memristive mechanism gets activated at the external stimulus of bias and regime II is observable. This threshold voltage defines the minimum SET Voltage, \( V_{SET,min} \) of our Pt|SrTiO\(_{3-\delta}\)|Pt device. The device switches from its equilibrated high resistance state, \( HRS_{eq} \) (OFF), to its equilibrated low resistance state, \( LRS_{eq} \) (ON), as depicted in the equivalent circuit diagram for regime II, \( LRS_{eq} < R(t) < HRS_{eq} \). From today’s common understanding of oxygen vacancy migration as responsible resistive switching mechanism in anionic memristive devices,\(^8\) we conclude oxygen vacancy motion lowers the overall electronic resistance of the device in regime II. It has to be mentioned that this critical threshold voltage of the resistive switching mechanism is not accessible via cyclic voltammetry experiments, but defines a fundamental new material parameter for resistive switching devices. Especially for the discussion and improvement of required switching voltages and non-volatility in final devices this material characteristic threshold voltage might be crucial. Increasing the bias magnitude reduces the time interval of regime II. A detailed discussion of the time characteristics and diffusion coefficients of the processes will form the basis of the subsequent chapter.
Regime III \( \left( \frac{dl}{dt} \approx 0 \right) \): In the final state \( dl/dt \) equals zero and a stable limiting current, \( I_{lim} \), prevails, as quantified in relation to the field strength in Figure 7.4c. The device reaches an equilibrated state at which the electronic conduction is constant, \( R(t) = LRS_{eq} \). Therefore, assuming a redistribution of oxygen vacancies as cause for the increase of the conductivity in regime II we can also conclude that this redistribution has reached a final state by a drift-diffusion equilibrium of oxygen vacancies at the according bias in regime III. The resistance in this equilibrium state defines the limiting lowest accessible resistance state, \( LRS_{eq} \), in cyclic voltammetry and pulsed experiments for a SET operation in relation to the corresponding bias and electric field strength for the materials involved and device geometry. We analyze an exponential dependency of the limiting current on field strength and bias applied for the low resistance state (ON), see Figure 7.4c. For common sweep rates in cyclic voltammetry experiments usually a non-equilibrated resistance value between \( LRS_{eq} \) and \( HRS_{eq} \) is measured depending on the field strength and charge carrier flux history. This characteristic data is especially interesting to compare material combinations and processing to improve the ON/OFF ratio of resistive switches and to study accessible multilevel switching states for a certain device.

7.5. Bias-dependent Kinetic Analysis of Carrier Diffusion for a Memristive Pt|SrTiO\(_{3-\delta}\)|Pt bit via Chronoamperometry Measurements: The Memristor-based Cottrell Analysis

On the basis of the suggested circuit model of a parallel memristor-capacitor to represent the Pt|SrTiO\(_{3-\delta}\)|Pt bit, we will determine the time constant, \( \tau \), of regime II, \( \left( \frac{dl}{dt} > 0 \right) \) relative to bias for kinetic analysis of diffusing carriers in the following.

For the analysis of diffusion kinetics in chronoamperometry experiments classically the Cottrell equation (Equation 7.1) is applied which describes the change in diffusion-controlled current response with respect to a constant potential:
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\[ i_j = \frac{nFAc_j^0 \sqrt{D_j}}{\sqrt{\pi t}} \quad \text{Equation 7.1} \]

where \( i_j \) represents the diffusion current, \( n \) the number of electrons transferred, \( F \) the Faraday constant, \( A \) the geometric electrode area, \( t \) the time, \( c_j^0 \) the bulk concentration of the diffusive species and \( D_j \) the chemical diffusion coefficient. In a classic electrochemical system (e.g. a redox couple in a battery) one measures a diffusion current resulting in a current drop to zero for time approaching infinity with \( i_j \propto t^{-0.5} \) in accordance to Fick’s law.\(^{81}\) In contrast to the classic behavior, the chronoamperometry results for our memristive Pt|SrTiO\(_3\)-δ|Pt device reveal for the regime II in Figure 7.4a an increasing current over time indicating the memristive nature and switching of high to low resistance state upon bias which makes an adaption of the Cottrell equation necessary.

The total electric current, \( i_{\text{total}} \), can be described by the sum of the electronic, \( i_e \), and \( i_{h^+} \), and oxygen ionic currents, \( i_{\text{O}^\text{v}^\text{v}} \), of SrTiO\(_3\)-δ, namely,

\[ i_{\text{total}} = i_e + i_{h^+} + i_{\text{O}^\text{v}^\text{v}} \quad \text{Equation 7.2} \]

In particular, the current density, \( j_{\text{total}} \), is dictated by the mobility, \( \eta_j \), and concentration, \( c_j \), of the single charge carrier species, \( j \), and the elementary charge, \( q \), at the electric field, \( E \):

\[ j_{\text{total}} = E(q\eta_{h^+}c_{h^+} - q\eta_ec_e + 2q\eta_{\text{O}^\text{v}^\text{v}}c_{\text{O}^\text{v}^\text{v}}) \quad \text{Equation 7.3} \]

The total concentration of oxygen vacancies, \( c_{\text{O}^\text{v}^\text{v}} \), in SrTiO\(_3\)-δ can be described according to the oxygen exchange reaction:

\[ \text{V}_{\text{O}^\text{v}^\text{v}} + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{O}_\text{e}^+ + 2\text{h}^+ \quad \text{Equation 7.4} \]
Here, the Kröger-Vink notation is used and (g) is referred to the gas phase.

Based on the careful analysis of the bias-dependent activation energy of transport in the Pt|SrTiO$_{3-x}$|Pt bits we account electronic carriers, namely p-type, to be predominant. Although the current is mainly carried by electronic carriers, we suggest in accordance with today’s common understanding oxygen vacancy drift and diffusion as responsible switching mechanism in anionic-electronic devices. Therefore, we account for the memristive nature in regime II by a modification of the Cottrell equation to describe the time constant characteristic relative to bias, see Figure 7.5a-d. For a memristive system the increase in current over time till a limiting current is reached (e.g. region II, Figure 7.4a) can be defined by a differential current, $I_d$:

$$I_d(t) = I_{lim} - I(t) \quad \text{Equation 7.5}$$

We can now rearrange the classic Cottrell equation, Equation 7.1, use the differential transient memristor current data to evaluate the diffusion coefficient, $D_m$, by defining a Memristor-based Cottrell equation accounting for the valence change mechanism:

$$D_m = \left( \frac{I_d \sqrt{t}}{nFAc} \right)^2 \quad \text{Equation 7.6}$$

Here, the time, $\tau$, is a material-dependent time constant and is defined as at which $I \sqrt{t}$ has its maximum with respect to bias given by:

$$t(\tau) := \left[ \left( I_{lim} - I(t) \right) \sqrt{t} \right]_{max} \quad \text{Equation 7.7}$$

This maximum approach is typically used in literature to extract diffusion constants from chronoamperometry experiments. On the basis of Equation 5 to 7, the time constant can be analyzed with respect to bias for the valence-change memristor bit. In Figure 7.5a-d, we exemplify the analysis for a set bias of +2.4 V and extract a time constant of 291 s.
Figure 7.5: Example of kinetic analysis steps to calculate with the Memristor-based Cottrell equation the material specific time constant for the memristive regime II for a constant applied bias on Pt|SrTiO$_3$-δ|Pt bits: a) Measurement data of chronoamperometry experiment for an applied bias of +2.4 V to the top electrode in logarithmic scale. b) Differential current, $I_d$, allowing to analyze the oxygen diffusion. c) The plotted $I_d(t)$ vs. $t^{0.5}$ curve. d) The $I_d(t) t^{0.5}$ vs. $t^{0.5}$ curve to derive the material specific time constant for the memristive regime II.
Figure 7.6: Analysis of specific time and diffusion constants for a memristive Pt|SrTiO$_{3-\delta}$|Pt bit via the Memristor-based Cottrell equation: a) Analyzed time constant, $\tau$, determined via the Memristor-based Cottrell equation for the memristive oxide SrTiO$_{3-\delta}$ with respect to electric field strength and bias at room temperature. b) Calculated oxygen vacancy diffusion constant, $D_v$, for the memristive oxide SrTiO$_{3-\delta}$ with respect to electric field strength and bias at room temperature. Extrapolation of literature vacancy diffusion constants to room temperature without electric field, see references $^{106,112,119,181}$, including De Souza’s$^{106}$ derived global expression (red triangle) is added for comparison. c) Schematic of resistive switching in SrTiO$_{3-\delta}$ caused by oxygen vacancy redistribution under high electric field at room temperature. In the OFF state the memristive oxide remains unchanged in its high resistance state. At a specific threshold voltage the oxygen vacancies start to redistribute within the oxide decreasing the resistance. In the equilibrated low resistance state the redistribution has reached a final state by a drift-diffusion equilibrium of oxygen vacancies at the according bias.
The time constants are displayed for the measured bias range of 1.2 V to 3.9 V in Figure 7.6a. A decrease in time constants of about a factor seven (876 to 129 s) is measured for an increase in bias up to +3.9 V for a Pt|SrTiO$_{3-δ}$|Pt bit. Assuming that the whole oxide volume between the electrodes contributes to the memristive current increase under bias, the diffusion coefficient is evaluated using the time constants derived in Equation 7.6 and 7.7 according to the Memristor-based Cottrell equation see Figure 7.6b. We base our calculation on an experimentally determined diffusion length of 620 nm electrode distance by SEM and profilometry for one Pt|SrTiO$_{3-δ}$|Pt bit. We observe a maximum in diffusion coefficient of 3×10$^{-15}$ m$^2$s$^{-1}$ at 3.8 V bias which reduces to 4×10$^{-16}$ m$^2$s$^{-1}$ for 1.2 V bias at room temperature. This dependency reveals how strong the oxygen migration is facilitated by the electric field. Literature comparison to chemical oxygen vacancy diffusion data of SrTiO$_3$ single crystals for high temperature without bias as driving force were extrapolated to ambient conditions$^{106,112,119,181}$ and result in diffusion coefficients in the range of 6×10$^{-17}$ m$^2$s$^{-1}$ – 4×10$^{-19}$ m$^2$s$^{-1}$, Figure 7.6b. Interestingly, this reveals that the diffusion coefficients derived in this study for the memristive bits are of comparable magnitude and in agreement with De Souza`s global expression of diffusion coefficient for room temperature and zero bias extrapolation.$^{106}$ This implies that indeed oxygen vacancy diffusion is responsible for the resistance changes in the memristive regime for the Pt|SrTiO$_{3-δ}$|Pt bits. Here, local changes in oxygen non-stoichiometry of the oxide result and are balanced with electronic carriers at high electric field strength, as depicted in the schematic of Figure 7.6c.

The extrapolation of diffusion data additionally shows, that an increase of an order of magnitude of the diffusion coefficient equals about ~30 °C increase in temperature. Therefore, we exclude Joule heating as responsible memristive switching mechanism for the given materials and bit structure as larger differences would have been observed within the investigated bias range.

It is promising that based on the Memristor-based Cottrell equation diffusion coefficients can be analyzed over the whole range of bias and electric field based on chronoamperometry measurements. These are
complementary and give important new material characteristics for mixed anionic-electronic conducting oxides for memristive devices. Additionally, the threshold electric field strength initiating the switch from a capacitive to a memristive behavior can clearly be defined from the transients on the example of the Pt|$\text{SrTiO}_{3.0}$|Pt bit \((i.e. \ 1.9\times10^6 \ \text{Vm}^{-1})\) towards the equilibrium limiting currents of the devices. For classic memristor characterization, \textit{e.g.} cyclic voltammetry, the equilibration and limiting currents remain unknown. Through the new approach demonstrated we can clearly define the diffusion coefficient, minimum field strength and limiting currents for the memristive regime of a Pt|$\text{SrTiO}_{3.0}$|Pt bit. These are important material characteristics that directly implicate the device design and optimized operation of mixed anionic-electronic oxide-based memristors \textit{vs.} carrier flux.
8 Conclusion

In this work, we demonstrate that chronoamperometry and bias-dependent activation energy measurements are powerful methods for gaining complementary insights on material-dependent carrier characteristics for mixed anionic-electronic conducting oxides in memristive devices. Successfully fabricated 2-terminal Pt|SrTiO$_{3-\delta}$|Pt-based multi-bit cross-bar structures enable us to define the model oxide constituents in terms of their mixed defects and to investigate the effect of electric field strength and carrier flux on devices memristance. Our results for the Pt|SrTiO$_{3-\delta}$|Pt bits show reproducible and stable resistive switching for state-of-the art cyclic voltammetry measurements on several Pt|SrTiO$_{3-\delta}$|Pt bits for $V_{\text{SET,RESET}} = \pm 4$ V at field strength of $6.5 \times 10^6$ Vm$^{-1}$. To date, memristor-based kinetic analysis of carriers is focused primarily on one type of defect (cationic) and analyzed via the Randles-Sevcik equation of cyclic voltammetry only. By careful analysis and discussion we highlight the limitations of this classic methodology in characterizing memristance for mixed anionic-electronic oxide-based memristor bits; e.g. it is impossible to determine materials-dependent limiting currents, equilibrium defect states, or diffusion characteristics as the involved anionic vs. electronic carrier contributions cannot be separated. This accounts for the development of a comprehensive theory on carrier contribution and kinetics in memristive devices based on oxides with mixed anionic-electronic transport. We overcome these limitations by the use of a combination of complementary methods to identify the oxide material-dependent dominant carrier defect types contributing to the low and high resistance states, and to extract diffusion coefficients with respect to the local electric field strength and write/read voltages of the memristive bits:

First, we investigated the temperature dependence of electric conductivity and calculated activation energies for a rather unusually wide bias range. These measurements revealed a severe decay of activation energy from 1.4 eV down to 1.16 eV for higher biases and an asymmetry with respect to bias polarization as the Schottky barrier is lowered. Based on the activation energies, a predominant p-type electronic conduction balanced
by oxygen vacancies of the oxide is a reasonable model to account for the resistive switching in the Pt|SrTiO$_{3.0}$|Pt bits in air.

Second, we introduce chronoamperometry to identify the electric field dependence of the capacitive to memristive regimes of the device. Here we applied constant SET and RESET biases to the device during which the memristor bits equilibrate at either low or high resistance states. Oxide-material characteristic time-constants could be measured for which the memristive current evolution dominates in the device with respect to field strength. For example at a specific threshold voltage of 1.2 V corresponding to an electric field strength of 1.9×10$^6$ Vm$^{-1}$ is found for SrTiO$_{3.0}$ thin films at which the resistive switching mechanism gets thermodynamically activated at room temperature. Correlating the limiting current to the electric field strength the mixed oxygen anionic-electronic diffusion kinetics were probed via the newly suggested Memristor-based Cottrell equation. We found faster diffusion kinetics at higher electric fields with diffusion coefficients ranging from 4×10$^{-16}$ m$^2$s$^{-1}$ to 3×10$^{-15}$ m$^2$s$^{-1}$ for a bias increase from 1.2 V to 3.8 V respectively. Comparison to De Souza’s global expression of diffusion coefficients for SrTiO$_3$ resulting in 2×10$^{-17}$ m$^2$s$^{-1}$ reveals a good agreement.$^{106}$

To date, memristor-based kinetic analysis of carriers is focused primarily on one type of defect (cationic) and analyzed via the Randles-Sevcik equation from cyclic voltammetry only. We demonstrate an extended strategy to analyze memristive oxide devices kinetics for two types of charge carriers, namely, anionic and electronic carriers based on the Memristor-based Cottrell analysis and the method of chronoamperometry. Here, classic kinetic analysis via the Randles-Sevcik equation would no longer be valid as the involved anionic vs. electronic carrier contributions cannot be separated. This accounts for the development of a comprehensive theory on carrier contribution and kinetics in memristive devices based on oxides with mixed anionic-electronic transport.

The development of high performance oxide-based memristive devices may be the cornerstone of the next generation of information storage
devices replacing transistors or even allowing neuromorphic computing. Through our work we suggest new complementary tools to probe the oxide materials characteristic diffusion coefficients, dominant carrier types and limiting currents on the example of mixed two-carrier conducting Pt|SrTiO$_{3-x}$|Pt bits. All of the latter material characteristics would not be accessible with state-of-the-art methodology of cyclic voltammetry and pulse experiments for memristors. However, these characteristics allow comparing and improving material selection and directly implicate field strength requirements to optimize operation in the memristive regime towards enhanced performance specifications for valence-change memristive devices.
9 Follow-up Chapter II

This chapter briefly summarizes the scientific progress on the topic of Chapter II after publication.

Recently other material studies on resistive switching started to apply chronoamperometry measurements to their devices for example on amorphous-SrTiO$_3$, CeO$_2$ and WoO$_3$. Here, the general aim of the authors is to extract diffusion constants under bias, and to depict the memristive vs. capacitive contributions for their resistive switching oxides materials.

Nili et al. investigated the defect chemistry of amorphous strontium titanate, a-SrTiO$_3$, in detail and its impact on the resistive switching performance including the effect on doping with niobium. They measured for stoichiometric a-SrTiO$_3$ an activation energy from Arrhenius plots of the electrical conductivity of 1.48 eV similar to the results for polycrystalline SrTiO$_3$, as reported in this Chapter II, being at 1.4 eV. For oxygen deficient Nb doped a-SrTiO$_3$ the activation energy was reduced to 1.39 eV. Additionally, a similar methodology as described in thesis Chapter II was applied to Pt|a-SrTiO$_3$|Pt devices with an oxide thickness of 100 nm including the Memristor-based Cottrell Analysis. Here the authors adapted the experimental protocol presented in Chapter II and additionally measured the high and low resistance state of their device after every chronoamperometry measurement at constant bias by a $10^4$ s long reading measurement at 100 mV. They derived a diffusion constant of $5.27 \times 10^{-15}$ m$^2$s$^{-1}$ for the devices, which is added to the Figure 9.1 for comparison.

Younis et al. investigated the resistive switching characteristics of CeO$_2$-based devices in detail by chronoamperometry measurements and applied the Memristor-based Cottrell analysis. Here the authors focused on the ion migration under weak-programming conditions in the bias range of 0.2 V to 3.8 V. Similar to the presented results in Chapter II they observed increasing diffusion constants at increasing field strength. For their Au|CeO$_2$|Au|Si devices with an oxide thickness of 250 nm they
II Defect Kinetics in Resistive Switching Devices – Follow-up

exemplarily estimated a time constant of 221s at 1.2×10^7 Vm⁻¹, see Figure 9.1. Interestingly they found a SET threshold voltage, U_{SET}, of 1.4 V a lot smaller than the voltage of ~4.2 V at which resistive switching occurred during their cycling voltammetry experiments at different sweep rates.

Tan et al.¹⁸²,¹⁸³ and Shi et al.¹⁸⁴ studied the resistive switching of WoO_{3-x} in detail via chronoamperometry measurements and applied the Memristor-based Cottrell analysis. Here Tan et al.¹⁸²,¹⁸³ estimated for Pt|WoO_{3-x}|Pt structures a diffusion constant of 2.4×10⁻¹⁷ m²s⁻¹ for oxygen vacancies at an electrical field strength of 3.3×10⁶ Vm⁻¹, see Figure 9.1. The rather high diffusion constant compared to previous reports on WoO_{3-x}¹⁸⁵,¹⁸⁶ they assigned to the simplification of taking the whole film thickness as diffusion length, whereas in this system the vacancies only have to move the distance between the conductive Magnéli phase and the counter electrode which is only a small fraction of the film thickness. Shi et al.¹⁸⁴ determined for Pt|WoO_{3-x}|fluorine doped tin oxide structures with a oxide thickness of 500 nm a relative high diffusion coefficient of ~3.7×10⁻¹⁶ m²s⁻¹. Nevertheless they pointed out the possibility of overestimation of the diffusion length, a local electrical field enhanced diffusion within the oxide film, a possible existence of fast diffusion path in the material or Joule heating during the switching responsible for enhanced oxygen vacancy diffusion.

In the recent review on NbOₓ by Nico et al.¹⁸⁷ they identified this material due to its properties and few studies regarding resistive switching on niobium oxides as promising candidate for resistive switching devices and emphasized the necessity of a detailed bias dependent chronoamperometry analysis on NbOₓ-based devices.

Marrochelli et al.¹³² extrapolated in their simulation study oxygen diffusion on SrTiO₃ constants from high temperature data to room temperature similar as reported in this thesis Chapter II.

In conclusion, the presented work of Chapter II of this thesis was implemented to other colleagues work. The methodology of Memristor-based Cottrell Analysis became useful to analyze the capacitive to
memristive components and diffusion constants under bias for various oxides. This permits a direct comparison of bias and electric field dependent diffusion coefficients in resistive switching, which allows now a discussion such as the influence of microstructure or doping across the studies.

Figure 9.1: Calculated oxygen vacancy diffusion constants of different memristive oxides, $D_V$, with respect to electric field strength and bias at room temperature via the Memristor-based Cottrell analysis: polycrystalline SrTiO$_3$-$\delta$ (blue), amorphous a-SrTiO$_3$ (green), CeO$_2$ (orange) and WoO$_3$ (cyan). Extrapolation of literature vacancy diffusion constants of SrTiO$_3$-$\delta$ to room temperature without electric field, see references$^{106,112,119,181}$, including De Souza’s$^{106}$ derived global expression (red) is added for comparison.
III Influence of Moisture

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Abstract
Memristors based on anionic-electronic resistive switches represent a promising alternative to replace transistor-based memories due to their scalability and low power consumption. To date, studies on resistive switching focus on oxygen anionic or electronic defects leaving protonic charge carrier contributions out of the picture despite the fact that many resistive switching oxides are well-established materials in resistive humidity sensors. We study how memristance is affected by moisture for the model material strontium titanate. First, we thoroughly characterize own-processed Pt|SrTiO$_{3-δ}$|Pt bits via cyclic voltammetry under ambient conditions. Based on the high stability of our non-volatile device structures we investigate the impact of relative humidity to the current-voltage profiles. We find that Pt|SrTiO$_{3-δ}$|Pt strongly modifies the resistance states by up to 4 orders of magnitude as well as the device’s current-voltage profile shape, number of crossings and switching capability with the moisture level exposure. Furthermore, we demonstrate for the first time a reversible transition from classic memristive behavior at ambient humidity to a capacitive dominated one in dry atmosphere for which the resistive switching completely vanishes. We discuss the results in relation to the changed Schottky barrier by adsorbed surface water molecules and its interplay with the charge transfer in the oxide.
10 Introduction

Memory technologies based on electronically-operated transistors, e.g. DRAM and flash memory, are currently reaching their physical limits in scalability.\textsuperscript{7} Driven by the growing demand on fast data transfer, increased computational speed and memory density, the development of novel material structures and operation concepts is one of the major challenges of the 21\textsuperscript{st} century. Here, memristors deployed as Resistive Random Access Memory (ReRAM) represent a promising alternative to replace state-of-the-art transistor-based memories in the near future.\textsuperscript{7} In these ReRAMs, ionic carriers are moved under high electric fields besides electronic ones, resulting in superior memory storage with fast ns-read/write speeds, low energy consumption and high retention.\textsuperscript{22} The potential of these ionically controlled resistive switches is amplified by multiple accessible resistance states even going beyond binary logics.\textsuperscript{22} While the first demonstration of rapid resistance changes in oxides upon bias pulses dates back to the 1960s,\textsuperscript{16} only in 2008 Strukov and co-workers\textsuperscript{19} connected the experimental results of their fabricated Pt|TiO$_2$|Pt resistive switches to the memristor theory by Chua.\textsuperscript{9} Today it is generally accepted, that simple metal|oxide|metal structures under high local electric field strengths (>10$^6$ Vm$^{-1}$)\textsuperscript{8,22} can show memristive behavior and different resistive states can be addressed via the current flux history. There exist mainly two types of oxide-based ReRAMs, namely cationic and anionic resistive switches, differing in their main ionic carrier contribution accountable for the memristance.\textsuperscript{8} In anionic-electronic resistive switches migration of oxygen anions over defects, i.e. oxygen vacancies, facilitated under high electrical fields are responsible for controlled resistance changes. These resistive switches operate via local valence-changes of the transition metal oxide balanced by electronic carriers. The electric conductivity, $\sigma_{\text{tot}}$, for an anionic-electronic resistive switching oxide can be described using the Kröger-Vink notation by:

$$\sigma_{\text{tot}} = q\eta_{h^+}c_{h^+} + q\eta_{e^-}c_{e^-} + 2q\eta_{V_{O^2}}c_{V_{O^2}}$$

Equation 10.1
where $q$ denotes the elementary charge, $\eta_j$ the mobility and $c_j$ the concentration, of the single charge carrier species, $j$. $h^*$ are the holes, $e'$ the electrons and $V_{\text{O}^{**}}$ the oxygen vacancies.

Material examples include SrTiO$_3$, SrZrO$_3$, ZrO$_2$, TiO$_2$, SiO$_2$, HfO$_{2-\delta}$, SnO$_2$, Ta$_2$O$_{5-\delta}$, BaTiO$_3$, (La,Sr)MnO$_3$, (Pr,Ca)MnO$_3$, (La,Sr)(Co,Fe)O$_3$, CaCu$_3$Ti$_4$O$_{12}$ with metallic or oxide electrodes like Pt, Au, Ni, Pd, Nb:SrTiO$_3$ or SrRuO$_3$.

In this study, we work with strontium titanate, SrTiO$_{3-\delta}$, as resistive switching oxide which is a well-suited model material to investigate the role of defects and charge carriers on the resistive switching phenomena due to the following reasons:

i.) SrTiO$_{3-\delta}$ shows promising non-volatile oxygen anionic-type controlled resistive switching at electric field strengths of more than $10^6$ Vm$^{-1}$ with $R_{\text{off}}/R_{\text{on}}$ ratios up to 100, a retention of $10^5$ s and an endurance of $10^6$ cycles. Recently, we reported the successful distinction of capacitive and memristive contributions to the resistive switching and a facilitated oxygen migration for memristive conditions with diffusion constants of up to $3\times10^{-15}$ m$^2$s$^{-1}$ at electric field strengths of $6.2\times10^6$ Vm$^{-1}$ for Pt|SrTiO$_{3-\delta}$|Pt bits.

ii.) The oxide has a single phase cubic perovskite structure stable over a large temperature range of 105-1913 K, and for oxygen non-stoichiometry down to SrTiO$_{2.5}$.

iii) The defect chemistry, especially for high temperatures, is well established and the mixed oxygen anionic-electronic conduction mechanism is well understood. At ambient conditions it is a predominant p-type conductor with an electrolytic domain boundary at lower oxygen partial pressures of roughly $10^{-3}$ atm. Very recently, first reports on changes in the local dislocation concentrations altering oxygen diffusion coefficients under high fields during switching, and their direct implication on electronic carrier diffusion are discussed in theory and supported by transient transport experiments for SrTiO$_{3-\delta}$. 
Despite the many reports on resistive switching of SrTiO$_3$ the detailed resistive switching mechanism remains under debate.$^{68,71,91}$ To date, fundamental resistive switching studies on SrTiO$_3$ focus primarily on the anion contribution, namely defects in the anionic sublattice as oxygen vacancies, V$_O$$^{--}$, and the location of these defects in the resistive switches.$^{8,27,28}$ For example, the role of the Schottky barrier at the metal|oxide interfaces was highlighted by Sawa$^{71}$, whereas e.g. Waser and coworkers$^{68}$ emphasized the formation and rupture of conductive filaments as responsible for the resistive switching. Typical analyzing methods to characterize the resistive switching involve cyclic voltammetry$^8$, conducting atomic force microscopy$^{62,67,91}$ chronoamperometry$^{46,95}$, impedance spectroscopy$^{62}$, oxygen tracer diffusion$^{131}$ and electro-coloration experiments$^{189}$. As such, these experiments predominantly address the role of the main charge carriers of electrons and oxygen anions on the several orders of magnitude switchable resistance states. However, many of these experiments may not allow direct determination of the predominant charge carrier type for two- or even more charge carrier types. Importantly, this leaves protonic charge carrier species or interaction with hydroxyl groups created by ambient moisture exposure out of the picture. Even for SrTiO$_3$, one of the best investigated materials in anionic-electronic resistive switching, it remains unknown whether moisture can affect resistive switching and the physical property of memristance.

Interestingly, numerous oxides currently used as resistive switching oxides are known to vary their resistance upon moisture exposure at low electric field strength. Examples include the tunable ohmic resistance states upon humidity exposure of the oxides SrTiO$_3$$^{137}$, CeO$_2$$^{190,191}$, TiO$_2$, BaTiO$_3$, SnO$_2$$^{192}$ and Y$_2$O$_3$:ZrO$_2$$^{193}$. In these materials, the capability of incorporating hydroxyl ions (i.e. OH intermediates) to these oxide surfaces and bulk via interaction with oxygen vacancies have formed the technological base for today’s ceramic humidity sensors.$^{135,137,194,195}$

The reaction of oxygen deficient SrTiO$_{3-\delta}$ with moisture reveals clear interaction of anionic, electronic and protonic carriers, see references$^{109,133,134}$ for details. Water molecules from the gas phase are
first adsorbed at the surface and can subsequently be incorporated into an oxide’s bulk via the following hydration reaction:109,133,134

\[ H_2O + O^* + V_{O}^{**} \rightleftharpoons 2OH^* \]  

Equation 10.2

With taking the protonic contribution into account the total conductivity of the switching oxide, Equation 10.1, has to be extended to:

\[ \sigma_{\text{total}} = q\eta_{h^*}c_{h^*} + q\eta_{e}c_{e^*} + 2q\eta_{V_o^{**}}c_{V_o^{**}} + q\eta_{OH^*}c_{OH^*} \]  

Equation 10.3

where \( OH^* \) indicates a proton bound to oxygen in the metal-oxide. Rather than bulk protonic conduction, in oxides, often surface, interface or grain boundary conduction of protons are relevant for conductivity changes of oxide at elevated water concentrations.135,136 \textit{i.e.}, water interacts with the metal oxide resulting in a first layer being chemically adsorbed as hydroxyl group, whereby even subsequent water layers may become physically adsorbed to the oxide’s lattice. For this state, protonic defects can diffuse over hydroxyl groups, cascading as additional protonic conductivity via the "Grotthuss mechanism" besides oxygen anionic and electronic contributions.136,196-200 It is important to note that conductivity changes by moisture depend strongly on temperature and porosity of the metal oxide135,137, and can also be influenced by reactions of other ambient gases at the interface, \textit{e.g.} reactions with CO or CO\(_2\).137

Additionally to the conductivity changes due to moisture, a possible water splitting reaction could interfere with the memristance activated through the extreme conditions prevailing in resistive switching devices, namely the high electrical field strength. Despite the evidence for the active modulation principles of ohmic resistances and surface potentials of oxides used in ceramic humidity sensors, the effect of moisture and hydroxyl group interaction with oxygen vacancies and electrons on the physical property of memristance for anionic-electronic resistive switches was so far not elucidated.

This is in contrast to recent advances in the field of cationic-electronic resistive switches: First reports show that the injection of copper cations from the electrode into the oxide and the resulting formation of metallic filaments, \textit{i.e.} Cu-filaments in a Cu|SiO\(_2\)|Pt resistive switch, proceeds in
parallel to reduction of moisture acting as a counter/charge reaction at the platinum electrode, see Waser group$^{80,201}$. Additionally, Tsuruoka et al.$^{201}$ reported amongst others through comparison of Cu$|$SiO$_2$$|$Pt and Cu$|$Ta$_2$O$_3$$|$Pt cationic-electronic devices, that a hydrogen-bond network formed by moisture adsorption facilitates the Cu ionic migration along the grain boundaries of the oxide. Here, the forming, SET and RESET voltages were significantly altered by the relative humidity for the cationic-electronic resistive switches.

From a fundamental perspective it is exciting to uncover if and how the basic property of memristance is affected by moisture and protons as additional carrier species interacting with oxygen anions and electrons for anionic-electronic resistive switches. For decades mixed conducting oxides have been researched in their ohmic resistance and interface resistive modulations with respect to humidity exposure. In this work we turn now to memristive anionic-electronic switches and investigate for the oxide material constituents the interplay of oxygen anionic, electronic and protonic charge carriers and fluxes. These can play a key role in understanding how atomistic defects interact at surfaces and bulk of the oxide compound and whether adsorbing ambient species contribute to the property of memristance in oxide-based switches. Therefore, we need to examine carefully how this may inflict future material selection and engineering strategies for enhanced performing ReRAMs.

In this work we investigate and demonstrate the controlled modulation of memristance upon humidity exposure in strontium titanate-based switches. For this we fabricate model 2-terminal Pt$|$SrTiO$_{3-x}$-$x$Pt resistive switching bits with cross-bar array structures and single micro-electrodes. By adopting the relative humidity level during stable operation of the model switches in cyclic voltammetry experiments we probe for the first time an oxide model system with oxygen vacancies and electronic carriers the direct implication of moisture on the non-equilibrium states of the resistive switch. The current-voltage ($I$-$V$) profiles, their low to high resistance state ratio, switching capability and overall conduction changes are investigated relative to moisture and electric field strength variation. Hence, the experimental approach gives first insights to the fundamental question whether memristance is and may even actively be affected by
atmospheric changes for anionic-electronic resistive switches exemplified on SrTiO$_{3.8}$. Implication on the redox-kinetics and carriers involved is discussed also in view of future device operation and integration for SrTiO$_3$-based anionic-electronic ReRAMs.
11 Experimental Section

11.1. Sample Preparation and Characterization

The electrodes were structured via standard photolithography process on round sapphire substrates. Here, the micro patterning of the electrodes was carried out in a ISO class 4 cleanroom using AZ nLOF 2070 (1:0.4) negative photoresist (Microchemicals, Germany) which was spun at a speed of 4750 RPM for 45 s and afterwards soft baked at 110 °C for 180 s. The samples were then rehydrated for at least 10 minutes before aligned and exposed with ultraviolet light dose of 210 mJ/cm² in mask aligner (Karl-Suss MJ3B) using a custom made foil mask (Selba, Switzerland). Finally the structures were developed with MIF 726 developer for 90 s and rinsed in water. An O₂ plasma Asher (Technics Plasma TePla 100 Asher system) was employed for 60 s at 100 W to clean the samples surfaces of any organic residues before the metal depositions. The bottom electrodes consist of a titanium adhesion layer with 5 nm in thickness and 80 nm thick platinum layer deposited via electron beam evaporation (Plassys MEB 550). The top electrodes with an area of 500 μm × 500 μm consist of pure platinum and were deposited alike. The 760 nm thick strontium titanate film was deposited via pulsed laser deposition (Surface Advanced PLD technology; KrF excimer laser, 248 nm) with a laser energy of 46 mJ per pulse and a deposition frequency of 10 Hz under a constant oxygen flow at a pressure of 0.0267 mbar at 700 °C. The thin film layer thicknesses were confirmed by cross-view electron scanning images (LEO 1530, Zeiss) and profilometer measurements (Dektak XT Advanced profilometer, Bruker). The sample fabrication process is described in further detail in our previous work. All samples and PLD targets were characterized via x-ray diffraction (Bruker, D8, CuKα) and cubic phase was confirmed, see Supporting Information Figure 23.1. For structural characterization one sample was cleaved after electrical characterization and 5 nm platinum was sputtered onto it to record cross-view scanning electron microscope images (LEO 1530, Zeiss) with an acceleration voltage of 3 kV.
11.2. Electrical Characterization

All electrical measurements were carried out with either Keithley Source Meter Unit 2601b or Keithley High Resistance Meter 6517b. The electrodes were contacted with platinum contact needles controlled by micro positioners employing a stereo light microscope (Nikon SMZ 1500). The top electrodes were set as working electrode and the bottom electrodes were grounded. To avoid complicated conduction path interpretation, e.g. sneak paths \(^{202}\), all data shown in this study were measured on single Pt|SrTiO\(_{3.8}\)|Pt bits. If not other noted the cyclic voltammetry was carried out between ±4 V at a constant sweep rate of 50 mVs\(^{-1}\) at room temperature. Before any measurements the pristine electrodes were cycled at least 15 times to reach a stable switching state, no additional electroforming was necessary and applied. To verify reproducibility at least three electrodes were measured under same conditions. The cyclic voltammetry measurements under different humidity levels were carried out in a custom made closed high vacuum microprobe station (Everbeeing Taiwan and Electrochemical Materials ETH Zurich Switzerland). For a humidity level of 35-45% relative humidity electrical measurements were carried out under ambient atmosphere. A dry atmosphere with 0% relative humidity was achieved by evacuation of the microprobe station to 2×10\(^{-2}\) mbar with flushing the chamber with synthetic air (20% O\(_2\), 80% N\(_2\), H\(_2\)O < 3 ppm). The evacuation and flushing step was repeated for three times to assure a dry atmosphere. The electrical measurement was carried under a constant gas flow of 1 sccm at ambient pressure. For the measurements with 100% relative humidity the synthetic air was passed through a gas wash bottled filled with H\(_2\)O before entering the microprobe station.
12.1. Resistive Switching Performance under Ambient Conditions

We studied the resistive switching based on oxygen anionic-electronic transfer with own fabricated bit structures in cross-plane configuration of two platinum electrodes separated by a SrTiO$_{3-\delta}$ thin film, see Figure 12.1a.

![Figure 12.1](image)

**Figure 12.1:** a) Schematic representation of a single Pt|SrTiO$_{3-\delta}$|Pt memristive bit exposed to humidified air with its corresponding circuit symbol. b) Photograph of the measured sample showing several electrodes for cross-plane electrical measurements including a multi-bit crossbar array. c) Scanning electron microscope image of the thin film cross-section showing the polycrystalline columnar growth during pulsed laser deposition. d) Results of cyclic voltammetry measurements of 200 consecutive cycles with a constant sweep rate of 50 mVs$^{-1}$ show a very stable and robust resistive switching behavior.

Several micro-electrodes are structured onto the sample to characterize the memristive behavior and assure reproducibility of the resistive switching measurements including a close to application multi-bit crossbar array, see **Figure 12.1b**. The scanning electron image of the cross-section of a single bit is shown in **Figure 12.1c**. It reveals good adhesion...
between the Pt electrodes and the oxide film and also a crack-free and dense SrTiO$_{3-\delta}$ film microstructure of 760 nm in thickness. The SrTiO$_{3-\delta}$ film exhibits a typical polycrystalline and columnar microstructure for pulsed laser deposition thin film growth$^{127,179,203}$. The cubic perovskite phase of the thin film was confirmed by X-ray diffraction measurements in accordance to literature$^{176}$, see Supporting Information Figure 22.1.

In a first step, we detail the resistive switching characteristics via cyclic voltammetry under ambient conditions for the Pt|$\text{SrTiO}_{3-\delta}$|Pt bits, Figure 12.1d. We measure hysteretic and bipolar$^8$ I-V profile for constant voltage sweep rates of 50 mVs$^{-1}$ and maximum bias of ±4 V per bit. During the positive voltage sweep the conductivity increases and switches the resistance of the device to a lowered value; viz. the switch is set to ON state for > +2.5 V. Cycling to negative voltages the conductivity decreases again and the Pt|$\text{SrTiO}_{3-\delta}$|Pt bit switches back to its high resistance state; the switch is set to OFF state at < -1.8 V. We obtain a resistance ratio of up to 43 for the hysteresis at +3 V. The corresponding critical electrical field strength of 3.5×10$^6$ Vm$^{-1}$ is in agreement with earlier reports for the anionic-electronic resistive switching material of SrTiO$_{3-\delta}$.$^{27,45,46,49,51,53,63,68}$ The hysteretic I-V profiles for a bias of ±4 V show an asymmetry which is typical for bipolar anionic-electronic switches$^{204}$; i.e. the absolute measured value of $I_{SET}$, defined by the maximum positive current, is up to two orders of magnitudes larger than the absolute value $I_{RESET}$, defined by the highest negative current. The general mechanism discussed in literature explain the observed resistive switching characteristics at ambient through changes of the valence state of the titanium transition metal ion under the high electrical field. In turn, this leads to changes in the oxygen anionic and electronic defect concentration profiles and their mobilities upon bias polarity change, see our earlier work for details.$^{46}$ We demonstrate stable and non-volatile resistive switching stability for more than 200 consecutive cycles, Figure 12.1d. It is interesting to note that the here fabricated Pt|$\text{SrTiO}_{3-\delta}$|Pt resistive switching bits required no preforming step as often found necessary.$^{51}$ After 20 initial cycles during which the switching stabilizes in its set and reset currents, namely $I_{SET}$ and $I_{RESET}$, see Supporting Information Figure 22.2, the structures can be operated with high reproducibility as demonstrated in Figure 12.1d. Furthermore,
we repeat the experiment applying the same bias sweep conditions for five microelectrode sets, denoted as $E1$ to $E5$ in Figure 12.2a, confirming the high reproducibility of bit-device structures processed for the bipolar switches. By the nature of the capacitor like structure of the sample the $I$-$V$ profile is not pinned to the origin, but the zero-crossing of the current is clearly shifted by capacitive contributions. To get a better understanding of this capacitive behavior we carried out cyclic voltammetry measurements with voltages set to ±2 V, which are below the switching threshold voltage for a constant sweep rate of 50 mVs$^{-1}$, see Figure 12.2b-c. Here, the $I$-$V$ profiles show no non-volatile resistive switching, but a similar zero-crossing shift as for voltages of ±4 V. These resulting $I$-$V$ profiles of a slightly distorted circle in clockwise direction correspond to the typical charging and discharging of a capacitor with a parallel resistor in cyclic voltammetry experiments. Based on this experimental evidence we deduce that these capacitive contributions are not linked to the resistive switching mechanism itself. These capacitive contributions fit well to our earlier reported chronoamperometry results and the suggested equivalent circuit models being a memristor in parallel with a capacitor for such devices.$^{46}$

We can conclude from these cyclic voltammetry results in ambient atmosphere that we successfully fabricated Pt|$\text{SrTiO}_3$-$\delta$|Pt bits, which exhibit bipolar resistive switching with memristive and capacitive contributions depending on the applied bias range. This basic electrical characterization of our devices demonstrates the good reproducibility with a high uniformity. Stable resistive switching under constant conditions enabled us now through the following to study the effect of humidity.
Figure 12.2: Uniformity of the device and capacitive contributions: a) Cyclic voltammetry measurements on five different microelectrode sets, E1 to E5, between ±4 V showing uniformity and no differences in switching between the single electrodes. b) and c) Cyclic voltammetry measurements for a bias of ±2 V in log and linear scale, respectively.

12.2. Impact of Humidity on Resistive Switching
To identify the influence of moisture on resistive switching, we examine the effect of relative humidity change on the cyclic voltammetry characteristics of the Pt|SrTiO$_3$|$\delta$|Pt bits. The characteristic resistive switching cyclic voltammetry I-V profile varies systematically with the relative humidity and atmospheric humidity cycles applied (I-VI), see Figure 12.3:

i. Initially, we display the characteristic I-V hysteresis as measured in ambient air for a relative humidity around 40% for the atmosphere cycle (I) of Figure 12.3. The I-V profile is non-volatile with a counterclock-wise switching and characteristic resistance ON and OFF states being in agreement with the I-V profiles of Figure 12.3d.

ii. By exposing to a dry atmosphere, both the shape of the I-V profile and the switching is strongly modified: we observe a change from the original anticlockwise switching to a capacitive hysteresis without crossover; viz. the non-volatile memory characteristic vanishes under dry air (0% relative humidity, atmosphere cycle II, Figure 12.3). The absolute conductivity
increases as expected from theory due to decreased protonic conduction for oxides.\textsuperscript{136}

\textit{iii.} By increasing the relative humidity to 100\% in atmosphere cycle (III) the conductivity strongly increases and a third type of \textit{I-V} profile shape is observable. Here, non-linear fluctuating currents can be observed. Moreover, an \textit{I-V} profile with multiple crossings is measured and no hysteresis behavior is any more observable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.3.png}
\caption{This figure shows five consecutive \textit{I-V} profiles under three different humidity levels: i.) Laboratory air with 35-45\% relative humidity (atmosphere cycle I&VI). ii.) Synthetic air with 0\% relative humidity (atmosphere cycle II&IV). iii.) Humidified synthetic air with 100\% relative humidity (atmosphere cycle III&V). Blue lines show increasing voltage branch and red lines decreasing, respectively. Depending on the humidity level the conductivity and the \textit{I-V} profile shape changes drastically and without humidity no resistive switching is observable. Comparison of the same humidity, e.g. humidity exposure cycles I&VI, shows that this process is fully reversible.}
\end{figure}

We also repeat the experiment applying the same relative atmospheric humidity changes, now measuring the Pt|SrTiO\textsubscript{3.8}|Pt resistive switch response after re-equilibration to dry atmosphere and for subsequent 100\% and 40\% of relative humidity exposure and equilibration, see
atmospheric cycles IV-VI in Figure 12.3. Here, the current-voltage profiles of the resistive switches show clearly the same switching directions and shapes, effective maximum current values and also for the hysteretic profiles comparable $R_{OFF}/R_{ON}$ ratios with respect to the relative humidity exposure after an atmosphere equilibration time of 15 minutes. From this, we conclude that the interactions of the SrTiO$_{3-\delta}$ thin film with moisture and synthetic vs. laboratory air are fully reversible and the bit device structures very robust. Excitingly, the resistive switch response can be fully tuned from a hysteretic current-voltage profile with addressable resistance states for relative humidity levels around 40% (Figure 12.3, atmosphere cycles I&VI) to a capacitive hysteresis without crossover (Figure 12.3, atmosphere cycles II&IV) or almost non-hysteretic $I-V$ profile with multiple crossings (Figure 12.3, atmosphere cycles III&V) for either completely dried or fully moisturized atmosphere. These results indicate that a certain amount of moisture or traces of gases inexistent in synthetic air are required to achieve anionic-electronic resistive switching in the metal-oxide films. The reversibility of the interaction of moisture with the memristance and the stable $I-V$ profiles measured at 100% relative humidity show that a possible water splitting reaction does not take place at the field strengths applied. In accordance to literature\textsuperscript{136}, we observe a decreased relative conductivity of the Pt|$\text{SrTiO}_{3-\delta}$|Pt resistive switch in the fully dried atmosphere, which increases for the 100% relative humidity.
III Influence of Moisture – Results & Discussion

Figure 12.4: a) This figure shows $I_{SET}$ referring to the maximum current at a single I-V profile for the six different measured atmosphere cycles. The higher the relative humidity the higher the conductivity covering a range of four orders of magnitude. b) $I_{RESET}$ referring to the highest negative current at a single I-V profile. c) Ratio of resistance states at +3 V for the different atmosphere cycles showing non-volatile resistive switching solely for intermediate relative humidity levels.

We summarize the absolute switching currents $I_{SET}$ and $I_{RESET}$ for the atmospheric cycles, Figure 12.4a-b. For $I_{SET}$ at ambient conditions (atmosphere cycles I&VI) a value of $1.4 \times 10^{-6}$ A is measured, which corresponds to a current density of 5.6 Am$^{-2}$. At dry conditions (atmosphere cycles II&IV) $I_{SET}$ decreases by ~2 orders of magnitude to $5.5 \times 10^{-8}$ A (resp. 0.22 Am$^{-2}$) and for 100% relative humidity a current as
high as $3.2 \times 10^{-4}$ A (resp. $1.3 \times 10^{3}$ Am$^{-2}$) was recorded. It can be concluded that $I_{SET}$ can vary impressively over 4 orders of magnitude depending of the humidity level at room temperature for electric field strength of $5.5 \times 10^{6}$ Vm$^{-1}$ for the resistive switch. In contrast $I_{RESET}$ is much less sensitive to the humidity than $I_{SET}$ and did not show such a significant difference for ambient ($-1.9 \times 10^{-7}$ A) and dry conditions ($-5.0 \times 10^{-7}$ A). Only at 100% relative humidity a higher current of $-9.3 \times 10^{-5}$ A, similar to the large change for $I_{SET}$ is measured. This might arise from the fact that the conductivity at negative voltage might be defined by the bottom electrode, which is not as exposed to the ambient humidity as the top electrode and therefore shows less sensitivity. The analysis of the resistance states at +3 V for the different atmosphere cycles show that for 40% humidity a resistance ratio of up to 43 was measured and neither for 0% nor 100% relative humidity (ratio $\approx$ 1) resistive switching was observable, see Figure 12.4c.

The results show that moisture indeed plays an important role in anionic-electronic memristive devices and has to be taken into account also in switching models. The interaction of moisture with oxide surfaces and the corresponding reaction mechanism and transport processes are well studied at high temperatures, for details see references\textsuperscript{190,200}, and through this study for ambient at room temperature. Here, the incorporation of water molecules in oxygen vacancies, splitting of water molecules as well as electronic processes play a crucial role. Excitingly, the resistance switch characteristics such as the memristance and its hysteretic current-voltage profile can be fully transferred to predominant capacitive characteristics dependent on humidity exposure.
Figure 12.5: a) Schematic illustration of the interference of moisture with memristance. Water molecules are incorporated into the oxide through oxygen vacancies at the surface. The space charge region and the Schottky barrier is modulated by this adsorption process and interferes with the memristance itself. The I-V profiles get modulated by moisture and vary from a capacitive like behavior (0% rel. humidity) to memristive switching behavior (40% rel. humidity).

Fundamentally, for anionic-electronic resistive switching at moderate temperatures under high electrical fields similar reactions are likely to occur as for high temperature and humidity exposed oxides. In line, it is reasonable that moisture influences the overall electronic structure at the space charge region of the metal|oxide interface, see schematic of Figure 12.5. Here a multi-step electrochemical reaction starts, namely: In a first step, the gas water molecule is absorbed to the Pt|SrTiO$_3$ resistive switch surface. Secondly, the adsorbed hydroxyl group interacts with the oxygen anionic/electronic transfer across the interface and at the space charge region. Finally, the bulk oxygen anionic/electronic migration sets in, altering in dependence to the moisture degree the resistive switching response from either memristive (hysteretic current-voltage profile, 40% rel. humidity) to capacitive (0% rel. humidity). In conclusion, the electronic structure and Schottky barrier is altered by both, the
memristance itself and the interaction of moisture with the oxide, resulting that moisture interferes with the memristance of the oxide.
13 Conclusion

In this work, we successfully fabricated Pt|SrTiO$_{3-δ}$|Pt bits which show stable resistive switching characteristics over 200 cycles under ambient conditions. With a model experiment we demonstrated for the first time that moisture has a strong impact on resistive switching for oxygen anionic-electronic switching metal-oxides such as SrTiO$_3$ being fully reversible. We show that the basic property of memristance is dependent on moisture, which is in line with earlier humidity sensing studies at lower electrical fields. At higher electrical fields not only the overall conductivity changes over ~4 orders of magnitude, but also the $I$-$V$ profile shape, number of crossings and switching capability can be modified with humidity.

In contrast to the measurable memristive behavior at ambient conditions, capacitive contributions and no resistive switching was observable in dry synthetic air which could be turned to a non-hysteretic $I$-$V$ profile with multiple crossings by increasing to 100% relative humidity. This consequently implies an impact on the development of more precise switching models, material studies, as well as for final device geometries. First of all, today's switching models do primarily not consider any effects of moisture, and the surface species interaction with hydroxyl groups from ambient and solely focus on the anionic defects. Here, our experimental results clearly demonstrate that moisture, resulting in formation of hydroxyl groups at oxide material surfaces, has to be taken into account for the development of more precise switching models, materials and their involved charge carriers. We consider the interaction of moisture with the Schottky barrier at the oxide interface as the most likely origin of the interference with the memristance. Secondly the humidity level has to be controlled for material and device studies, e.g. doping of metal-oxides, to get comparable results and to draw correct conclusions from electrical measurements for diffusion models under high electric fields for resistive switch development. Therefore we suggest tracking the humidity level for anionic-electronic resistive switching studies similar to cationic switches.$^{80}$ A capping layer to maintain a constant moisture influence on the oxide and to avoid
switching variations during time or on the device itself arising from changes in humidity during operation might become crucial for anionic-electronic resistive switching devices. Despite the recent advances in the field of oxygen anionic-based switches a breakthrough on industrial scale could not be achieved yet, mainly because of missing control concerning uniformity and variability of the devices. Here, the discussion is so far restricted to microstructure and surface roughness. The impact of moisture on uniformity and variability of metal-oxide ReRAM devices was only rarely considered so far, although it plays a crucial role as we demonstrate for the case of the oxygen anionic-electronic resistive switching material of strontium titanate.

From a fundamental perspective, these results show that moisture cannot be neglected in the development of anionic-electronic resistive switches as hydroxyl interaction seems to be crucial to the basic property of memristance. These new insights on moisture controlling the current-voltage profile transition from classic memristive behavior to a fully capacitive one allows us to formulate future novel device design guidelines to tweak the resistance ratios and their addressable states and to engineer high-performance anionic-electronic resistive switches.
14 Follow-up Chapter III

This chapter briefly summarizes the scientific progress on the topic of Chapter III after publication.

Lübben et al.\textsuperscript{79}, Tsuoroka et al.\textsuperscript{201,207} and Mannequin et al.\textsuperscript{208} studied the influence on humidity on Ta$_2$O$_5$ thin films during resistive switching. As moisture is strongly bound to this oxide Lübben et al.\textsuperscript{79} annealed Pt$|$Ta$_2$O$_5$$|$Pt samples at 650 K in vacuum to remove the bonded water and compared the cyclic voltammetry experiments to the non-annealed samples. Here, they could observe that the Ta$_2$O$_5$ also did not show any resistive switching after removing the bound water and only capacitive behavior, identical to the findings of Chapter III. By exposing the annealed samples again to moisture the devices showed resistive switching again, confirming the reversibility of the process in agreement with the presented findings on SrTiO$_3$ in this thesis.

Additionally Tsuoroka et al.\textsuperscript{207} found drastic changes in cyclic voltammetry experiments on Cu$|$Ta$_2$O$_5$$|$Pt structures for relative humidity levels from 5 to 85%. They identified significant contributions of proton conduction to the ionic transport at higher relative humidity altering the switching properties. This study highlights the importance of water uptake and control also for Ta$_2$O$_5$-based resistive switching device.

Yang et al.\textsuperscript{209} investigated moisture effects on Ag$|$MoO$_{3-x}$$|$fluorine-doped tin oxide (FTO) switching devices based on the electrochemical metallization mechanism with focus on the Ag$|$MoO$_{3-x}$ interface. Here, it was demonstrated that the ambient moisture has a significant effect on the valence change memories like switching behavior. Hydroxyl groups created by ambient moisture exposure facilitated the anodic passivation of the Ag electrode, in which the AgO$_{x/2}$ layer was formed at the Ag/MoO$_{3-x}$. The anodic passivation blocked the Ag$^+$ migration into the films, and then transformed the electrochemical metallization switching into the valence change-like switching through the valence change between Mo$^{6+}$/Mo$^{5+}$ and the AgO$_{x/2}$ layer formation/dissolution.
Qiaonan et al.\textsuperscript{210} studied the influence of humidity on Pt|TiO$_{2-x}$|Pt unipolar resistive switching devices. They observed a similar current increase with higher humidity during cycling voltammetry experiments, indicating an increase of ionic conduction in these devices. Additionally, a bubble formation and electrode delamination during resistive switching in humid environment was observed for these devices attributed to electrochemical reaction forming H$_2$. This delamination process seemed to be independent of the resistive switching process. Nevertheless the authors could not rule out the possibility of a general hydration and incooperation of hydrogen ions into the oxide influencing the electrical and resistive switching properties. As Jameson et al.\textsuperscript{211} showed prior to this work that in TiO$_2$ hydrogen ions play a role in this material system and is even considered to be the dominating species for resistive switching. Such behavior could also be present in SrTiO$_3$-based systems.

Sun et al.\textsuperscript{212} were investigating moisture effects on Pt/Ir|NiO|Pt thin film resistive switching amongst others. In contrast to Ta$_2$O$_5$\textsuperscript{79,207}, TiO$_2$\textsuperscript{210}, MoO$_3$\textsuperscript{x}\textsuperscript{209} and SrTiO$_3$-$\delta$ for NiO no effect on the switching properties induced by moisture was found and only constant R$_{OFF}$/R$_{ON}$ ratios were measured.

Lai et al.\textsuperscript{213} kept the water vapor pressure constant during the electrical characterization of their ZrO$_2$-based resistive switches to exclude the effect of moisture on the switching characteristics as found for SrTiO$_3$ in this thesis.

Di Martino et al.\textsuperscript{214} focused on the formation of filaments in Ag|SiO$_2$|Au electrochemical metallization cells using a nanoparticle-on-mirror geometry to study isolated plasmonic junctions. Here they considered moisture as involved of the counter reaction to the formation of Ag$^+$-ions during switching.

Shang et al.\textsuperscript{215} investigated Cu|Si|Pt electrochemical metallization cells, where reversibly a CuO$_x$ layer formed in atmosphere conditions responsible for the resistive switching. The authors highlight that from a technological point of view the environment effect on resistive switching properties as presented in Chapter III, make it difficult to use as real
memory devices. Here, they see it challenging to incorporate environmental factors like oxygen gas and water molecules in a controlled way making it incompatible with the present semiconductor fabrication process.

Additional to the recent progress on the effect of moisture on resistive switching Saraf et al.\textsuperscript{216} observed similar zero-crossing shift in cyclic voltammetry experiments for Sr(Fe\textsubscript{0.01}Ti\textsubscript{99.99})O\textsubscript{3}-based resistive switching devices as reported in this thesis chapter.

In conclusion, this paper related to this third thesis Chapter has contributed to the discussion in the field as a follow up various valence change materials used as oxides in resistive switches based on Ta\textsubscript{2}O\textsubscript{5},\textsuperscript{79,207,208} MoO\textsubscript{3-x},\textsuperscript{209} TiO\textsubscript{2},\textsuperscript{210} and NiO\textsuperscript{212} have been subjected to electrochemical testing to probe whether the switching is affected by humidity exposure. Here, similar observations as reported in this thesis for SrTiO\textsubscript{3} modulation of resistive switching behavior have been also confirmed to occur for these materials.
IV Memristance Crosses Humidity Sensing

This thesis chapter is planned to be submitted as "When Memristance Crosses the Path with Resistive Humidity Sensing", F. Messerschmitt, M. Jansen, J.L.M Rupp. 2016

Abstract

Resistive switching devices based on oxides have outstanding properties making them a promising candidate to replace today’s transistor-based computer memories as non-volatile valence change memories and can even find future application in neuromorphic computing. Unlike transistors these devices do not solely rely in their function on electrons but depend in their switching characteristics on defect contributions in the oxide film. To date the scientific discussion on valence change-based resistive switching is so far mainly restricted to oxygen vacancy contributions disregarding the role of protonic defects. In this work we study the effect of moisture and protonic contributions upon resistive switching properties by changes in the surface to bulk ratio and oxide surface exposure of the oxide SrTiO₃. For this, we fabricate Pt|SrTiO₃₄|Pt model memory arrays which only differ in their oxide thickness to be close and far from their Debye length and study the role of capping layer on resistive switching with respect to humidity exposure. Here, we find a linear to exponential SET current density dependency when changing the film thickness from 170 nm to 740 nm for the SrTiO₃, whereby the surface to bulk ratio of the oxide is significantly changed. We discuss this behavior in terms of differences in total concentration of oxygen vacancies and their interplay with moisture. From a fundamental point of view we demonstrate the importance of protonic defects beside oxygen vacancies for resistive switching devices. Through this experimental approach we demonstrate that the sensitivity towards moisture in resistive switching devices can be tuned over a wide range. This demonstrated moisture sensitivity raises new challenges to control resistive switching...
but also gives new opportunities as an additional handle to actively tune the switching performance or even exploit it for novel sensing devices.
15 Introduction

Resistive switching devices, often also referred to as memristors\textsuperscript{19}, are a promising alternative to replace today's transistor-based memory technology due to its superior properties like low power consumption, high switching speed, non-volatility and scalability.\textsuperscript{7} Resistive switching devices are even considered to be a crucial part in artificial neural networks and in neuromorphic computing hardware because of their outstanding properties, spike timing dependent plasticity and the capability of multi-level data storage.\textsuperscript{10} These devices consist of a simple metal$|$oxide$|$metal structure, for which in valence change memories the metal-electrodes are selected to be inert, \textit{e.g.} by the choice of platinum.\textsuperscript{8} Here, under high electrical field, typically in the range of $>10^6 \text{ Vm}^{-1}$,\textsuperscript{8,22} the defects become mobile within the metal oxide and are altering the overall resistance state of the device. Despite the exciting switching performances reported in literature there are still many obstacles to overcome like endurance, variability and uniformity issues.\textsuperscript{205} Therefore it is essential to get a better understanding of the resistive switching fundamentals and to unveil the defect chemistry of metal oxide-based thin films under high electrical fields at ambient conditions in detail. In particular the role of defects, \textit{i.e.} oxygen vacancies, protonic species, and electronic carriers within the metal oxide require attention as they define the final resistive switching characteristics. The resistive switching behavior is typically characterized by pinched current-voltage hysteresis measurable in cyclic voltammetry experiments.\textsuperscript{20} Here, changes in the derivative of the current-voltage relation define the state and number of addressable resistances for these non-volatile resistive switching devices.\textsuperscript{9} As such these studies predominantly address the interplay of oxygen vacancies and electronic carriers within the metal-oxide towards resistive switching. However, from a fundamental perspective contributions of protonic defects and their interplay with oxygen vacancies and electronic carriers are only rarely considered. Even though the omnipresence of protonic defects in metal oxide thin films which are either introduced during the fabrication process and handling of the devices or through the reaction of atmospheric species like moisture during operation. Through
this work we therefore focus on bipolar resistive switching valence change memories to study the role of protonic defects to resistive switching and its electric response on strontium titanate.

For this, we fabricate switching devices based on strontium titanate, SrTiO$_3$, which is a well-suited model resistive switching metal oxide. The selected oxide is a mixed conductor with electronic p-type conduction at ambient conditions with a well-known low cation mobility compared to the mobility of oxygen anions in the material.$^{107,108}$ The cubic perovskite crystal structure of SrTiO$_3$ is stable over a wide range of oxygen partial pressure and temperature.$^{99,100}$ Hence, resistance changes due to phase changes of the oxide by local Joule heating induced by the high electrical fields can be ruled out. This is an important aspect since it allows simplifying the mechanistic discussion to the valence change mechanism. The defect chemistry of SrTiO$_3$ especially for high temperatures and low electrical fields is well-established, e.g. we refer here for details to the excellent work of De Souza et al.$^{138}$ and Merkle and Maier$^{109}$. Additionally, there exists many reports in literature pointing out the switching capabilities of SrTiO$_3$ with remarkable ratios of high and low resistance states, $R_{\text{OFF}}/R_{\text{ON}}$, of up to $10^5$$^{54}$, switching speeds of $<100$ ns$^{68}$, retention $>10$ years$^{52}$, endurance of $>10^6$ cycles$^{52}$. Moreover, the wealth of experience in working with SrTiO$_3$ as a transistor gate oxide on a chip$^{148}$ makes its integration into future memory devices highly feasible.

On closer literature inspection it is obvious that the resistive switching mechanism of SrTiO$_3$-based devices was already addressed in numerous experimental and theoretical studies in prior art, we refer here to Waser et al.$^8$ and Menzel et al.$^{68}$. A common view is that positive charged oxygen vacancies are accumulating in locally defined sites through the external electrical field applied forming conductive filaments lowering the overall resistance of the device. By applying the opposite polarity to the device these filaments get partially dissolved again resetting the device back to a high resistance state, which results in bipolar resistive switching. The importance of oxygen vacancy diffusion and oxygen vacancy-based filaments in SrTiO$_3$-based resistive switching devices was shown in electrocoloration$^{189}$, conductive atomic force microscopy$^{62,91}$ and in numerous cyclic voltammetry experiments$^{46,47,52,54,217}$. It should be
mentioned that for SrTiO$_3$ devices these filaments do not give a complete picture of the oxygen vacancy defect chemistry involved in the switching.

A second counteracting mechanism with a reverse bias polarity dependency and slower kinetics$^{72}$ than the filament formation can be triggered either by applying higher electrical fields than necessary for the formation of filaments$^{55,72,91}$ or slower sweeping rates$^{72}$ in cyclic voltammetry experiments.

Despite these fundamental studies, there exist only a few reports examining the defect chemistry, kinetics and additional types of defects such as protonic defects contributing to the resistive switching. For example, electrochemical impedance spectroscopy was applied to measure the impact of electric field strength and to study the defect kinetics in epitaxial SrTiO$_3$ thin films for equilibrium and off-equilibrium states.$^{62,72}$ Very recently, the Memristor-based Cottrell analysis was suggested$^{46}$ which allows to measure and determine oxygen vacancy diffusion constants in dependence of high electrical fields, e.g. constants of up to $3 \times 10^{-15}$ m$^2$s$^{-1}$ and $5.27 \times 10^{-15}$ m$^2$s$^{-1}$ at up to 6 MVm$^{-1}$ were measured for polycrystalline$^{46}$ and amorphous$^{84}$ SrTiO$_3$ at room temperature, respectively. Nevertheless, these established mechanistic discussions on resistive switching in oxide-based valence change devices are only limited to the oxygen vacancy defects in the oxide and even though the cations are considered immobile at the usual switching conditions$^{107,108}$, as mentioned before, additional defects like protonic defects have to be considered as they might influence the resistance changes in these devices. For example, SrTiO$_3$ is a well-known material to be sensitive to vary its charge transport and electrical behavior with respect to atmospheric species like moisture$^{218}$ which also holds for many other resistive switching oxides like e.g. CeO$_2$$^{191,219,220}$, TiO$_2$$^{221}$, BaTiO$_3$$^{222}$, SnO$_2$$^{223}$, etc. This dependency is for example even exploited in resistive humidity sensors where protonic defects are altering the overall conductivity and electrical properties of the oxide.$^{137,195,224}$ Most of such commercial available humidity sensors are based on the impedance change of the oxide upon moisture and operated in the range of 10-95% relative humidity at room temperature up to 400°C with typical response
times of 20-30s.\textsuperscript{225} For an excellent overview on the recent progress of ceramic based humidity sensors we refer to \textsuperscript{225}.

In the sensor literature the defect chemistry including the reaction of SrTiO\textsubscript{3} to humidity changes and role of its protonic defects is well described for small external electrical fields, see for details\textsuperscript{109,200,226}. It was found that the increased conductivity of oxides upon moisture exposure can origin from various conduction mechanisms; Firstly, chemisorbed water molecules on the surface of the oxide can facilitate the proton conduction via the “Grotthuss mechanism” on the surface.\textsuperscript{136,196-200} Depending on the water coverage at the surface additional physisorbed water can increase the conductivity.\textsuperscript{227} The role of the oxides’ surfaces in the incorporation of protons and protonic conduction can also be seen in conductivity changes of metal oxides in dependence of their porosity and grain boundary density.\textsuperscript{135,137} Secondly, the water can be incorporated within the bulk through a hydration reaction increasing the protonic carrier concentration in the oxide. Here water from the gas phase dissociates into a hydroxide ion and a proton.\textsuperscript{109,133,134} Experiments with minor doped iron SrTiO\textsubscript{3} single crystal samples revealed at low electrical fields non-monotonous conductivity changes through the bulk caused by the three defect diffusion equilibrium of holes, protons and oxygen vacancies.\textsuperscript{226,228} These changes in impedance upon moisture exposure in the metal oxide are then exploited in humidity sensors.

Unfortunately, the interaction of the surface with humidity is rarely investigated for resistive switches at high electrical fields and ambient conditions, even though it is known from catalysis that it can severely define (i.) the formation of oxygen defects at surface and bulk, and (ii.) the incorporation of protonic defects into the lattice as third carrier species besides oxygen ions and electrons. Therefore we focus in this study on the protonic contribution to resistive switching and the interplay of moisture from the atmosphere with the resistive switching oxide. In general, such protonic defect contributions are omnipresent for oxide-based resistive switching devices, since it is difficult to fully avoid moisture due to its strong adhesion. For example, chemisorbed water on SrTiO\textsubscript{3} single crystalline samples was reported even for temperatures higher than 550 °C and for a high vacuum atmosphere of 2×10\textsuperscript{-7} bar.\textsuperscript{229}
Moisture is typically present in the fabrication process of resistive switching devices, for example during the photolithography in nanostructuring of the devices.\textsuperscript{215} Additionally, prototype devices in fundamental studies are usually not encapsulated and therefore moisture from the atmosphere can freely interact with the samples during operation at ambient conditions.

The high importance of protonic defects in resistive switching devices was already highlighted by Jameson \textit{et al.}\textsuperscript{211} which even considered protons as the responsible species for resistive switching in TiO$_2$. Very recently it was shown for valence change resistive switches, that at operating conditions present during resistive switching, in particular under high local electrical fields and room temperature, moisture shows to have a direct effect on the electrical properties and the resistive switching characteristics exemplified for SrTiO$_3$.\textsuperscript{74} For example the memristive behavior vanished during cyclic voltammetry experiments in dry atmosphere (H$_2$O < 3ppm) and showed complicated multi-crossing current-voltage curves in humidified atmosphere. The maximum conductivity of the device shifted by 4 orders of magnitude for a change in relative humidity from 0\% to 100\% at room temperature. These results demonstrate first direct implication of the surface dissociation of water on SrTiO$_3$ and interplay with the overall charge balance in the oxide towards oxygen vacancies and electronic carriers. We conclude based on these findings that not only oxygen vacancies but atmospheric effects are interfering with the resistive switching performance and highlight that resistive switching cannot solely be explained by oxygen vacancy kinetics for SrTiO$_3$-based devices which is also supported by other studies on other valence change oxides, \textit{e.g.} on TaO$_2$\textsuperscript{207} and TiO$_2$\textsuperscript{210}. In addition, such dramatic conductivity changes at high electrical fields upon moisture exposure could be interesting for sensing applications.

From these studies the following important points remain unclear which we want to address in this study: i.) Does such protonic lattice incorporation and involved charge balance change the overall bulk charge carrier concentration of the oxide thin film or does it occur particularly at the vicinity of the electrode|oxide interface and therefore alters the space charge region resulting in such changes of the resistive switching
behavior? ii) Where is the precise transition region of relative humidity situated at which the resistive switching property vanishes and solely capacitive behavior of the resistive switching devices is observed? iii) How does the electrical field applied during the resistive switching at ambient conditions interfere with such surface dissociation reaction? iv) Finally, can such parasitic atmosphere sensitivity be controlled for memory application?

In essence, it is desired to understand the detailed mechanism how the moisture is affecting the resistive switching and the exact role of protonic defects interfering with oxygen vacancies at high electrical fields to assure a good and controllable resistive switching performance and possibly even extend the range of application of such structures for novel sensing devices.

To this end we turn to SrTiO$_3$ and design a model experiment by fabricating two sets of resistive switching arrays via pulsed laser deposition, which exclusively differ in their thickness. Therefore we can assure that the total number of defects within the oxide thin films is significantly different as well as the effective surface to bulk ratio without changing the underlying resistive switching mechanism. By choosing thin film layer thickness far away of the Debye length$^{230,231}$ and one close to it we are able to study the influence of the Pt|SrTiO$_3$ interface. Here for the first time we investigate the role of protonic defects towards resistive switching by changing the relative humidity by small increments over a wide range of 0%-80% during cycling voltammetry experiments on oxide based valence change memories. Through this experimental we want to elucidate the precise transition region at which the resistive behavior upon moisture exposure vanishes. In addition these devices have a significant fourfold surface to bulk ratio difference and local electric field strength at the same measurement conditions for the thin set of samples. The oxide layers were not patterned, therefore a direct reaction path of the atmosphere with the bottom electrode can be ruled out for these model device structures. Furthermore, we fabricate a set of Pt|SrTiO$_3$|Pt samples with equivalent oxide thickness but encapsulate the single switching bits by fabricating an additional not patterned SrTiO$_3$ capping layer on top. This allows to study how the electrical field interferes with the moisture
incorporation into the oxide and if the resistive switching can be controlled with such an encapsulation approach for memory application.

We analyze and discuss in detail the resistive switching behavior of these memory arrays with respect to changes in current density, hysteretic $I-V$ behavior, and sensitivity to moisture. Through this approach we are able to demonstrate that the sensitivity upon moisture during resistive switching is highly tunable in oxide-based valence change memories and we elucidate the importance of understanding protonic contributions toward resistive switching mechanism. Ultimately, the results contribute to the understanding on how humidity interacts with the resistive switching material under bias such as by the nature of protonic species coupling at the oxide surface and towards its bulk. In addition, our results imply possibilities of Pt|$\text{SrTiO}_3$|Pt structures to be exploited either as pure highly responsive moisture sensors or combined resistive switching and moisture sensing devices within one simple structure for novel applications in the future.
16 Materials and Methods

16.1. Sample Preparation and Characterization
The resistive switches were fabricated on randomly cut sapphire substrates (Stettler, Switzerland) with a diameter of \( \varnothing = 35 \) mm. The electrodes were fabricated through standard photolithography process in an ISO 4 class cleanroom. Here, AZ nLOF 2070 (1:0.4) negative photoresist (Microchemicals, Germany) was dripped onto the substrate and spun with 4750 rpm for 45 s. The photoresist was then soft baked at 110 °C for 180 s with a rehydration step in air of at least 10 min. Afterwards the electrode pattern was put on by illuminating the photoresist with UV light (constant energy mode of 210 mJ cm\(^{-2}\)) with a mask aligner (Karl-Zeiss MJ3B) through customized designed foil masks (Selba, Switzerland). A post bake by 110 °C for 180 s was applied. In the end the photoresist was developed with MIF 726 developer for 90 s and rinsed in H\(_2\)O. Prior to electrode deposition the patterned substrate was cleaned for 60 s at 100 W in an O\(_2\) plasma asher (Technics Plasma TePla 100 Asher system). The 80 nm thick platinum bottom electrodes with a 5 nm titanium adhesion layer were deposited via electron beam evaporation (Plassys MEB 550). The final lift off was done in acetone. The top electrodes were fabricated alike without deposition of the titanium adhesion layer. The electrodes consisting of the cross points of bottom and top electrode have an area of 500 μm x 500 μm for the samples without a capping layer and 50 μm x 50 μm for samples with a SrTiO\(_3\) capping layer.

For the preparation of the strontium titanate, SrTiO\(_3\), target for the pulsed laser deposition commercial SrTiO\(_3\) (>99.5 %, Aldrich Chemistry) was uniaxial pressed in a \( \varnothing = 3\) cm steel press mold with 140 kN for 150 s. Additionally the green body was isostatically pressed in an oil press for 2 min with 1000 kN. The target was then sintered for 5 h at 1350 °C with a heating/cooling rate of 2 K min\(^{-1}\). The SrTiO\(_3\) thin film layers were deposited via pulsed laser deposition (Surface Advanced PLD technology; KrF excimer laser, 248nm) at 650 °C with a heating rate of 10 K min\(^{-1}\) at a pressure of 0.0267 mbar under a constant oxygen flow. The energy laser density was 0.6 J cm\(^{-2}\) with a deposition frequency of
10 Hz. The thickness of the thin films was measured by profilometer measurements (Dektak XT Advanced profilometer, Bruker) directly after deposition. Additionally was the thickness and microstructure confirmed by taking scanning electron microscopy (LEO 1530, Zeiss) images of cross-sections after electrical characterization with an acceleration voltage of 3 kV. For this, the samples were cleaved by a diamond pen and a 5 nm platinum layer was sputtered on the prepared samples to avoid charging. Additionally were all thin film samples characterized by X-ray diffraction (Bruker, D8, Cu Kα) confirming the cubic perovskite crystal structure of pure SrTiO₃.

16.2. Electrical Characterization under Different Relative Humidity Levels

All electrical measurements were carried out using impedance bridges being a Solatron 1260 and 1287 (Ametek Ultra Precision Technologies), as well as a Gamry Reference 600 (Gamry Instruments). To prevent any permanent damage to the samples a compliance current of 5 mA was set. If not otherwise stated in the manuscript the cyclic voltammetry was done in the voltage range of ±4 V with a constant sweep rate of 50 mV s⁻¹. The microelectrodes were contacted via custom-made platinum contact needles with a diameter of ~20 μm which were positioned by manually controlled micro positioners employing a stereo light microscope (Nikon SMZ 1500). The top electrodes were set as the working electrode and the bottom electrode was set to ground. Every set of electrodes measured was initially stabilized before any further measurements by cycling it 25 times between ±4 V under laboratory conditions where typically a slight decrease in conductivity over cycling was observed before a stable behavior was achieved. This is in agreement with our observations reported earlier, see reference⁴⁶. The measurements were conducted in a closed custom made high vacuum microprobe stations (Everbeeing Taiwan and Electrochemical Materials ETH Zurich Switzerland). The temperature during all measurements was kept constant at 22 °C ±2 °C. The relative humidity inside the vacuum chamber was increased by guiding dry synthetic air (20 % O₂, 80 % N₂, H₂O< 3ppm) through a gas wash bottle containing H₂O before being guided in the chamber. To decrease the relative humidity the synthetic air was directly guided into the chamber,
after changing the moisture level inside the chamber the samples were equilibrated at least for 30 min prior measurements. The relative humidity was measured with an accuracy of ±2% by a humidity sensor (SHT21, Sensirion) placed inside of the chamber. We verified that the changes are induced by the change of humidity and not by other changes in the atmosphere by setting the humidity level to the same value in the synthetic air as present in the laboratory, see Supporting Information Figure 23.2. Here we measured during cyclic voltammetry experiments the exact same behavior for both atmospheres. Therefore effects from other minor gases present in laboratory air can be ruled out and the further discussion can be solely restricted to changes in humidity.
17 Results & Discussion

17.1. Sample Preparation and Structural Characterization
For this work we successfully fabricated two sets of samples which exclusively differ in their thickness with a fourfold surface to bulk ratio difference which allows us to allowing us to gain insights on the bulk contribution on moisture sensitivity of resistive switching devices. We prepared two sets of 2-terminal Pt|SrTiO$_3$|Pt memory arrays where one reveals a low oxide thickness of 170 nm of the oxide close to the Debye length$^{130}$ and the second much larger one with a 4 times increased thickness of 740 nm, see schematic in Figure 17.1a. The prepared thin films have a thickness which prevents undesired direct short circuiting of the devices by pin holes in the thin film structure or interference with the resistive switching of similar macroscopic defects. To study the influence of free surfaces on the exchange with humid atmosphere under high electrical fields on the property of resistive switching we also add a reference sample of equivalent small oxide thickness of 150 nm and engineer a capping layer on top (viz. a second SrTiO$_3$ oxide film of 150 nm), Figure 17.1a. The oxide layers, including the capping layer, were not patterned and have a diameter of 2 cm, therefore a direct reaction path of the atmosphere with the bottom electrode can be ruled out for these model device structures.

We engineer, for this model experiment various electrode configurations on the memory arrays to enable access to each single Pt top electrode of a "switching bit" in the configuration of Pt|SrTiO$_3$|Pt independently on the oxide size and whether a capping layer is employed or not. Here, we keep always the cross-measurement geometry, measuring across the SrTiO$_3$ oxide layer accessing over a bottom Pt electrode and top Pt electrode, denoted by the shorts "BE" and "TE" as electrodes in Figure 17.1b. For this, the metal oxide films were fabricated via pulsed laser deposition (PLD) with the same deposition parameters, only the number of laser shots was varied and consequently similar microstructures of SrTiO$_3$ are expected.$^{127,177}$ This fabrication approach ensures that the sets of samples only differ in their thickness and atmosphere exposure level during the measurements, allowing us to limit the discussion of differences in their
resistive switching behavior to these two factors in the given model experiment.

Figure 17.1: a) Schematic representation of the three sets of SrTiO$_3$ thin film samples to vary the reaction pathways towards humidity during resistive switching experiments. For this, the prime model samples differ in (i.) thickness and (ii.) with variation of the occurrence of the SrTiO$_3$ capping layer for resistive switching measurements carried out with respect to moisture levels. b) Top view optical microscopy images of the three model samples showing the electrode designs with electrode areas of 500$^2$ $\mu$m$^2$ and 25$^2$ $\mu$m$^2$. c) SEM cross-view images of uncapped samples (left & middle) and TEM image of a capped sample (right) showing the polycrystalline columnar microstructure of oxide thin films and stack thereof.
Figure 17.1c shows the scanning electron microscopy images and transmission electron microscopy image for the cross-section of the samples verifying the targeted film thickness of the fabricated devices. The cross-section images confirm a dense equivalent polycrystalline columnar microstructure for all three sets of samples as expected from PLD growth on sapphire substrates. The images were taken after the electrical measurements showing no microstructural change in the oxide and intact electrodes. The cubic perovskite crystal structure of SrTiO₃ with a <111> preferential grain orientation was confirmed for all samples without any additional phases by X-ray diffraction measurements, see Supporting Information Figure 23.1.

17.2. Influence of Oxide Film Thickness and Atmosphere Exposure of Single Bits upon Moisture during Resistive Switching

In the following, we investigate two aspects: i.) the influence of surface to bulk ratio on resistive switching in dependence of the moisture exposure. ii.) the influence of an additional oxide capping layer on resistive switching. For this the relative humidity in the range of 0% to 70% is systematically varied and the resistive switching behavior is measured via cyclic voltammetry for the fabricated Pt|SrTiO₃|Pt memory arrays at room temperature (22 °C).

In Figure 17.2 exemplary cyclic voltammetry results of the samples at 70% relative humidity (in blue) and 5% relative humidity (in yellow) are shown for comparison. It is to be noted from an experimental point of view that we verified that the changes in resistive switching behavior presented in Figure 17.2 are induced solely by the change of humidity and not by other atmospheric species, e.g. CO₂ or CO, by setting the moisture level to the same value, i.e. 42% relative humidity, in the synthetic air as present in the laboratory, see Supporting Information Figure 23.2. Here, we measured similar I-V profiles and conductivities for both atmospheres and therefore the mechanistic discussion in this study can be solely restricted to changes in humidity.

All three sets of samples show at a humidity range >10% typical⁴⁶,⁶⁰,⁷² pinched hysteretic behavior with counter-clockwise bipolar resistive
switching. This means the devices switches at positive polarity from high resistance state to low resistance state and by applying the opposite polarity the devices switch back to the high resistance state resetting the single Pt|SrTiO$_3$|Pt bit. The hysteretic $I$-$V$ profiles for all three sets of samples show an asymmetry as typical for such devices, i.e. at positive bias the SET currents, $I_{\text{SET}}$, are up to 5 orders of magnitude higher than the reset currents, $I_{\text{RESET}}$, at negative bias. For constant experimental conditions the hysteretic behavior of a single bit was stable and showed no degradation over cycling, shown exemplarily by the 10 consecutive cycles for a given condition in Figure 17.2.

![Figure 17.2: Exemplary cyclic voltammetry results of the three sets of samples measured in two extreme moisture exposure levels of 5 and 70% relative humidity. Each dataset shown here includes 10 consecutive cycles indicating low variability in a constant atmosphere in contrast to the strong variation by moisture on the hysteretic behavior.](image)

First we want to analyze the effect of oxide thickness on the exchange reaction with humid atmosphere by comparing the switching behavior of the samples with 170 nm and 740 nm in thickness without a capping layer. Here, the asymmetry for positive and negative bias is more pronounced for the thinner oxide samples (Figure 17.2 middle) independent on the moisture exposure level when compared to the fourfold thicker oxide samples (Figure 17.2 left). We explain this behavior by the enhanced influence of the Schottky barrier and the
suppressed bulk contribution of the thinner sample. The thinner set of samples showed in general a higher current density at positive voltage in the range of \( 1 \text{ Acm}^{-2} \) at +4 V and a lower high resistance to low resistance ratio, indicated by the smaller opening of the hysteresis, compared to the thick sample with a current density between \( 10^{-3} \text{ Acm}^{-2} \) to \( 10^{-6} \text{ Acm}^{-2} \) at +4 V. The threshold SET voltage at which the current increases and the devices switch from their high to its low resistant state is for these cyclic voltammetry conditions for the thin sample at \(~1.3\) V and for the thick sample at \(~2.4\) V which corresponds to an electric field strength of \( 8 \text{ MVm}^{-1} \) and \( 3 \text{ MVm}^{-1} \), respectively. Both sets of samples showed expected\textsuperscript{74,136} higher \( I_{\text{SET}} \) conductivity at increased moisture exposure, but the thinner set of samples is a lot less sensitive to moisture with a current density difference of one order of magnitude for a relative humidity change of 5% to 70% compared to the thick samples changing three orders of magnitude. For low relative humidity in the range of 0%-5% the thick sample showed only capacitive behavior and no resistive switching in accordance to recent studies.\textsuperscript{74,79}

Excitingly in addition to being less sensitive to moisture concerning \( I_{\text{SET}} \) the thin samples did still show hysteretic behavior and the resistive switching was preserved at these low moisture exposure levels in contrast to thick samples. These results show that bipolar resistive switching behavior occurs in SrTiO\(_3\) over a wide range of 5%-70% of relative humidity for thinner oxide films and the drastic changes in resistive switching behavior observed for thick oxide films can be controlled by tuning the oxide film thickness. These differences between the thin and the thick samples concerning their reaction to water exposure shown in Figure 17.2 can be either explained by the important role of the bulk in the resistive switching behavior which suits as an oxygen vacancy reservoir increasing the moisture effect and the incorporation of protonic defects. Additionally the generally higher conductivity of the thin samples could overlay the effects of moisture compared to the thick samples. These findings indicate that metal oxide thin films with a thickness closer to the Debye length are more suitable to suppress the moisture sensitivity for memory applications with the downside of smaller high resistance to low resistance ratio. But to exploit the moisture sensing
behavior with a high sensitivity a minimum film thickness of such Pt|SrTiO$_3$|Pt structures seems to be beneficial as could be shown by the 740 nm thick samples.

Now we turn to the influence of moisture on resistive switching behavior of exposed metal oxide and top electrode to the atmosphere. Therefore we compare the $I$-$V$ profiles of the both set of samples with equivalent thickness and microstructure but one set with Pt|SrTiO$_3$|Pt bits directly exposed to the atmosphere (Figure 17.2 middle) and one where the single bits are covered by an additional SrTiO$_3$ capping layer (Figure 17.2 right). Here, the $I$-$V$ profiles look qualitatively similar and all samples show stable resistive switching in the relative humidity range of 5-70%.

In contrast to the resistive switching bits directly exposed to the atmosphere the samples with a capping layer show no change of resistive switching behavior upon change to the relative humidity conditions in the range of 5%-70%, see Figure 17.2 right. Also after long equilibration times of several days in humid atmosphere did the resistive switching behavior not change of the capped Pt|SrTiO$_3$|Pt devices during cyclic voltammetry experiments. This finding clearly shows that the incorporation of protonic defects into the metal oxide layer is facilitated by the external applied electric field and the diffusion of protonic defects within the SrTiO$_3$ thin film without an external electrical field is in comparison rather slow at room temperature. Furthermore, it shows that by fabricating devices with a capping layer parasitic atmospheric influences can be controlled and avoided for final applications.

The thin capped devices showed similar to the thick samples a lower current density of $\sim 10^{-2}$ Acm$^{-2}$ at +4 V in comparison to the uncapped devices with similar thickness with a current density of 10 Acm$^{-2}$ at +4 V. Therefore, we can conclude that the increased current density observed in this study for thinner oxide films cannot solely be attributed to reduced thickness but also to the atmosphere exposure. It has to be mentioned that the samples with the capping layer were fabricated via standard photolithography process and therefore chemisorbed water and protonic defects within the buried oxide layer are to be expected.\textsuperscript{215,229}
explains why also all capped resistive switching bits showed hysteretic $I$-$V$ profiles in contrast to the thick samples measured in dry atmospheres.

17.3. Sensitivity of SET Current to Moisture Exposure
Now we want to analyze this newly found sensitivity to moisture in dependence of the thickness of the oxide film during cycling voltammetry experiments in more detail. Therefore we systematically varied the relative humidity stepwise over a broad range of 0%-80%. Figure 17.3 shows clearly the drastic change of the SET current density, $I_{\text{SET}}$, at +4 V upon moisture level exposure in dependence of the thickness. Here, the thick samples were very sensitive towards moisture and showed an exponential dependency of $I_{\text{SET}}$ (Figure 17.3a), whereas the thin samples only show a linear increase of $I_{\text{SET}}$ by increasing the relative humidity (Figure 17.3a&b). The samples with a capping layer showed no change in conductivity with respect to humidity for the range of 5% to 60%, see Figure 17.3b. This conductivity sensitivity towards moisture of Pt|SrTiO$_3$|Pt bits presented here were fully reversible and could be measured over several humidity cycles, see Supporting Information Figure 23.3.

These results show that by tuning the oxide film thickness the sensitivity can be suppressed by using oxide layer thickness closer to the Debye length, but also be enhanced by an oxide layer thickness far away of it. This drastic enhancement and reversible change in the $I_{\text{SET}}$ behavior could be potentially exploited in ceramic humidity sensors but as presented in this work also in totally new device hybrids where memory can be stored and the humidity be sensed within single Pt|SrTiO$_3$|Pt resistive switching bits.
Figure 17.3: a) Current at SET voltage of +4 V, $I_{SET}$, for different moisture levels of 740 nm thick sample shows an exponential behavior in contrast to a linear dependency of the 170 nm thick samples. b) $I_{SET}$ of the capped sample with equivalent thickness of 150 nm as reference specimen shows no change with moisture level.

These conductivity values measured at a constant relative humidity are strongly dependent on the measurement conditions during the cyclic voltammetry experiments like the sweep rate, in this work always kept at 50 mVs$^{-1}$, which is an intrinsic property of resistive switching devices.$^{46,68}$ Therefore we also looked in this study into the kinetics of the exchange reaction of moisture and conduct chronoamperometry measurements at +2 V during which we changed the humidity, see Supporting Information Figure 23.3. Here, a faster response time was measured for the 740 nm thick samples, which means the conductivity was increasing faster by increasing the relative humidity compared to recovery time when the relative humidity was decreased again. The measured equilibration time after changing the atmosphere was in the time range of hours whereas in the first minutes a strong increase of conductivity and then a slow decrease of it was observed similar to experiments on single crystals on SrTiO$_3$,$^{226}$ see Supporting Information Figure 23.4. This
non-monotonous behavior can be attributed to the equilibrium of the three defects in diffusion, namely, holes, protons and oxygen vacancies, for the oxide.\textsuperscript{226,228}

17.4. Capacitive Behavior in Dry Conditions
Until now recent resistive switching studies on valence change oxide-based memories could show that in dry atmospheres resistive switching devices can lose their switching capabilities and that protonic defects have an important impact on resistive switching behavior as presented in Figure 17.2 (left). Nevertheless it remained unclear when the transition between resistive switching and pure capacitive behavior takes place. In this work we were able to directly observe this transition at a specific relative humidity level of 5\%, see Figure 17.4. In this particular cyclic voltammetry measurement on a thick 740 nm sample the relative humidity was set to 5\% and the capacitive behavior was measured in the initial cycle, shown in Figure 17.4 (left). During cycling the humidity increased slightly in the chamber below the detection limit of the humidity sensor and the evolution of a slight hysteresis could already be observed. This signifies that already a small amount of water is enough to trigger the resistive switching behavior for this set of samples and the bipolar hysteretic behavior is restored. In addition it demonstrates that our structures under switching conditions show a sensitivity limit towards moisture which is below standard ceramic based humidity sensors, <10\% relative humidity.\textsuperscript{225}
17.5. Reset Behavior as Function of Relative Humidity

It is important to note that not only the set processes at positive bias are affected by moisture induced effects but also the reset process at negative bias is influenced by changes in the relative humidity. Even though the $I_{\text{RESET}}$ dependency upon moisture at $-4 \, \text{V}$ was weaker and more variable as the $I_{\text{SET}}$ during the change of humidity in general an increased $I_{\text{RESET}}$ could be measured in this study at higher relative humidity. But more interestingly the typical non-monotonous conductivity decrease during the resetting is strongly reduced at drier atmospheres, see Figure 17.5. Valov et al.\textsuperscript{79} attributed this feature in cyclic voltammetry experiments to the partially re-oxidation, passivation, of the filaments resulting in a first resistance increase in the device. Our results indicate that this behavior is also strongly interfering with the protonic defects present and not restricted to the discussion of oxygen vacancy filaments. It could even be that not the re-oxidation of filaments but the rearrangement of protonic defects is the source of this relaxation process in the device.
Figure 17.5: Analysis of the reset process in cyclic voltammetry experiments of the 170 nm SrTiO\textsubscript{3} sample without capping layer shows an enhanced reaction for higher relative humidity in this voltage region.

The in this study presented strong dependency of the conductivity of resistive switching devices on the moisture level during the SET and RESET process has severe implications on further research on such devices, on the understanding of the underlying fundamental resistive switching mechanistic as well on final device designs. Figure 17.6 summarizes the interplay of moisture exposure with metal-oxide thin films under high electric fields and its electric behavior. SrTiO\textsubscript{3} thin films with a thickness larger than the Debye length, d<<\lambda_d, react intensive and reversible with moisture exposure. Here, oxygen vacancies from the bulk, which acts as a defect reservoir, contribute either to an increased water incorporation at the Pt|SrTiO\textsubscript{3} interface as hydroxyl species changing the Schottky barrier altering the electric behavior, see Figure 17.6a (i). Potentially these oxygen vacancies from the bulk could also be responsible for an overall increased incorporation of protonic defects within the thin film as depicted in Figure 17.6a (ii). As the thickness is decreased and therefore the effect of the bulk is suppressed the sensitivity upon moisture is strongly decreased. Here, for an oxide film thickness close to the Debye length, d \approx\lambda_d, the water alters the electronic structure at the interface solely and changes reversible the Schottky barrier therein upon moisture exposure, see Figure 17.6b. Such increased incorporation of protonic defects does not take place without an external electric field as could show in this study by introducing a capping layer. Here the total
concentration of protonic defects remains unchanged independent of the moisture exposure.

Such a capping layer could be essential, as for the comparison and control of oxide-based valence change resistive switching devices it is essential to control the atmosphere during experiments and the protonic defects within the metal-oxide thin film. Additionally the presented results show that the resistive switching cannot be purely explained by the interaction of oxygen vacancies with the external electrical field but additionally the interplay with protonic defects has to be taken into consideration in all resistive switching models for such moisture sensitive oxides. As shown in this study by the oxide thickness dependency upon the moisture incorporation reaction can the sensitivity towards humidity be controlled and the overall oxygen vacancy concentration in the bulk plays an important role and defines the protonic contribution during resistive switching. This highly sensitive moisture dependency can be even leveraged for novel device applications where resistive switching and moisture sensing is possible within one single device structure.
Figure 17.6: Schematic overview of the interplay of moisture exposure and the metal-oxide thin film under high electric fields and its electric behavior. 

a) SrTiO$_3$ thin films with a thickness larger than the Debye length, $d \ll \lambda_d$, react reversible with moisture exposure. Here, oxygen vacancies from the bulk, which acts as a defect reservoir, contribute either to an increased water incorporation at the Pt|SrTiO$_3$ interface as hydroxyl species changing the Schottky barrier altering the electric behavior (i). Potentially these oxygen vacancies from the bulk could also be responsible for an overall increased incorporation of protonic defects within the thin film (ii).

b) For an oxide film thickness close to the Debye length, $d \approx \lambda_d$, the water alters the electronic structure at the interface solely and changes the Schottky barrier therein upon moisture exposure.

c) Such increased incorporation of protonic defects does not take place without an external electric field as could show by introducing a capping layer.
18 Conclusion

In this work, we studied the role of protons defects during resistive switching in dependence of oxide film thickness and the influence of free surface on the exchange with humid atmosphere. Therefore we fabricated two sets of Pt|SrTiO₃|Pt resistive switching arrays which exclusively differ in their thickness. By this approach we could assure that the total number of defects within the oxide is significantly different, as well as the surface to bulk ratio without changing the underlying resistive switching mechanism. We studied resistive switching behavior of these model devices in dependence of the relative humidity over a wide range. By this approach we were able to demonstrate how changing the oxide film thickness of resistive switching devices allows to tune the sensitivity upon moisture during resistive switching operation. Furthermore, we fabricated a set of Pt|SrTiO₃|Pt sample with equivalent oxide thickness but encapsulate the single switching bits by fabricating an additional not patterned SrTiO₃ capping layer on top. This allowed us to study how the electrical field interferes with the moisture incorporation into the oxide.

First, we investigated the SET current density sensitivity upon moisture exposure via cyclic voltammetry experiments. Here, an exponential dependency to the exposed moisture level for 740 nm thick samples is found and the SET current density changes 3 orders of magnitude for a relative humidity change from 5% to 70%. In contrast the thinner 170 nm samples show only a linear dependency and a change of one order of magnitude in SET current density. These results show that by tuning the oxide film thickness the sensitivity can be either suppressed, but also be enhanced. This enhancement might even be utilized in new hybrid devices for memory storage and humidity sensing within one single Pt|SrTiO₃|Pt bit. Additionally it is possible by utilizing oxide capping layer to fully suppress the moisture sensitivity in resistive switching devices as experimentally shown in this study. Here, the incorporation reaction is very slow without high electrical fields and therefore show buried memory arrays resistive switching independent of the moisture exposure level.
Secondly, we could observe for the first time the transition of pure capacitive behavior to resistive switching behavior at a relative humidity of 5% demonstrating that only in very dry conditions the resistive switching disappears in such oxide-based valence change memories. This means already a few protonic defects can trigger the resistive switching, but are essential for the underlying switching mechanism in SrTiO$_3$.

Thirdly, also the reset process at negative bias during cycling voltammetry measurements is strongly affected by the moisture exposure level. Here, the non-monotonous conductivity decrease during resetting a Pt|$\text{SrTiO}_3$|Pt bit, usually attributed to a partial re-oxidation of the oxygen vacancies, is strongly reduced at drier atmospheres. Therefore these results indicate that this passivation process is also strongly interfering with the protonic defects present and not solely restricted to oxygen vacancy filaments.

From a fundamental point of view these results demonstrate the importance of protonic defects in the resistive switching mechanism in general which have to be carefully considered in the development of models besides oxygen vacancies. In particular the overall oxygen vacancy concentration in the bulk plays an important role for the incorporation reaction of moisture at high electrical fields and defines the protonic contribution during resistive switching. In essence, by controlling the protonic contributions during resistive switching we have a new handle by hand to improve and tune the resistive switching phenomena in oxide-based valence change memories.
Summary and Outlook

This chapter critically summarizes the findings of this thesis and briefly discusses scientific questions, which were raised during this thesis and remain to be elucidated concerning the fundamental resistive switching mechanisms in valence change memories.

19 General Conclusion

The objective of this project was to gain a better understanding of the fundamental resistive switching mechanisms in valence change memories with the focus on the kinetics of the defect chemistry and charge transport involved during the resistive switching of SrTiO$_3$. By a critical review of resistive switching literature and defect models present, SrTiO$_3$ was considered to be a suitable model material for this study. This resistive switching oxide material is not to be expected to undergo phase transitions at switching conditions, is known for its resistive switching capabilities and is in general already well described concerning its defect chemistry in literature especially for high temperatures and low electrical fields, which allows benefiting from this accessible knowledge for this study.

In this project different 2-terminal Pt|$\text{SrTiO}_3$|$\delta$|Pt multi-bit arrays were successfully fabricated via PLD and standard photolithography processes. A thoroughly characterization by standard material science methods like XRD, SEM and TEM allowed to control the fabrication process and to ensure a proper understanding of the fabricated devices. The experimental results for the Pt|$\text{SrTiO}_3$|$\delta$|Pt bits show reproducible and very stable resistive switching for cyclic voltammetry measurements for $V_{\text{SET,RESET}} = \pm 4 \, \text{V}$ at field strength of $6.5 \times 10^6 \, \text{VM}^{-1}$ for hundreds of cycles. By sweep rate dependent cyclic voltammetry measurements the limitations of this state-of-the-art method to gain further insights into the kinetics of valence change memories are carefully analyzed and
highlighted; e.g. it is impossible to determine materials-dependent limiting currents, equilibrium defect states, or diffusion characteristics as the involved anionic vs. electronic carrier contributions cannot be separated. Therefore, chronoamperometry and bias-dependent activation energy measurements are proposed to the field for gaining complementary insights on material-dependent carrier characteristics for mixed anionic-electronic conducting oxides in resistive switching devices.

In this work the temperature dependence of electric conductivity is investigated and calculated activation energies for a rather unusually wide bias range are determined. These measurements reveal a severe decay of activation energy from 1.4 eV down to 1.16 eV for higher biases and an asymmetry with respect to bias polarization as the Schottky barrier is lowered. Additionally, chronoamperometry measurements are introduced to identify the electric field dependence of the capacitive to memristive regimes of the device. Here, a specific threshold voltage of 1.2 V corresponding to an electric field strength of 1.9×10^6 Vm^{-1} is found for SrTiO$_3$ thin films at which the resistive switching mechanism gets thermodynamically activated at room temperature. Oxide-material characteristic time-constants could be measured for which the memristive current evolution dominates in the device with respect to field strength. Correlating the limiting current to the electric field strength the mixed oxygen anionic-electronic diffusion kinetics were probed via the newly suggested Memristor-based Cottrell analysis. Faster diffusion kinetics at higher electric fields are found with diffusion coefficients ranging from 4×10^{-16} m^2s^{-1} to 3×10^{-15} m^2s^{-1} for a bias increase from 1.2 V to 3.8 V respectively. These new complementary tools were also recently applied to other material systems like amorphous-SrTiO$_3$, CeO$_2$ and WoO$_3$. The authors of these studies highlighted the possibility of an overestimation of the diffusion length, i.e. the resistive switching film thickness. Nevertheless, these newly obtained switching characteristics allow comparing and improving material selection and directly implicate field strength requirements to optimize operation towards enhanced performance specifications for valence-change resistive switching devices.
Resistive switching studies on oxide-based valence change memories focus predominantly on the kinetics of the defect chemistry and charge transport on oxygen anionic or electronic defects involved during the resistive switching. Despite the fact that many of the resistive switching oxides are well-established materials in resistive humidity sensors, hydroxyl or protonic charge carrier contributions are left out of the picture in the field of resistive switching. In general, the impact of moisture on uniformity and variability of metal-oxide ReRAM devices was only rarely considered so far. Therefore, humidification effects on resistive switching devices are discussed in this thesis based on the high stability of the fabricated non-volatile SrTiO$_3$-based device structures.

Here, the impact of relative humidity to the current-voltage profiles during cyclic voltammetry experiments is investigated in detail by systematic exposure to different moisture levels for the first time. In this experimental study, the resistance states, the current-voltage profile and switching capability are strongly affected by the moisture exposure level. In particular it is shown that the overall resistance states of Pt|SrTiO$_{3-x}$|Pt devices are strongly modified by up to four orders of magnitude as well as the device`s current-voltage profile shape, number of crossings and switching capability with the moisture exposure level. It is demonstrated in this work that this moisture sensitivity can be tuned by changing the oxide film thickness and the atmosphere exposure level of the devices. An exponential conductivity change is observed as function of moisture level for thick samples in contrast to a linear dependency for thinner samples. This study attributes the influence of moisture on resistive switching to the changed Schottky barrier by adsorbed surface water molecules and its interplay with the charge transfer of oxygen anionic-electronic charge carriers in the bulk oxide.

Furthermore, a reversible transition is demonstrated for the first time from classic memristive behavior at ambient humidity to a capacitive dominated one in dry atmosphere for which the resistive switching completely vanishes. This memristive dependency as function of relative humidity is fully reversible and was also recently verified for Ta$_2$O$_5$.\textsuperscript{79}
From a fundamental perspective, these new results show that moisture cannot be neglected in the development of anionic-electronic resistive switches as hydroxyl interaction with the oxide layer seems to be crucial to the basic property of memristance. This consequently implies an impact on the development of more precise switching models, material studies, as well as for final device geometries.

In conclusion, the presented thesis has proposed novel tools to analyze on the one hand memristive processes and diffusion kinetics for mixed anionic electronic valence change memories such as by the Memristor based Cottrell analysis, and discusses in detail the role of charge carriers such as hydroxyl species besides classic electronic/oxygen vacancies ones for SrTiO$_3$ resistive switches.

20 Outlook

Despite these findings on the fundamentals of resistive switching on SrTiO$_3$-based valence change devices during this project urgent scientific questions remain unanswered. Therefore an outlook for potential experimental studies is given in the following.

In general the exchange reactions with ambient species, \textit{i.e.} oxygen and water, under high electrical fields remain to be elucidated in more detail. Here $^{18}$O experiments including SIMS measurements could give more insights.\cite{232,233} By exposing the resistive switching device to $^{18}$O atmosphere at different switching conditions the oxygen incorporation reactions with respect of high electrical fields could be studied. Similar experiments with H$_2^{18}$O and/or D$_2$O would be helpful to better understand the protonic contribution towards resistive switching and the reaction of moisture and the resistive switching oxide. Answering the exact incorporation reactions at ambient under high electrical fields could also be helpful to better understand the inherent asymmetry within the Pt$|$SrTiO$_{3-\delta}$|$Pt$ structures and its bipolar switching.
Additionally such isotope experiments could give insights into the discussion on the overestimation of the diffusion length of oxygen vacancies in the proposed Memristor-based Cottrell analysis by assuming the full thin film thickness as discussed in Chapter II and highlighted by other authors.\textsuperscript{84,182-184} Furthermore could be the diffusion length validated by a systematic thickness study on a model resistive switching oxide in combination with the Memristor-based Cottrell analysis.

Answering the question how in detail the derived parameters from chronoamperometry experiments as presented in Chapter II can be interpreted for pulsed experiments and final application conditions a better understanding of the dependency of electrical field strength and switching duration might be helpful in future. Here, it has to be answered if the same switching mechanisms are present for long time scales and during short electrical pulse experiments. This could be achieved by a series of experiments for which the applied bias and the time scales are systematically varied down to the nanosecond range and the resistant states are analyzed in detail. With the ultimate goal to be able to give a general guideline for a given switching device with its specific material switching properties how to operate it concerning resistance state, pulse duration and bias applied.

A question which is closely linked to this matter is the exact electrical field within the oxide during resistive switching. Here, fabricating reference electrodes due to a multilayer approach could be successful. Therefore a multilayer of the switching oxide and thin metal layers as reference electrodes could be deposited \textit{via} PLD in a first step. By employing a shadow mask during the metal depositions the reference electrodes could be fabricated in a way that they only partially extend into the switching oxide. Afterwards these reference electrodes can be made accessible by cutting through the multilayer structure in a diagonal way, for example by focused ion beam (FIB) cutting. Finally, these reference electrodes could make the electrical field within the oxide during resistive switching visible by measuring the different potentials at the reference electrodes \textit{via} c-AFM during resistive switching.
Additionally, the exact temperature in the switching oxide when the high electrical fields are applied remains unclear and how much Joule heating is influencing the resistive switching. Even though it is difficult to experimentally measure the temperature without distorting the device in such a small volume like the switching oxide thin film layer, especially if it only heats up in very confined volume like filaments, this parameter is crucial to give a complete physical description of the resistive switching mechanism. Here, resistive switching experiments over a large range of temperature could give first insights. Additionally in situ experiments measuring the temperature through atomic vibrations might be promising shedding light into this matter. For example near field Raman measurements and mapping the anti-Stokes/Stokes ratio in operando during resistive switching could be a feasible approach.
Appendix

21 Supporting Information Chapter II

21.1. XRD Scan of SrTiO$_{3-\delta}$ Thin Film Samples
Detailed $\theta$-2$\theta$ scan of a reference SrTiO$_{3-\delta}$ thin film sample was recorded and is displayed in Figure 21.1. The pattern shows all characteristic peaks in agreement with reference$^{176}$, indicating the cubic phase and no impurities.

![XRD Scan of SrTiO$_{3-\delta}$ Thin Film Samples](image)

Figure 21.1: XRD $\theta$-2$\theta$ scan of SrTiO$_{3-\delta}$ thin film sample.

21.2. Switching Endurance During Cyclic Voltammetry Experiments
The switching endurance was confirmed for more than 200 consecutive cycles in the cyclic voltammetry measurements as shown in Figure 21.2. The endurance experiments revealed that at latest after 50 consecutive cycles the single bits stabilize. All bits were cycled with a constant sweep rate of 50 mVs$^{-1}$ and $V_{\text{SET,RESET}}$ of $\pm$4 V until a stable $I$-$V$ profile was recorded as an initial electroforming step to set the bit in a stable state before any further electrical characterization was carried out analogue as reported in literature.$^{49,90,167,173}$
Figure 21.2: Change of maximum conductivity per cycle ($\sigma_{SET}$) during cyclic voltammetry with a constant sweep rate of 50 mVs$^{-1}$ and $V_{SET,RESET} \pm 4$ V for 200 cycles shows that after 50 cycles the single bit stabilizes and stable hysteretic I-V profiles are measured.
22 Supporting Information Chapter III

22.1. XRD Scan of SrTiO$_{3.5}$ Thin Film Samples
Detailed θ-2θ scan of the Pt|SrTiO$_{3.5}$|Pt thin film sample verifying the cubic perovskite phase of SrTiO$_3$ according to reference$^{176}$. The two peaks marked with an asterisk can be assigned to the sapphire substrate, additionally verified via XRD scans of the sapphire next to the SrTiO$_3$ thin-film and tilting of the sample.

![XRD scan](image)

Figure 22.1: XRD scan of Pt|SrTiO$_{3.5}$|Pt thin film sample verifying the cubic phase in accordance to reference$^{176}$.

22.2. Switching Endurance
The switching endurance of the Pt| SrTiO$_{3.5}$|Pt bits was studied by 200 consecutive cyclic voltammetry measurements between ±4 V at a constant sweep rate of 50 mV s$^{-1}$, which corresponds to a measurement time >17 h. The switching current I$_{SET}$, defined by the maximum positive current, increases during the initial cycles before the Pt|SrTiO$_{3.5}$|Pt bits stabilize and I$_{SET}$ gets constant, see Figure 22.2a. Therefore, all measured bits in this study were cycled 15 times at least for equilibration before further electrical characterization was carried out. The switching current I$_{RESET}$, defined by the maximum negative current, equilibrates faster than
ISET and shows no strong variation during the endurance experiment, see Figure 22.2b. These endurance results show that any changes of the resistive switching within this cycle range up to 200 cycles do not arise from degradation due to electrical stress.

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23 Supporting Information Chapter IV

23.1. XRD Scan of SrTiO$_{3.5}$ Thin Film Samples
Detailed 0-20 scan of the Pt|SrTiO$_{3.5}$|Pt thin film sample verifying the cubic perovskite phase of SrTiO$_3$ according to reference$^{234}$. The two peaks marked with an asterisk can be assigned to the sapphire substrate, additionally verified via XRD scans of the sapphire next to the SrTiO$_3$ thin-film and tilting of the sample.

![XRD Scan](image)

Figure 23.1: XRD scan of Pt|SrTiO$_{3.5}$|Pt thin film sample verifying the cubic phase in accordance to reference$^{234}$.

23.2. Influence of Minor Gases in Air to Resistive Switching
In this study we varied the relative humidity during the experiments by flushing dry synthetic air (80%N$_2$, 20% O$_2$, H$_2$O < 3 ppm) through a water filled gas wash bottle. For validation of the experimental setup and to rule out any influence of the differences of synthetic air compared to uncontrolled laboratory air we run cyclic voltammetry experiments under identical relative humidity and temperature. The results presented in Figure 23.2 show that the minor differences in atmosphere composition had no impact and therefore all results presented in this work can be attributed to the change in relative humidity during measurements.
Figure 23.2: Exemplary cyclic voltammetry results of the 740 nm thick samples of 10 consecutive cycles at 42% relative humidity measured in uncontrolled laboratory air and moisture synthetic air showing no difference in its resistive switching behavior.

23.3. Response/Recovery Time to Moisture Exposure

In this chronoamperometry experiment at +2 V we changed the relative humidity after equilibration at 10% RH to 85% relative humidity. A fast response in conductivity on the atmosphere change could be measured with a steady slow decrease was observed. By changing the atmosphere back again to dry conditions the conductivity decreased again to its initial value but the recovery process took longer than the response process. The reversibility and the stability of the samples of the interaction with moisture was tested by carrying out several humidity cycles where two consecutive cycles are shown here.
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23.4. Relaxation Behavior after Moisture Exposure
A chronoamperometry long time measurement at +1.8 V shown here shows that the relaxation time of the samples until an equilibrated state is reached after the atmosphere is changed from dry conditions, 10% relative humidity, to a moisturized atmosphere, 50% relative humidity, is >200 minutes. This non-monotonous current evolution can be explained by the three defect diffusion equilibrium of holes, oxygen vacancies and protons similar to observations made in single crystals.  

Figure 23.4: Chronoamperometry measurements by changing the relative humidity from 10% to 50% shows how the conductivity first increases rapidly and then decreases again slowly over time and does not get into an equilibrated state after more than 200 minutes.
Financial Support

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Bibliography

1. Freeman, C. & Louçã, F. *As Time Goes By: From the Industrial Revolutions to the Information Revolution.* (Oxford University Press, 2002).


<table>
<thead>
<tr>
<th>Page</th>
<th>Reference</th>
</tr>
</thead>
</table>


75 Bruchhaus, R. & Waser, R. in *Thin Film Metal-Oxides* (ed Shriram Ramanathan) Ch. 4, 131-167 (2010).


Steinsvik, S. Hydrogen Ion Conduction in Iron-Substituted Strontium Titanate, SrTi$_{1-x}$Fe$_x$O$_{3-x/2}$ $(0 \leq x \leq 0.8)$. *Solid State Ionics* **143**, 103-116 (2001).


219 Ruiz-Trejo, E. & Kilner, J. A. Possible Proton Conduction in Ce$_{0.9}$Gd$_{0.1}$O$_{2-δ}$ Nanoceramics. *Journal of Applied Electrochemistry* **39**, 523-528 (2009).


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Nomenclature

AES: Auger electron spectroscopy
BRS: bipolar resistive switching
cAFM: conductive atomic force microscopy
CBRAM: conductive bridge resistive access memory
cc.: compliance current
c_j: concentration of charge carrier species j
CMOS: complementary metal oxide semiconductor
CPUs: central processing units
CV: cyclic voltammetry
DFT: density functional theory simulation
D_j: chemical diffusion coefficient of species j
D-MATL: department of Materials ETH Zurich
DRAM: dynamic random access memory
EBPVD: electron beam physical vapor deposition
ECM: electro chemical metallization cells
EDX: energy dispersive x-ray spectroscopy
EELS: electron energy loss spectroscopy
F: Faraday constant, 96 485 sAmol$^{-1}$
FeRAM: ferroelectric random access memory
FIB: focused ion beam
FTO: fluorine-doped tin oxide
GPUs: graphics processing units
Hall: Hall measurements
HRS: high resistance state
HRS$_{eq.}$: Equilibrated high resistance state
HR-XPS: micro-beam X-ray photoemission spectroscopy
I: current
$I_{\text{lim}}$: stable equilibrated limiting current
Imp.: impedance spectroscopy
j: diffusion current
LRS: low resistance state
LRS$_{eq.}$: Equilibrated low resistance state
MOSFET: metal oxide semiconductor filled effect transistors
n: number of electrons transferred
PCM: phase change memory
PLD: pulsed laser deposition
q: elementary charge, $1.602 \times 10^{-19}$ C
Raman: Raman spectroscopy
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
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<tbody>
<tr>
<td>ReRAM:</td>
<td>Resistive random access memory</td>
</tr>
<tr>
<td>$R_{\text{OFF}}$:</td>
<td>electrical resistance in the off-state of the device</td>
</tr>
<tr>
<td>$R_{\text{ON}}$:</td>
<td>electrical resistance in the on-state of the device</td>
</tr>
<tr>
<td>RPM:</td>
<td>revolutions per minute</td>
</tr>
<tr>
<td>RT:</td>
<td>room temperature</td>
</tr>
<tr>
<td>SCNAT:</td>
<td>Swiss Academy of Science</td>
</tr>
<tr>
<td>SCS:</td>
<td>Swiss Chemical Society</td>
</tr>
<tr>
<td>SEM:</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS:</td>
<td>secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>SMD:</td>
<td>numerical simulations based on semiconductor with mobile dopants</td>
</tr>
<tr>
<td>SNSF:</td>
<td>Swiss National Science Foundation</td>
</tr>
<tr>
<td>SSEC:</td>
<td>Swiss Society for Food Chemistry</td>
</tr>
<tr>
<td>STM:</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>$t$:</td>
<td>time</td>
</tr>
<tr>
<td>TEM:</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>$U_{\text{RESET}}$:</td>
<td>voltage the device is reset to its HRS</td>
</tr>
<tr>
<td>URS:</td>
<td>unipolar resistive switching</td>
</tr>
<tr>
<td>$U_{\text{SET, min}}$:</td>
<td>minimum switching voltage</td>
</tr>
<tr>
<td>$U_{\text{SET}}$:</td>
<td>voltage the device is set to its LRS</td>
</tr>
<tr>
<td>V:</td>
<td>voltage</td>
</tr>
<tr>
<td>vac.:</td>
<td>oxygen vacancies</td>
</tr>
<tr>
<td>VCM:</td>
<td>valence change mechanism cells</td>
</tr>
<tr>
<td>VP:</td>
<td>voltage Pulse Experiments</td>
</tr>
<tr>
<td>XANES:</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XPS:</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD:</td>
<td>x-ray diffraction spectroscopy</td>
</tr>
<tr>
<td>$\eta_j$:</td>
<td>mobility of charge carrier species j</td>
</tr>
<tr>
<td>$\sigma$:</td>
<td>electrical conductivity</td>
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Publications

1. Messerschmitt, F.; Schmitt R., Nenning A., Rupp J.L.M.,
   “Electrical Probing Techniques for Solid State Resistive Switches: an
   Electrochemist’s Review”,
   *(to be submitted 2016)*

2. Messerschmitt, F.; Sediva, E.; Alec, T.; Rupp J.L.M.,
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   Influence of Doping on Memristance Dynamics”,
   *(to be submitted 2016)*

3. Messerschmitt, F.; Jansen, M.; Rupp, J.L.M.,
   “When Memristance Crosses the Path with Resistive Humidity
   Sensing”,
   *(to be submitted 2016)*

4. Kubicek, M.; Schmitt, R.; Messerschmitt, F.; Rupp, J.L.M.,
   „Uncovering Two Competing Switching Mechanisms for Epitaxial
   and Ultra-Thin Strontium Titanate-Based Resistive Switching Bits”,
   *ACS Nano, 9, 11, 10737 (2015)*

5. Messerschmitt, F.; Kubicek, M.; Rupp, J.L.M.,
   „How does Moisture affect the Physical Property of Memristance for
   Anionic-Electronic Resistive Switching Memories?”,
   *Advanced Functional Materials, 25, 32, 5117 (2015)*

6. Messerschmitt, F.; Kubicek, M.; Schweiger S.; Rupp, J.L.M.,
   „Memristor Kinetics and Diffusion Characteristics for Mixed
   Anionic-Electronic SrTiO$_{3.8}$: The Memristor-based Cottrell Analysis
   Connecting Material to Device Performance”,
   *Advanced Functional Materials, 24, 47, 7448 (2014)*

7. Schweiger, S.; Kubicek, M.; Messerschmitt, F.; Murer, C.; Rupp,
   J.L.M., „A Micro-Dot Multilayer Oxide Device: Let’s Tune the
   Strain-Ionic Transport Interaction”,
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Patents


Conference Contributions


- Messerschmitt, F; Kubicek, M; Jansen, M; Rupp, J.L.M., „Resistive switching in SrTi$_x$Fe$_{1-x}$O$_3$ Solid Solution Thin Films: The influence of doping on memristance dynamics”, E-MRS Spring Meeting, Lille, France Poster 05/2016
• Messerschmitt F; Schmitt, R; Schweiger S.; Sediva E; Korobko R.; Rupp J.L.M, „Oxide-based Resistive Switches: Understanding Fundamentals to Design new Device Concepts”, 
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  Invited Oral Presentation

• Messerschmitt, F; Kubicek, M; Rupp, J.L.M., “How does Moisture affect the Physical Property of Memristance for Anionic-Electronic Resistive Switching Memories?”, 
  *MRS Fall Meeting, Boston, USA*
  Poster

• Messerschmitt, F; Kubicek, M; Rupp, J.L.M., „How does Moisture affect the Physical Property of Memristance for Anionic-Electronic Resistive Switching Memories?”, 
  *Advances in ReRAM: Materials & Interfaces, Chania, Crete, Greece*
  Oral Presentation

• Messerschmitt, F; Kubicek, M; Schweiger, S.; Rupp, J.L.M., „Memristor Kinetics and Diffusion Characteristics for Mixed Anionic-Electronic SrTiO$_{3-\delta}$ Bits: The Memristor-Based Cottrell Analysis Connecting Material to Device Performance”, 
  *MRS Fall Meeting, Boston, USA*
  Oral Presentation

• Messerschmitt, F; Kubicek, M; Schweiger, S.; Rupp, J.L.M., “ReRAM the Next Generation of Memory: Connecting Material Properties to Device Performance”, *Industry Day 2014, Zürich, Switzerland* Poster

• Messerschmitt, F; Kubicek, M; Ezbiri, M; Fompeyrine, J.; Marchiori, C.; Rupp, J.L.M., “Chronoamperometry: a tool to test new resistive oxide materials towards switching voltages and switching kinetics”, *E-MRS Spring Meeting, Lille, France* Oral Presentation

• Messerschmitt, F; Kubicek, M; Schweiger, S.; Rupp, J.L.M., „Resistive switching in SrTi$_x$Fe$_{1-x}$O$_3$ Solid Solution Thin Films: Chronoamperometry as new Tool to Describe Defect Kinetics in Memristive Systems”, *E-MRS Spring Meeting, Lille, France* Oral Presentation
Supervised Students

Tibor Alec, “The Effect of Iron Doping on the Electrical Behavior of SrTiO$_{3-\delta}$ Memristive Thin Films”
*Master Project I* 03/2016 (3 months)

Maximilian Jansen, ”The Effect of Humidity on the Electrical Behavior of SrTiO$_3$ Thin Films for Memristor Application”
*Master Project I* 08/2015 (3 months)

*Master Project I* 11/2014 (3 months)

Miriam Ezbiri, “Electric transport of epitaxial and heterostructured SrTiO$_3$ films for non-volatile information logics”
*Master Thesis*, supervised with Abel S., Fompeyrine J. and Machiori C. 01/2014 (6 months)

Mathias Steinacher, “Electrical Characterization of Strontium Iron Oxide Pulsed Laser Deposition Thin Films for Potential ReRAM Applications”
*Master Project I* 02/2013 (3 months)

Jan Aeschlimann, “Electrical Characterization of Strontium Titanate Pulsed Laser Deposition Thin Films for Potential ReRAM Applications”
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