Memristive Systems Based on Metal Oxide Nanowires

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ABSTRACT

The digitalisation in the present day and age has lead to a tremendous boost of the development and engineering of nanosized components for computer technologies. The demand for new approaches which are able to go beyond the von Neumann bottleneck has furthermore become an important key factor for big data processing and artificial neural network. Memristor (portmanteau of memory and resistor) devices are thereby deemed possible candidates to overcome the von Neumann bottleneck, which has opened up a new, large research field. In this work, two different memristive systems based on metal oxide materials are demonstrated and the emulation of important synaptic functions are presented.

In order to understand the different memristive systems, typical memristive phenomena, i.e., unipolar, bipolar, and complementary switching are discussed at first, including the physical processes within the material and the fundamental driving forces. The memristive devices of this work are based on metal/insulator/metal (MIM) architectures with TiO$_2$ and Nb$_3$O$_7$(OH) as memristive material models. Hydrothermally grown TiO$_2$ nanowires are vertically standing on a fluorine doped tin oxide (FTO) substrate and are investigated by a self-built electrical characterization setup. The devices show a current-voltage behavior atypical for memristive devices, which can not be attributed to one of the known switching mechanism directly. It is rather assigned to a combination of electric field and temperature gradients competing against an increasing concentration gradient of n-type oxygen vacancies. Time-dependent decay measurements of different resistance states affirm the oxygen vacancy accumulation and redistribution model and show lifetimes of few seconds to up to 20 min. Accordingly, these findings are used to mimic the short- to long-term memory transition of the human brain, which is linked to the plasticity of the biological synapses. Additional important synaptic functions like the spike-rate dependent plasticity, paired-pulse facilitation, and excitatory postsynaptic currents could be emulated in a second step, which paves the way for building artificial synapses based on the TiO$_2$ nanowires.

Finally, the switching behavior of hydrothermally grown Nb$_3$O$_7$(OH) nanowire memristive devices is compared to the previous material system. Nb$_3$O$_7$(OH) nanowires show a complementary resistive switching (CRS) behavior, which is explained by the oxygen vacancy migration model for resistive switching in a similar approach to the previous considerations. An oxygen plasma treatment is used to verify the influence of the oxygen vacancies on the memristive switching behavior by reducing the vacancy concentration. Additionally, the destructive readout current common for CRS cells is demonstrated and the tunability of the
destruction time of a resistance state is established by choosing suitable voltage amplitude and duration. However, particular differences of the \( \text{Nb}_3\text{O}_7(\text{OH}) \) defect structure compared to \( \text{TiO}_2 \) lead to a somewhat different switching behavior, underlining the great impact of crystallographic defects on the memristive switching mechanism.

Altogether, we were able to deepen the understanding of memristive switching properties in different materials and configurations which allows to advance the field of memristive systems towards the development of artificial synapses.
ZUSAMMENFASSUNG


Insgesamt konnten wir das Verständnis von memristiven Schalteigenschaften erweitern, indem verschiedene Materialien und Konfigurationen verwendet wurden. Dies erlaubt es das Gebiet von memristiven System in Richtung künstliche Synapse voranzutreiben.
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1. Introduction

Memristive devices are indispensable nowadays when thinking about artificial intelligence and neuromorphic computing, where efficient signal processing on a small area is essential to process big data sets [1]. The memristor was first theoretically described by L. Chua in 1971 [2], as the fourth missing basic circuit element, adding to the three fundamental elements resistor, capacitor, and inductor. In 2008, 37 years later, the research group around Stanley Williams announced to have found an experimental demonstration of the missing memristor [3]. This started a controversy, whether the ideal memristor described by Chua has really been found or not [4]. It has been shown that, by now, this is indeed not the case and any as memristor labeled real device does not fulfill the requirements for the ideal memristor described by Chua [5, 6]. Y. Pershin and M. di Ventra [6] have therefore developed a test to check if the device is really an ideal memristor and found, that to date none of the presented devices can pass this test. The experimentally demonstrated devices with similar memristor functionalities are therefore commonly named memristive devices, systems, or elements. The rather new research field of memristive elements has expanded quite fast since 2008 [7], which is mainly driven by the demand for alternative computing technologies, going beyond the limited von Neumann architectures. The von Neumann technology is based on separated memory and computation units. A central processing unit (CPU) is responsible for computation (arithmetic logic unit) and for data transfer (control unit) from and to the storage unit (random-access memory(RAM)), which limits the speed and scalability of this conventional technology [8]. Memristive devices have shown great potential to overcome these limitations by enabling parallel and analog computing with a local memory and are called memristor processing units (MPU) [9]. The memristive material is manufactured in a crossbar array structure, where, for example, the inputs are connected to the rows of the array and the outputs are connected to the columns [10–14]. Furthermore, this architecture is applicable for the realization of artificial neural networks (ANNs) [1, 15–18] and, as a special case of ANNs, for pattern recognition [19, 20]. The role of the memristive materials in the ANN is emulating an artificial synapse to connect artificial neurons [21–27] or to operate as artificial neuron itself, called neuristor [28]. Not only researchers from all over the world are interested in this new development, but also large computer technology companies like Hewlett-Packard Enterprise, Samsung, International Business Machines Corporation (IBM), and Toshiba are aware of the potential of memristive devices for in-memory computing systems and neural
networks [29].

Moreover, memristive devices can be utilized in neuroscience to speed-up human brain simulations. In the European ‘Human Brain Project’ (HBP) neuroscientists, doctors, computer scientists, physicists, and mathematician from a total of 23 countries are working together on creating a virtual brain [30]. It started in 2013 and aims to emulate biological processes of the human brain to gain an overall better understanding, but also to compare a vital human brain to a diseased brain, which could help to develop and potentially test medicine [31]. Several approaches like the BrainScaleS project from Heidelberg [32], the SpiNNaker technology from Manchester [33], both being part of the HBP, are working on the realization of a simulation platform for the human brain. The recent approaches are all based on conventional computer technologies, whereas of course manycore supercomputer architectures are designed to realize the massive information processes. However, such machines require about 100 kW power, while memristive devices could enable energy efficient computation in a several watt regime [34, 35]. Nevertheless, not every two terminal system showing a memristive behavior is suitable for the neuromorphic computing approach as pointed out by Di Ventra and Pershin [36], and Islam et al. [37]. Beside a salable parallel architecture, sufficiently long durability, a low sample-to-sample variation, and high stability against variations of the environment are requirements for memristive elements intended for neuromorphic computing systems.

To build memristive devices, different approaches have been developed so far. Typical systems are phase change memories (PCM), electrochemical metallization memories (ECM), redox-based valence change memories (VCM), and thermochemical memories (TCM), which are found in metal oxide [38, 39], organic [40–42], but also perovskite materials [43, 44]. PCMs change rapidly between an amorphous and crystalline phase, having a different conductivity each, and are mostly found in chalcogenides and antimony compounds [45]. In ECM cells, an electrochemically active electrode, e.g. silver (Ag), and an inert counter electrode, e.g. platinum (Pt), sandwiches a host insulator (i.e. SiO$_2$, GeS) [46]. An applied voltage oxidizes Ag$^+$ ions which then drift to the counter electrode and form a highly conductive silver filament [47]. This process is reversible by applying the opposite voltage and dissolve the filament. In TCM cells local Joule heating effects lead to a variation of the stoichiometry, which leads to a change of the the resistance of the materials, which is most likely ZrO$_x$, TiO$_x$, CoO, CuO, NiO [38, 48, 49]. VCMs are oxide materials, like TiO$_x$, TaO$_x$, HfO$_x$, Nb$_3$O$_7$(OH), which are based on the migration of most likely n-type oxygen vacancies (O$_{vac}$) due to an applied electric field [50, 51]. Thereby, either an interface-type switching (often also called area-switching), where O$_{vac}$ assemble at the electrode interface, or a growth of a conductive filament of O$_{vac}$ through the device leads to a change in the conductivity. The resistive switching mechanism is typically tested by current-voltage measurements, which can result in either unipolar, bipolar, or complementary resistive switching (URS, BRS, and CRS, respectively). Unipolar switching, occurring in TCM cells, is only current dependent
and therefore, just one voltage polarity is necessary to observe switching. For bipolar and complementary switching a polarity change of the applied voltage is necessary to switch between two states.

In this work however, a metastable resistive switching (MRS) states for the TiO$_2$ nanowire arrays is observed, where the resistance state degrade over time. Diffusive resistance states can occur in VCM, TCM, and ECM cells [52–55]. The relaxation process, as found here for TiO$_x$ nanowire arrays, is attributed to a concentration gradient and electromotive force driven redistribution of oxygen vacancies [56, 57]. A clear dependence of the oxygen vacancy density, the voltage amplitude, and pulse duration on the lifetime of the states has been found here. Fitting the decay dynamic by Kohlrausch’s equation provides the respective lifetime of the resistance states, which is a common method for ion redistribution mechanism [58–60]. The lifetimes show parameters rang between milliseconds to several minutes, which is similar to the memory function of biological synapses. Additional important synaptic functions, i.e. the spike-rate dependent plasticity (SRDP), paired pulse facilitation (PPF) and excitatory postsynaptic currents (EPSC) [61], are demonstrated with the TiO$_x$ nanowires, showing the possibility for them to be used as artificial synapses.

For comparison, a different metal oxide compound is presented. Single Nb$_3$O$_7$(OH) nanowires are investigated regarding their memristive behavior. Nb$_3$O$_7$(OH) is quite a similar material to TiO$_2$ and is also often used for dye-sensitized solar cell applications, or as active material for photo-catalytic water splitting [62–71]. It has furthermore shown promising memristive switching behaviors [72] and are therefore been chosen as alternative metal oxide system. However, the present single Nb$_3$O$_7$(OH) nanowires show a CRS behavior, which has been observed before in NbO$_2$ layers [72]. CRS devices typically face the problem of a destructive readout process. The readout procedure results in a destruction of the resistance state, so that the state needs to be rewritten afterwards. We have found, that it is of quite importance to figure out the perfect readout voltage and polarity, as an asymmetric distribution of the defects result in a slower or faster readout destruction. However, it could be demonstrated, that the O$_{vac}$ migration model can be adapted from TiO$_x$ nanowires to Nb$_3$O$_7$(OH) nanowires. Yet, the different crystal structure and defect arrangement lead to a different type of switching behavior, which will be discussed in Section 5 and Section 6.
Background

I briefly want to introduce the origin and the interesting development of this topic, which will additionally provide literature recommendations to gain a deeper background of the dealt materials.

TiO$_2$ is a widely investigated material due to its multiple advantageous properties like a high chemical stability, non-toxicity, and various alterable electric and optoelectronic features [73–75]. In the form of nanostructure it is utilized as white pigment in paints, toothpastes, sun milks, food, etc. [76, 77] whereas it furthermore shows great potential in photocatalytic activities [66, 67, 78], sensing possibilities [79–81], as UV detector applications [82], super-capacitors [83], light-emitting diodes (LEDs) [84], hybrid solar cells [85–87] and many more. It can be manufactured in different forms like thin-films, nanowires, nanotubes, with the different crystal structures rutile, anatase, brookite, and amorphous, and can be produced on various substrates (f.e. FTO, TiO$_2$ single crystal) [88–90]. Furthermore, its functional properties can be influenced by appropriate defect engineering like post-annealing processes, plasma treatments, acid etching, ultra violet (UV) treatment, doping, and more [91–95]. In our research group however, a lot of work on manufacturing methods, defect engineering, understanding crystal growth mechanism, and investigating their electronic and optoelectronic properties has been done. Eugen Zimmermann, for example, built an atmospheric pressure - spatial atomic layer deposition (AP-SALD) setup for controlled TiO$_2$ thin-film layer growth with additional Sn doping possibilities as part of his PhD project [96]. Julian Kalb investigated the hydrothermal growth method of TiO$_2$ nanowires itself in detail, studied the growth on different substrates, and developed position controlled growth methods [90]. Not to forget the intense studies on TiO$_2$ thin films and nanostructures, including defect engineering and atomic structure regulation, for hybrid solar cell applications by Philipp Ehrenreich [97], Jonas Weickert [98], Haijan Sun [99], and James Dorman [100]. With the background of all these remarkable results, the aim of this work has been to develop a controlled defect engineering process and study its impact on the electronic and optoelectronic properties.

Therefore, the two metal oxides TiO$_2$ and Nb$_3$O$_7$(OH) nanowires are utilized as material model.

We started with the investigation of different post-annealing treatment of TiO$_2$ nanorod arrays in various atmospheres, to influence the defect density and arrangement of oxygen vacancies. Our findings about its impact on the conductivity of the materials are summarized in the bachelor work of Elise Sirotti [101] and Domenik Vögel [102]. Furthermore, as TiO$_2$ is the most popular candidate for electron transport layers in dye sensitized solar cell (DSC)
devices, the differently treated NRAs are studied regarding the impact on the DSC behaviors in a joint work, together with Maximilian Brochnow [103] and Charline Cuenot [104]. In all those works, one will find the later shown hystereses of the current-voltage measurements for the pristine, as-synthesized TiO$_2$ nanorod arrays. As no one of our group has seen such a behavior before, an explanation for the phenomena had to be found. Therefore, I did a great, extensive literature study and found the solution to the mystery: the memristor. As the devices show this fascinating metastable resistive switching behavior, we decided to proceed studies on the memristive devices in combination with the initial aim. Accordingly, the defect density controlled by the growth temperature is studied by means of the memristive behavior of the NRAs and compared to another metal oxide compound Nb$_3$O$_7$(OH), all summarized in this work. A great overview on the crystal structure, impacts on doping, etc. is given for TiO$_2$ in the afore mentioned works. For Nb$_3$O$_7$(OH) the works of Sophia Betzler [105–107] and Thomas Gänsler ([108], in preparation) are recommended.
2. Memristive Systems

A memristor is a two terminal metal/insulator/metal (MIM) device, which changes its resistance due to an applied electric field and is able to keep (memorize) this state. The scope of this chapter is to provide the theoretical background of ideal memristors, and the extension for real memristive systems and devices. The physical picture, which has been established over several years and experimentally proven for the respective devices, is shown and discussed in detail. Therefore, the nature of resistive switching in real devices is introduced, whereas the main focus lays on redox-based switching devices. The devices are then analyzed by simple current-voltage (I-V) measurements, which can result in different behaviors depending on the switching nature. Three forms of switching curves have been observed so far, i.e. unipolar, bipolar, and complementary resistive switching. Another type named metastable switching has been observed in this work, which is related to the volatility of the system, i.e. the resistance loss over time. Therefore, the theory for common relaxation processes in dielectric materials is described in the time-domain and examples of the literature are given. A full, detailed description and overview of all the switching types, mechanism, and recent findings can be further found in [38] and [109].
2.1. The Ideal Memistor, Memristive Systems and Devices

The first theoretical description of an ideal memristor was given by Leon Chua in 1971 [2] and was claimed as the fourth missing circuit element. It relates the voltage to the current similar to a resistor, but in a non-linear regime. Since the resistance change is non-volatile, the device ‘memorizes’, which is giving it the name memristor (memory - resistor). Chua also invented the electronic symbol for memristors, which is shown in Figure 1. It is commonly used as electronic symbol in integrated circuit diagrams in, for example, nanocrossbar array diagrams [11, 110], memristor based computer unit (MPU) diagrams [111], and all kinds of neuronal network diagrams [112–114].

Figure 1: **Electronic symbol of memristors.** The symbol has been invented by L. Chua in 1971 [2] and has since then been used in the memristor community.

In electrical devices the current is defined as the amount of charges per time

\[ I(t) = \frac{dQ}{dt}, \]  

whereas the time dependence of the voltage is given by the change of the magnetic flux per time

\[ U(t) = \frac{d\Phi}{dt}. \]  

This results in the equations for the fundamental circuit elements resistor, capacitor, and inductor, as well as the completion by the memristor equation, which are given in Table 1. The memristance \( M \) results in a hysteresis in current-voltage (I-V) measurements, since the resistance is sustainably changed upon applying a bias. The dependence is given by

\[ U(t) = M(q(t))I(t). \]  

<table>
<thead>
<tr>
<th>Electrical Voltage</th>
<th>Electrical Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistors: ( R = \frac{dU}{dt} = \frac{d\Phi}{dq} )</td>
<td>Capacitors: ( \frac{1}{C} = \frac{dU}{dq} = \frac{d\Phi}{dq} )</td>
</tr>
<tr>
<td>Inductors: ( L = \frac{d\Phi}{dt} = \frac{d\Phi}{dq} )</td>
<td>Memristors: ( M = \frac{d\Phi}{dq} )</td>
</tr>
</tbody>
</table>

Table 1: **Equations for the circuit elements.** The memristor equation completes the three fundamental electrical equations for the resistor, capacitor, and inductor. It is therefore often considered as the fourth missing circuit element.
For a linear dependence, the memristance $M(q(t))$ is equal to a resistor. Otherwise, two criteria constitute ideal memristors, which are on the one hand, that the area of the loop of the hysteresis has to decrease for increasing sweep frequencies and becomes linear for infinite sweeping speed approaches. On the other hand, the hysteresis has to be pinched at zero applied bias while sweeping. Those requirements are often used to verify real devices as memristor [115]. The non-volatility of memristors make them therefore promising candidates for data storage (resistive random access memory (ReRAM)) devices, where two different resistance states can be chosen to represent a bit, which can be 'ON' or 'OFF' (1 or 0, respectively). However, it has been shown, that real resistive switching devices can not be ideal memristors, wherefore they are often classified as memristive systems or memristive devices. The problem is, that the theoretical description of an ideal memristor violates the Landauer principle in real devices [116]. The Landauer principle is formulated for digital computing and claims, that every computing machine generates heat in the order of $kT$ per writing cycle [117]. Therefore, a generalized description of two-terminal devices, which change their resistance on an applied bias or a current flux is developed. It has been shown, that the dynamical system approach is well suited [34]. Dynamical systems, in reference to memristive devices, are described by the two equations

$$I = G(x, V, t) \cdot V \quad (4)$$

$$\dot{x} = f(x, V, t) \quad (5)$$

for a voltage-driven memristive system with the inverse memristance $G(x, V, t) = M(q(t))^{-1}$. The variable $x$ describes the state of the system, whereat for the special case of an ideal memristor $x = q(t)$. It is found, that in such real devices the state of the system depends on different variables, such as the flowed charge, the self-induced temperature, moving ions/species, chemical reactions, phase transitions, and/or gaps between electrodes and filaments. The general form of the mathematical model (Equation (4) and (5)) allows different types of hysteresis loops, like loops of the form of an horizontal '8' with the crossing at (0,0), or other self-crossing loops, as well as non-pinched hysteresis loops. Although a pinched hysteresis loop is referred to as the fingerprint of a memristive system [5, 34, 118], a theoretical description of non-pinched loops [119], as well as experimental results [120] have been found in 2013 and 2014, respectively. However, the multiple possibilities of the general memristive system equations gives multiple simulation possibilities for the measured I-V data. The generalization needs therefore to be specified for each investigated material and device. The interpretation of the I-V data without knowledge of the actual internal device physics is quite impossible. Since it is rather difficult to know the exact physical behavior, a so-called gray-box method is used, knowing some features of the dynamics and combining those with the observed I-V hysteresis [121]. With this method, many physical effects resulting in a memristive resistance change like phase change memories (PCM) [45, 122, 123], electrochemical
metallization (ECM) [46, 55, 124], valence change memory (VCM) [125–127], and thermochemical memory (TCM) [50, 128] have been described and studied quite well nowadays. However, the switching mechanism has to be investigated not only for the material type, but also by the device structure, since differences of the switching mechanism has been observed for thin films and nanostructures of the same material. However, switching is mostly attributed to oxygen vacancy movement, anion movement, as well as interface changes, which is discussed in the next parts.

2.2. Point Defects and Ionic Motion in Metal Oxide Memristive Devices

The electronic conductivity of metal oxide semiconductors can be influenced by suitable device engineering, which is done by the chemical introduction of dopants during the preparation process, or by creating point defects like atomic interstitials or vacancies [69, 129, 130]. In metal oxides, oxide or cation (metal) interstitials or vacancies are possible, whereas oxygen interstitials are energetically unfavorable, due to their large size. The defect density can be influenced by the preparation/growth process of the film or nanostructure, but also by post treatments like, for example, annealing at high temperatures in different atmospheres [94], or oxygen plasma treatments [131]. In many metal oxide memristive devices, oxygen vacancies are the main species to obtain resistive switching. Upon growth or defect engineering, oxygen vacancies tend to accumulate along existing grain boundaries (lattice defects, i.e. sequence of edge dislocations) or interfaces/surfaces [132, 133]. Otherwise, when the concentration is high enough, oxygen vacancies can agglomerate and form oxygen deficient Magnéli phases $\text{T}_n\text{O}_{2n-1}$. The removal of oxygen from the material into the atmosphere leaves two electrons behind, so that oxygen vacancies act as n-type dopant. Therefore, oxygen vacancies increase the conductivity of n-type metal oxides (in p-type conductors the conductivity is mostly reduced by increasing oxygen vacancy concentration [126]).

However, those oxygen vacancies are now able to migrate on a few nanometer scale through the material. It has been found, that thermally activated oxygen ions can hop to an empty nearest neighbor site due to Brownian motion. The diffusion term is given by

$$D_i = D_0 \exp \left( \frac{-E_A}{k_B T} \right)$$

with the temperature $T$, the Boltzman factor $k_B$, activation energy $E_A$, and the maximum diffusion coefficient $D_0 = \frac{1}{2} a^2 \omega_0$. $a$ is thereby the hopping distance and $\omega_0$ is the attempt-to-escape frequency, given by the vibration of the ion. The activation energy has been found to range between 0.3 and 3 eV and scatters around those values due to natural deviations of the bond angles and lattice distances. As only the metal oxide transports ionic and electron charge carriers and electrodes only carry electrons, a redox-process at the metal/semiconductor interface takes place, with oxidation at the anode and reduction at the cathode. The ions change their valence due to the electron loss or the added electron. The
ions are then blocked by the electrode and an accumulation or depletion at the electrodes is observed. However, resistive switching in metal oxide memristive devices is explained by the migration of those defects, forming conductive channels or filaments within the device or by accumulating at the metal electrode interface, lowering the Schottky barrier and increasing the device conductivity. The atomic rearrangement is then frozen-in into a metastable state. Three main driving force mechanism for oxygen anion and therefore also oxygen vacancy migration are the drift due to an electrical gradient due to the applied field giving the oxygen vacancy flux

\[ J_{\text{drift}} \approx Dnq \frac{E}{k_B T}, \]

(7)
diffusion due to a concentration gradient (Fick’s diffusion)

\[ J_{\text{Fick}} \approx -D \frac{dn}{dx}, \]

(8)
and thermophoresis (Soret diffusion)

\[ J_{\text{Soret}} \approx -DSn \frac{dT}{dx}, \]

(9)
upon local Joule heating and the induced temperature gradient \([128, 134]\). \(n\) is thereby the oxygen vacancy density, \(T\) is the local temperature, \(x\) is the location, \(D\) is the diffusion term as given in Equation (6), \(k_B\) is the Boltzman factor, and \(S\) is the Soret coefficient. All driving forces are schematically illustrated in Figure 2. In a), the ion ‘hops’ to its nearest free neighbor due to a concentration gradient. For an applied field, the hopping barrier to the right side in Figure 2 is reduced, so that the oxygen vacancy can overcome the energy barrier more easily. The temperature gradient in c) reduces the energy barrier for hopping as well, whereas the ion wants to get into the lowest possible energy state. Thermophoresis is the main driving force within unipolar switching devices, whereas the applied field mainly drives oxygen

![Figure 2: Schematic of the driving forces for oxygen vacancy motion. a) Fick’s diffusion, b) electrical drift, and c) Soret diffusion of oxygen vacancy ions. As oxygen ions move away from hot regions, oxygen vacancies move along the temperature gradient to the ‘hot’ region. \(a\) is the distance between two potential walls with energy barrier \(E_a\).](image-url)
2.3 Microscopic View on Redox-based Memristive Switching Mechanism

vacancy migration within bipolar and complementary switching devices (see Section 2.3.1). However, temperature effects have been shown to contribute to the electrical driving force in the latter two mentioned switching mechanism [135]. Moreover, the movement due to an electrical drift leads to an accumulation of oxygen vacancies, inducing a valence change at the filament/electrode interface and reducing the interface barrier. However, radial outward movements of oxygen ions from hot filament regions can lead to an insulator-to-metal phase transition, leaving a totally metallic Ti$_4$O$_7$ filament behind [136]. The transition has been verified by temperature dependent measurements, where the device shows an insulating or semiconducting behavior (conductivity increases for high temperatures), when no filament is present, whereas they show a metallic behavior (conductivity increases for decreasing temperatures), when filaments have been grown. However, the migration of oxygen vacancies of the afore mentioned effects results in increased local concentration areas of oxygen ions and oxygen vacancy areas. Therefore, a concentration gradient with the opposite direction to the electrical and temperature gradient is observed, leading to a counter movement of the migrating species. The resulting thermodynamically metastable states can lead to relaxation processes on different timescales. The retention of the devices is a key parameter for memristive devices, which defines application possibilities like non-volatile data storage, or emulating short- and long-term memories with volatile systems as discussed later in Section 2.3.3.

2.3. Microscopic View on Redox-based Memristive Switching Mechanism

The focus of this work lies on redox-based memristive switching mechanism in metal oxides, which are based on the formation of conductive filaments or metal electrode/memristor interface changes in oxide materials. Other mechanism like the phase change memory, where the memristive material undergoes phase transitions from crystalline to amorphous, or electrochemical metallization, where a conductive bridge of metal ions is formed, can be found for example in detail in the book of R. Waser [38]. The description and explanation of typical memristive switching behaviors are less based on fundamental physical models, but rather on consistent working hypotheses and pictures. Therefore, electrical current-voltage (I-V) curves are combined with high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) [137–139], atomic force microscopy (AFM) measurements, to image the grown filament or interface changes. Especially, AFM studies enabled the reconstruction of 3D-images of conductive filaments within redox-based memristive devices by scratching layer by layer through the memristor film and imaging the conductivity of each plane [48, 140–143]. However, it is found that the same material can show different switching behaviors, dependent on the atomic structure, amount and arrangement of defects, electrode configuration, or electroforming procedure [144–146]. Typically, an initial electroforming process is necessary to create such filaments or conductive areas and hence, observe a resistive switching behavior. Therefore, a voltage is applied to the device until a limiting
current compliance (cc) is reached. During electroforming high local temperatures along the
current flux are observed (the driving force for ion motion is described in Section 2.2), which
enable oxygen reduction processes, leading to the formation of n-conducting filaments. The
high temperatures can furthermore enable oxygen deficient phases, known as Magnéli phases,
which make the devices more conductive. The switching between two different states itself
is discussed in Section 2.3.1.
To make the discussion of the different switching mechanism easier, a brief introduction in
the main used denotations will be given. Most devices are first characterized by current-
voltage (I-V) measurements upon voltage cycling in a specified voltage range. The resulting
I-V behavior shows different hysteresis curves, leading to different resistance states for simi-
lar voltages, depending on the previously applied potential. The different possible switching
curve types are discussed in the following section. However, to determine the resistance
change in the I-V curves, a readout voltage is defined, at which two different conductive
states are observed. Typically, a small readout voltage is chosen, which does not induce
switching itself. The current at the readout voltage gives two possible resistance states, a
high and low resistance state, (HRS) and (LRS), respectively. The ratio of those two states
is called the on/off ratio and can give an indication of the device applicability. A further
requirement to the devices is a long endurance, which is tested by doing multiple (over 1000)
cycles and plotting the HRS and LRS at the readout voltage. Further characterization of
the devices is usually also done by time-dependent measurements. A write operation, to set
a specific state is applied for several seconds and probed by a read operation, mostly at the
afore mentioned readout voltage for the I-V measurements. It is here even more important
to use a small readout voltage, to prevent a change of the previously written state. The
retention of the readout current gives the device the possibility to store information. For
data storage application a non-volatile device with retention times greater than 10 years
is desired, wherefore retention investigations are inevitable. However, volatile devices are
applicable to emulate biological synaptic behavior like for example the short- and long-term
memory. Moreover, computing with memristive devices is found to be either analog or digi-
tal, dependent on the application purpose and device operation [147, 148]. Digital devices
can switch between two discrete states and often show high on/off ratios, whereas analog
device can be set into multiple resistance states in an analog way.

2.3.1. Unipolar, Bipolar, and Complementary Switching

Memristive elements are characterized by simple current-voltage (I-V) measurements, where
cycling between a high and a low voltage is carried out. The three main observed switching
characteristics are unipolar, where only one polarity is necessary to observe switching, bipolar
and complementary switching, where a polarity change is necessary to observe a switching
behavior. A forming process is typically needed beforehand. Especially, if the switching be-
2.3 Microscopic View on Redox-based Memristive Switching Mechanism

behavior is based on the growth of conductive filaments, this filament has to be formed before. Therefore, either the voltage is increased in small steps, until the current reaches a specified current compliance (cc), or a constant voltage is applied at which the current increase over time, until the cc is reached. Electroforming leads to morphological changes and/or the growth of conductive filaments due to high local temperatures upon localized currents and high electric fields. In oxide materials, it leads to a reduction of the oxide, resulting in n-conducting filaments or oxygen deficient phases like Magnéli phases. The different resistive switching curves for redox-based resistive switching of transition metal oxides are schematically drawn in Figure 3, including a picture of the ongoing process. However, the explanation is based on filamentary switching in transition metal oxide devices. Further switching mechanism are summarized in [126]. In unipolar switching cells, a sudden increase in the current occurs during electroforming due to a Joule heating induced redox reaction. Thermal gradients lead to an oxygen diffusion outward of the filamentary region, lateral to the electrodes, leaving n-type oxygen vacancies behind. This is similar to the SET procedure shown in Figure 3 process (2), where the voltage is increased to a current compliance to get the device from a high resistance state (HRS) (1) into a low resistance state (LRS) (3). Temperature dependent conductivity measurements for small voltages typically show an ohmic, metallic behavior for unipolar switching cells. The filaments are therefore reduced metallic phases. To RESET the device, the voltage with the same polarity is increased again, resulting in an ohmic increase of the current for small voltages. At a particular voltage, the current drops quickly, due to a rupture of the filament. Generally, the high current leads to a significant temperature increase, which results in a dissolution of the filament. The exact physical nature of the RESET process is still under investigation, with two processes under debate. On the one hand, it is assumed, that the free surface energy reduction of the filament leads to a dissolution of the filament, similar to the melting process of metal wires into spheres upon high temperatures. On the other hand, thermally activated re-oxidation could occur. Therefore, the local temperature needs to be lower than the temperature for the SET process, since this would result in a further oxidation of the filament [134]. Bipolar resistive switching is a field and temperature driven process. After electroforming, the current-voltage shows an eight-wise hysteresis behavior upon voltage cycling (Figure 3, middle). In metal oxide devices, the filament is formed by reducing the oxide material due to high local temperatures and voltages. During electroforming in bipolar switching cells, a filament is grown from the cathode to the anode. This results in an interface-based resistive switching, for bipolar resistive switching between the electrode and the end of the filament, shown in Figure 3 (A). Increasing the voltage leads to an attraction of n-type oxygen vacancies to the positively charged electrode (B). A reduction of the interface barrier and the formation of a conductive path leads to a higher conductivity after the filament is in contact with the electrode (C). To RESET the device, an opposite voltage is applied, which repels the positively charged oxygen vacancies again from the electrode, resulting in the HRS (D). However, as mentioned
Figure 3: Schematic current-voltage characteristics and a sketch of the process of unipolar (left), bipolar (middle), and complementary (right) switching. For unipolar switching, only one polarity is necessary, since it is based on thermochemical processes. Bipolar and complementary switching are field driven effects, accompanied by a thermochemical contribution and are therefore dependent on a polarity change [149].
2.3 Micorscopic View on Redox-based Memristive Switching Mechanism

before, also thermal effects occur during switching in bipolar switches. The thermal energy delivers the energy for oxygen ion migration [149], similar to unipolar switching. However, the strong field gradient leads to an additional perpendicular (relative to the electrode) ion motion [125, 126]. **Complementary resistive switching (CRS)** has first been introduced by E. Linn et al. in 2010 [11] by connecting two bipolar switching cells in series, to overcome the sneak path problem in nanocrossbar array systems [11]. Single material devices have been processed showing a CRS mechanism, for example niobium oxide devices [72], but also other materials, such as hafnium oxide by Nardi et al. [150], titanium oxide [151] by Lee et al., and many more [152, 153, 153] have been demonstrated. The switching mechanism for single material devices is shown in Figure 3 (right). The device is in a HRS for low voltages (I), followed by a LRS upon voltage increase and resulting filament growth (II). A sudden decrease of the current occurs for high voltages, which repels the oxygen vacancies from the electrode and leading to a HRS again (III). Changing the polarity leads to an attraction process of the oxygen vacancies back to the electrode again so that a filament is formed again (IV). Unfortunately, the CRS cells face the challenge of destructive readout currents. The readout of a specific state has to be at high voltages, as it is for low voltages always in the HRS, which leads to a destruction of the logic state. Therefore, the last state needs to be rewritten, which leads to an additional energy consumption. Several approaches to overcome the readout problem have been developed and can be found in [154].

2.3.2. Nanobattery Effect

Some metal-oxide devices show a non-pinched hysteresis loop. An extension of the theoretical model Equation (4) has been developed by I. Valov et al. [119] in 2013. The physical mechanism is ascribed to the nanobattery effect. The theory was therefore extended by the afore mentioned group and includes redox-based nanoionic-resistive memory cells. They form chemical potential gradients upon switching, generating an electromotive force (emf) of several hundred millivolts. They found three driving forces generating an internal cell voltage $V_{emf}$, which are the Nernst potential $V_N$, the diffusion potential $V_D$, and the Gibbs-Thompson potential $V_{GT}$. The Nernst potential arises due to a chemical potential difference at the interface of the electrodes and the memristive material. In general, two different electrode materials are used, leading to a chemical potential within the switching material. The diffusion potential arises due to an excess concentrations of charged species within the switching device. The Gibbs-Thompson potential is observed for filamentary switching, where a metallic filament from one electrode is already formed, but not connected to the other electrode (no short circuit). As a result, Equation (3) is extended to

$$I(t) = M(q(t)) \cdot (V - t_{ion}V_{emf}), \quad (10)$$
where \( t_{ion} \) represents the total ionic transference number, which is the fraction of the current carried by the electrolyte to the total electric current.

### 2.3.3. Volatile Switching

Relaxation in solid-state devices implies the removal of an applied stress and a recovery to a stable state in equilibrium over time. Dielectric materials, for example, are polarized in an electric field and depolarize if the field is removed. The electric field induces an orientation of the present dipole with the direction along the field. However, other types of dielectric responses can be caused by free movable charge carriers, trapping and detrapping of charge carriers, and the movement of mobile ions. This leads to different relaxation responses, as different physical mechanisms are involved. Memristive devices are either non-volatile, where the resistance state is stable infinitely or for more than ten years, or volatile, where the resistance state is lost within seconds or minutes. Mostly, the low or intermediate resistance state relaxes back into the high resistance state over time, which is known as the retention time. The following part summarizes the theory for relaxation processes with respect to memristive systems.

![Normalized relaxation curves of the three main relaxation laws for memristive switching devices.](image)

**Figure 4:** **Debye, Curie-von Schweidler, and Kohlrausch relaxation.** Normalized relaxation curves of the three main relaxation laws for memristive switching devices. For the Curie-von Schweidler law, as well as for Kohlrausch’s relaxation law, three curves with different decay constants and stretching parameters are shown, each.
2.3 Microscopic View on Redox-based Memristive Switching Mechanism

**Debye Relaxation**

The relaxation process of a dielectric placed in an electric field is described by the Debye relaxation, if there is only one type of dipole and the environment does not influence the relaxation. The electric field causes a polarization of the material, as the dipoles orient to the applied field. The rate of polarization $P(t)$ is proportional to the polarization

$$\frac{dP(t)}{dt} = -\frac{P(t)}{\tau}. \quad (11)$$

$t$ is thereby the time and $\tau$ is the relaxation time constant of the polarization. This leads to the time dependent polarization

$$P(t) = P_0(1 - \exp(-t/\tau)) \quad \text{and} \quad P(t) = P_0\exp(-t/\tau) \quad (12)$$

for charge and discharge processes, respectively. A temporal change of the polarization leads to a current, which is dependent on the dipole moments per volume and therefore, the current density $J(t)$ is given by

$$J(t) = \frac{dP}{dt} = -P_0\tau\exp(-t/\tau), \quad (13)$$

which is also known as the discharge current of a capacitor [60].

**Curie-von Schweidler Law**

A more general solution for several dipole types and therefore a number of relaxation processes is given by the Curie-von Schweidler equation

$$I(t) = I_{0,C}t^{-n} \quad (14)$$

with the decay constant $n$, with $0 < n < 1$ for dielectric materials, and the amplitude $I_{0,K}$. It is interpreted as a number of resistor-capacitor circuits by Jonscher et al. [60] and can be expressed as a sum of Debye relaxations. However, it is mostly used for electronic processes like trapping and detrapping of charges [155–157]. It is found, that the charges are detrapped in memristive devices, when the device is switched into a LRS. When measuring the resistance state at a low voltage over time (readout process), the charges get trapped again and reduce the conductivity of the device. It has furthermore been observed, that this effect happens at the memristor/electrode interface, leading to an additional increase of the Schottky barrier upon the readout procedure [155]. Compared to the Debye relaxation, see Figure 4, the Curie-von Schweidler law shows a faster decay for short times, followed by a slow decay, dependent on the decay constant $n$. 
Kohlrausch’s Relaxation Law

Another approach to describe relaxation processes is given by the stretched exponential function (SEF) [158], which is also known as Kohlrausch’s equation [58]. It assumes a stochastic nature of the relaxation processes, including an influence of the environment. It has been introduced for the discharge of a capacitor with a dielectric inside [58] and has been shown to be useful for disordered systems [159]. The function is given by

\[ I(t) = I_{0,K} \exp\left(-\frac{t}{\tau} \beta\right) \]  

where \( \beta \) is the relaxation factor and is restricted to \( 0 < \beta < 1 \) for a stretched exponential decay and \( I_{0,K} \) is the current amplitude. The probability distribution description suits therefore quite well for memristive devices in which switching is based on the migration of defects or ions, such as oxygen vacancies [160, 161]. The stretched exponential function shown in Figure 4 shows a fast decay for short times followed by a slow process, similar to the Curie-von Schweidler law. However, the slow component is still faster compared to the Curie-von Schweidler law, but is dependent on the stretching parameter \( \beta \). For \( \beta = 1 \) the Kohlrausch equation is simply an exponential function and follows the Debye relaxation.
3. Materials and Methods

In this chapter, the preparation and characterization methods of the memristive devices of this work are summarized. Therefore, a detailed description of the TiO$_2$ and Nb$_3$O$_7$(OH) sample preparation and the resulting structure is provided. Furthermore, a brief introduction in the standard structural characterization techniques scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray (EDX) spectroscopy is given. Current-voltage and time-dependent behaviors are performed in a characterization setup, built by our former group member J. Kalb, which is developed further in the course of this work. It is therefore described and presented in detail. STEM measurements are carried out at the Max Planck Institut für Eisenforschung in Düsseldorf by Joohyun Lim and Thomas Gänslers in the group of Prof. Dr. Christina Scheu. Furthermore, T. Gänslers manufactured the Nb$_3$O$_7$(OH) structures and sent them to us in powder form.
3.1 Material Preparation and Structure

Titanium dioxide structures, as well as niobium hydroxide structures are prepared by a hydrothermal growth method. The TiO$_2$ nanowires are grown vertically on top of a fluorine doped tin oxide (FTO) substrate. Since Nb$_3$O$_7$(OH) structures do not grow on FTO, single nanowires are filtered from the growth solution and dropped on top of gold finger electrode substrates from the Fraunhofer Institute. However, the preparation processes of both materials will be given in the following part.

3.1.1. Titanium Dioxide Nanorod Arrays

Figure 5: **Hydrothermal growth process of TiO$_2$ nanowires on FTO.** The growth solution is prepared in a Teflon liner by adding 350 µL Ti(OBu) dropwise to a 20 mL water/acid solution. After sealing the liner, the growth is initiated by temperatures higher than 120 °C. Vertically standing TiO$_2$ nanowires with a rutile crystal structures on top of the FTO substrates are observed.

The growth process of TiO$_2$ nanowires on fluorine doped tin oxide (FTO, TCO10-10, Solaronix SA, Aubonne, Switzerland, sheet resistance: $10 \Omega \text{cm}^{-2}$) is shown in Figure 5. 14 × 14 cm$^2$ FTO substrates are cleaned with deionized water, aceton, and isopropanol (IPA) in an ultrasonic bath, each for ten minutes. Afterwards, a nitrogen stream is used to dry the samples.
prior to an oxygen plasma (Diener electronic, Typ: Femto) cleaning process with seven minutes duration. A 20 mL water/HCL (hydrochloric acid, 37% from VWR Chemicals) solution with a 14.8% concentration is filled in a Teflon liner. 350 µL titanium butoxid (Ti(OBu)4 - (Bu = CH2CH2CH2CH3), 97% reagent grade, Sigma-Aldrich, Switzerland) is added dropwise while stirring the solution. The complete solution is stirred again for additional 10 min. After placing the FTO substrates on the sample holder inside the solution, the Teflon liner is sealed and fixed with a steel autoclave to prevent exchange with the surrounding and pressure release. A temperature greater than 120°C is necessary to initiate the growth process [90]. In our experiments, temperatures of 150, 180, and 220°C are used. The high temperature and pressure induce a growth of single TiO2 nanowires inside the solution and vertically standing nanowires on top of the FTO substrate, as schematically shown in Figure 5, middle. The growth results in rutile TiO2 structures, shown in Figure 6 a), whereas for the resulting crystal structure, atomic arrangement, and defect structure, which is shown by the following references [90, 91, 94, 162–164]. Other morphological structures are anatase and brookite crystal structure, which have been observed in TiO2 films, but also nanostructures [165]. Defects in titanium dioxide are mostly oxygen vacancies, but also titanium vacancies, oxygen and titanium interstitials, and other impurities are possible [88, 92, 130, 166, 167]. The main dominant defects within the nanowires have been related to n-type oxygen vacancies, which accumulate along the V-shaped grain boundary defects from the top to the bottom part of the nanowire, see schematically Figure 6 b) [162]. At the bottom part, the nanowire is fairly single crystalline, which could be reproduced in this work and its influence on the memristive behavior is discussed in Section 4.1.

3.1.2. Niobium Hydroxide Nanowires

Niobium hydroxide nanowires, Nb3O7(OH), are grown by Thomas Gänsler in the group of Prof. Dr. Christina Scheu at the Max-Planck-Institut für Eisenforschung in Düsseldorf. The growth process is shown in Figure 7. A 6 M HCl (Brenntag)/water solution is prepared

![Figure 6: Crystal structure of hydrothermally grown TiO2 nanowires. a) Rutil crystal structure, b) schematic of a single TiO2 nanowire grown on a FTO substrate.](image-url)
3.1 Material Preparation and Structure

at first. Afterwards, a niobium(IV)chloride–tetrahydrofuran (NbCl\(_5\)-THF) complex (0.2 g, 0.5 mmol, Sigma-Aldrich) is added to the solution. The Teflon liner is sealed in a steel autoclave and is placed in an oven at 200°C for 19 h. After cooling the solution down to room temperature, the growth product is separated from the growth solution and washed with water for several times. The powder is then dried and stored in small, sealed glass bottles.

For the electronic characterization, the samples are sent to the University of Konstanz, where I processed them further. First, few powder particles are dispersed in 2 mL ethanol (EtOH). To unravel clustering, the solution is put in an ultrasonic bath for 10 min. Meanwhile, a finger electrode substrates from Fraunhofer Institute (30 nm gold on top of 10 nm indium doped tin oxide (ITO), 230 nm SiO\(_2\), and n-doped (3 \times 10^{17} \text{cm}^{-3}, \text{altogether an top of a Si wafer}), with finger electrode distances of 2.5, 5, 10, and 20 \(\mu\text{m}\), four of each size \[168\]), are cleaned by placing the substrates into deionized water (DI), acetone, IPA, stepwise in an ultrasonic bath for 10 min, each. After drying the substrates with a nitrogen stream, 1 mL of the Nb\(_3\)O\(_7\)(OH) solution is dropped on the substrate and the ethanol is dried away. By chance, a single Nb\(_3\)O\(_7\)(OH) nanowire lays on top of the finger electrodes contacting two electrodes as shown in Figure 7, bottom. The growth product contains complex, three-dimensional

![Diagram](image)

Figure 7: Preparation method of single Nb\(_3\)O\(_7\)(OH) nanowires. Single Nb\(_3\)O\(_7\)(OH) nanowires are prepared in the laboratory of Prof. Dr. C. Scheu in Düsseldorf by T. Gänsler. A hydrothermal method is used with a HCl (6 M), NbCl\(_4\), tetrahydrofuran (THF) solution, which is heated at 200°C for 2 h. The washed product is then dissolved in ethanol and dropped on the finger electrode substrate at the University of Konstanz.

Nb\(_3\)O\(_7\)(OH) superstructures consisting of highly ordered nanowire networks, as well as single nanowires with lengths of several nanometers up to 30 \(\mu\text{m}\). The Nb\(_3\)O\(_7\)(OH) structures are present in an orthorhombic crystal structure consisting of blocks of corner-sharing NbO\(_6\) octahedra. Planar defects and oxygen vacancy defects are observed in the otherwise quite
defect free nanowires. A detailed analysis of the atomic structure of Nb$_3$O$_7$(OH) structures can be found in [106, 107, 169, 170].

3.2. Characterization Setups

In the following part the scanning electron microscope (SEM) with integrated energy dispersive X-ray (EDX) system, the scanning transmission electron microscope (STEM), and the current-voltage (I-V) setup for electronic characterization is explained. The structural characterization methods are kept short, since those are well known and commonly used devices. References to detailed literature is given for each part. However, the current-voltage setup is a self-built system and is therefore discussed in more detail.

3.2.1. Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy

A SEM is a standard device for sample imaging of resolutions up to few nanometers. Therefore, electrons are emitted by a cathode and accelerated to the sample by an electric field where they interact with the atoms of the investigated material. This leads to the emission of secondary electrons from the surface of the material, which can be detected by an InLens-detector. Furthermore, backscattered electrons can be detected by the backscattered electron (BSE) detector. This is mostly used for heavy elements, which show a strong backscattering effect of electrons. High contrast images can give information about the composition and arrangement of different constituent parts of the material. However, charging effects or different topographies of the sample can lead to misinterpretation of the contrast image, which should be taken into account while analyzing the data. Nevertheless, if the electrons of the cathode push another electron out of its atom, an electron from an higher energy orbital falls into the empty state of the emitted electron. The energy, which is becoming free due to the transmission from an electron of a higher state to a lower state, is emitted by X-ray, which can be detected by an energy dispersive X-ray (EDX) detector. The transition is element dependent, so that X-ray spectroscopy gives information about the element constitution of the material. A more detailed explanation of the measurement technique is given by Kühl et al [171]. However, the Gemini 500 from the Zeiss Company is a SEM equipped with an integrated EDX system at the University of Konstanz with acceleration voltages in the range of 0.02 to 30 keV. Furthermore, it has detectors for secondary electrons, as well as backscattered electrons. The EDX Ultim Max 100 detector is capable of already light elements, starting with beryllium.

3.2.2. Scanning Transmission Electron Microscope

Scanning transmission electron microscope (STEM) is a technique to image nanostructures and films on an atomic scale. The investigated structure needs to be thin enough, so that
3.2 Characterization Setups

Electrons can be transmitted through the investigated material. Therefore, again electrons are accelerated in an electric field and hit the sample, where the high energy electrons are transmitted through the thin film or nanostructure. The transmitted electrons are diffracted by the atoms (Rutherford scattering) of the material. If the material is amorph, no diffraction patterns is observed. However, for ordered systems a selected area (electron) diffraction (SAED) pattern is detected, which can be recalculated back to its origin and make the crystal structure of the material visible. A high resolution transmission electron microscopy (HRTEM) Zeiss CrossBeam 1540XB on a JEOL JEM-2100Plus, operated at 200 kV, as well as image-corrected Thermo Fisher Scientific Titan Themis 80–300 microscope, operated at 300 kV, is used at the University of Düsseldorf to image TiO$_2$ and Nb$_3$O$_7$(OH) structures on an atomic scale by Joohyun Lim and Thomas Gänsler, respectively. A more detail description of this technique can be found in [171].

3.2.3. Current-voltage Characterization Setup

The setup to characterize the memristive behavior of the niobium hydroxide and titanium dioxide samples is shown in Figure 8. The devices, prepared as described in Section 3.1, are placed inside a cubic chamber, which can be set under vacuum or filled with nitrogen. An electronic plug delivers cables from the digital multimeter Keithley 2401 from Tektronix to the electrodes of the samples. For TiO$_2$ NRAs, the FTO substrate is used as bottom electrode, whereas a large gold tip of 1 mm diameter is used as top electrode and connects several nanowires simultaneously. This method is studied before [172] and has been proofed as facile and suitable measurement system to characterize NRA samples. The single nanowires act as parallel resistances while measuring. The Nb$_3$O$_7$(OH) single nanowires, which are on the gold finger electrode substrate, as described before, can be connected directly to the electronic cables in the chamber. The multimeter is connected by a General Purpose Interface

![Figure 8: Measurement setup for electrical characterization.](image)

The setup consists of a nitrogen filled or vacuumized chamber, where electronic contacts are available, to connect the samples to the digital multimeter Keithley 2401. The multimeter itself is controlled by a computer program written by Eugen Zimmermann using the software Matlab R2016b.
Bus (GPIB) cable to a computer, where a Matlab program is used to apply electronic measurements. Besides standard I-V measurements, individual time-dependent measurements are possible. Therefore, a voltage can be applied for a chosen time and the current is measured simultaneously. This enables voltage pulse-probe measurements, which are used to investigate the possibility of biological synaptic function emulation and test the retention of the resistance states of the different devices.
4. Volatile Titanium Dioxide Nanorod Array Memristors

The following chapter is based on the paper *Hydrothermally Grown TiO$_2$ Nanorod Arrays with Volatile States* [173], which I have written as part of my PhD. All samples are prepared and electronic and SEM investigations are performed at the University of Konstanz. Joohyun Lim made STEM measurements at the *Max-Planck Institut für Eisenforschung GmbH* in Düsseldorf. All authors provided fruitful inputs during discussions and revised the manuscript. The work deals with a metastable resistive switching mechanism, different from the most common switching mechanism found in literature. Therefore, three samples with a different oxygen content are studied. All samples show a volatile behavior with different decay lifetimes. It is found, that the V-shaped defect structure in hydrothermally grown TiO$_2$ NRAs increase the oxygen vacancy mobility, which accumulate under an electric field and redistribute due to the concentration gradient. The increased defect density leads then to a faster disruption of the resistance state explaining the metastable switching phenomena. Individual text fragments are resumed partially from the mentioned paper and the figures are reprinted and adapted with permission from [173]. Copyright (2021) American Chemical Society.
4.1 Growth Temperature Dependent Defect Structures in TiO$_2$ Nanowires

SEM images of the different nanowires are shown in Figure 9 with growth temperatures of 150 °C, 180 °C, and 220 °C (see experimental part Section 3.1.1). Each growth temperature results in vertically standing TiO$_2$ nanowires of ~1 µm length covering the FTO substrates completely. The diameter of the nanowire increases with increasing growth temperature from ~70 nm (150 °C) to ~150 nm (180 °C) to ~200 nm (220 °C). In the upper part, a finger-like structure is observed, which is explained by the layer-by-layer growth model developed by Wisnet et al. [162] and Kalb et al. [164]. Folger et al. [93] further showed, that the fingers at the very top are separated by an open space incorporating O-H groups in between. In the middle part of the wire, the fingers merge together, resulting in edge dislocations most likely forming small angle grain boundaries. The bottom part is then observed to be single crystalline (STEM in Figure 9, bottom), which results in an overall V-shaped defect cascade within the whole nanowire. With increasing growth temperature, we observed an increase in the finger’s diameter resulting in a decreased density of edge dislocations and grain boundaries for those NRAs. A finger structure with relatively thin fingers can be seen for a growth temperature of 150 °C, which is confirmed by STEM images in Figure 9 (bottom images). The single fingers at the very top of the nanowires grown at 220 °C have been observed to be single crystalline [93, 174]. It has further been shown, that O$_{\text{vac}}$ are energetically favored to gather along grain boundaries [133]. Hence, a decreased density of O$_{\text{vac}}$ is expected for increasing growth temperatures. Furthermore, the grain boundaries at the bottom of the nanowire almost entirely disappear and only individual voids come up, whereas the outer part of the bottom nanowire seems defect free.
EDX measurements show the common oxygen and titanium peaks (Figure 10). Due to the low density of the nanowires, especially for the nanowires grown at 150 °C, a significant amount of the oxygen and tin from the FTO substrate appears in the EDX signal, which hinders the calculation of the Ti/O ratio in the nanowire. However, EDX results do not show any chlorine residuals or other impurity peaks for any samples, which have also been observed in previous reports [94]. Therefore, major effects due to growth residuals can be excluded in the further discussion.

![Figure 10: EDX measurements. EDX results of nanowires grown at 150 °C, top and nanowires grown at 220 °C, bottom. The tin peaks on the left image are from the FTO (fluorine doped tin oxide) substrate and are due to the lower density of the NRAs grown at 150 °C. Adapted with permission from [173]. Copyright (2021) American Chemical Society.](image)

### 4.2. Memristive Switching Behavior of TiO$_2$ Nanorod Arrays

The switching behavior of memristive devices is usually investigated by simple current-voltage (I-V) measurements. The typical memristive behaviors, e.g. unipolar, bipolar, or complementary switching, are described in Section 2.3.1. However, since a metastable I-V behavior with a temporal dependence is observed, additional time-dependent measurements are performed. Therefore, writing procedures of several seconds are used to set the resistance state of the device. Two resistance states per device are investigated by means of their decay dynamic. Using the gray-box method described in Section 2.3 a physical picture of the switching mechanism in the nanowire has been developed.
4.2 Memristive Switching Behavior of TiO$_2$ Nanorod Arrays

4.2.1. Current-Voltage Behavior

![Current-voltage (I-V) and polarity dependent I-V characteristics.](image)

The I-V characteristics for all growth temperatures are shown in Figure 11 a), b), c). The continuous line depicts the forward (negative to positive bias) measurement direction, whereas the dashed line depicts the reverse direction. The devices show typical memristive features like the change in the resistance upon voltage cycling and a pinched hysteresis loop (zero crossing) as described in Section 2.3 and [5]. However, the memristor hysteresis shown in Figure 11 does not follow typical unipolar, bipolar or complementary switching cycles. Instead, the I-V curves show different features like a self-crossing of in the curve and a temporal current evolution upon cycling. Three main features, labeled with I, II, and III define the I-V curve and are discussed in the following. I labels the asymmetric I-V behavior, II the current overshoot around 0.5 V, and III the current increase during cycling. The asymmetric I-V behavior (I) is observed for all growth temperatures and all of them show a higher conductivity for negative applied voltages. By applying a negative voltage, electrons have to move from the top gold tip electrode to the FTO. However, between the metal electrodes and the semiconducting NRAs, a Schottky contact is formed. Since gold and FTO have a similar work function of $\sim$5.1 eV [175, 176], the diode behavior is rather attributed to the difference of the top and bottom parts of the NRAs, than to the different electrode material. Furthermore, the STEM images show a higher grain boundary density at the top part of
the nanowire (shown in Figure 9 bottom and schematically in Figure 11 e), where n-type oxygen vacancies assemble [94, 132, 177–179]. Oxygen vacancies lower the Fermi level of the material by introducing shallow donor states below the conduction band [69]. Therefore, the Schottky barrier at the Au interface is lowered, resulting in the observed diode behavior. By applying a positive voltage, electrons have to overcome a higher energy barrier between the FTO electrode and the quite stoichiometric TiO₂ part, so that higher voltages are required to obtain a measurable current. Furthermore, at small positive applied bias, an overshoot (Figure 11, II) is observed, which is more distinct for higher growth temperatures. This current overshoot is defined by an increase in the current for an increasing voltage, followed by a negative differential resistance (NDR), hence, a decrease of the current for increasing voltages. Kim et al. mentioned a NDR for bipolar switching devices and explained it by a fast formation of a stoichiometric TiO₂ layer upon an applied voltage, which lead to a fast change of the resistance during cycling [180]. Others describe the NDR by a fast disruption of a conductive filament during switching, leading to a higher resistance state [145, 181–183], which did show common unipolar, bipolar, or complementary switching.

In order to understand this complex behavior in our system, split I-V curves, for a negative and a positive polarity cycle, are applied and shown in Figure 11 d). Ten cycles measured from negative bias to zero and back (left) and then ten cycles from zero to positive bias and back (right) are performed. Again, a hysteresis is observed, demonstrating that no polarity change is required to observed resistive switching. This, however, is necessary for field-driven BRS and CRS cells [184–187], so that an additional temperature effect is expected to be present, similar as in unipolar resistive switching devices [188, 189]. As the I-V curves are neither unipolar, the recent behavior is attributed to a metastable switching behavior with volatile resistance states in the following way: The split I-V curves show, that the resistance of the device decreases by increasing the bias to a higher positive/negative voltage amplitude. Then, the current remains at a high conductive state when the voltage is removed, whereas for rather small voltages the resistance relaxes back to its initial value. If the bias therefore goes below a threshold voltage, which is necessary to keep the material in its low resistance state, the system starts to relax to its initial, equilibrium state, which means that the LRS decays into the HRS. This furthermore explains the overshoot in Figure 11 II. It can be interpreted as a result of a non-completely back relaxed resistance state when cycling from negative to positive voltages. The current at small positive applied bias is therefore higher in forward direction than in backward direction. However, when increasing the bias to further high positive voltages, it can relax back into its HRS, so that a NDR is observed. The relaxation in that case is further supported by the now opposite applied electric field. For voltages (>~2 V) switching in the reverse direction starts, which brings the device again back to a lower resistance state. However, when decreasing the voltage below the threshold voltage in reverse direction, relaxation of the LRS starts again.
4.2 Memristive Switching Behavior of TiO$_2$ Nanorod Arrays

For higher growth temperatures the LRS in (II) does not relax back into the HRS completely, since the current in the NDR region does not go down to zero, as seen in Figure 11c). Therefore, switching is initiated again before the system has relaxed. This leads to the effect, that the overall conductivity increases per cycle (III). This effect is more dominant for higher growth temperatures, showing a different time-dependent behavior of the different growth temperatures. Accordingly, investigations regarding the decay dynamic of the different resistance states is performed in the following section.

4.2.2. The Volatile Dynamic

Figure 12: Write process. To set and reset the devices into a low and an intermediate resistance state, is done by applying a positive voltage or negative voltage for 300 s, respectively. Adapted with permission from [173]. Copyright (2021) American Chemical Society.

The temporal behavior of the nanorod array system is investigated for two different resistance states for each sample, a LRS and an intermediate resistance state (IRS). To write the respective states, a positive or negative voltage is applied for 300 s, respectively. The current-time evolution of the writing process is shown in Figure 12. To set a LRS, the maximum applied voltage from the I-V characteristics is applied for 300 s, whereas an intermediate resistance state (IRS) is obtained by applying the minimum applied voltage to all samples. The absolute current value increases for all devices and biases over time, showing a saturating behavior after approximately 100 s. For a positive bias, the current ranges between 0.1 and 2 mA, whereas for a negative bias, the current is about -0.1 to -0.2 mA. To probe the resistance states, 0.1 V pulses are applied with 1 s duration at a 2 s period. The probe voltage is chosen to be 0.1 V, since such a small bias is too low to influence the resistant state. As suggested in the I-V curve discussion, the devices show a volatile behavior, whereas current decays over time into the equilibrium high resistant state (HRS), shown in Figure 13.
Figure 13: Decay dynamics. The intermediate resistance state (IRS) decays for all devices faster into the high resistance state (HRS) compared to the low resistance state (LRS). However, the lifetime of the states increase with increasing growth temperatures. Reprinted with permission from [173]. Copyright (2021) American Chemical Society.

The relaxation contains two regions: a slow decay component in the beginning, which lasts from several seconds up to several minutes, followed by a fast abrupt drop within several seconds. After stimulating with a negative voltage, the system is set into an IRS with the current being lower than the LRS for the positive voltage writing procedure. The initial probe current values are ∼0.1 mA for the LRS and ∼8 × 10⁻¹ mA for the IRS of all samples. All signals decay into the HRS, whereas the decay is much faster for the IRS compared to the LRS in all samples. Furthermore, the lifetime increases with increasing cycle number when repeating the whole process several times, as shown in Figure 14 a), which is mostly observed for the nanowires grown at 220°C. For this high growth temperature a saturation of the lifetime is observed, whereas for the sample grown at 150°C the sample is already saturated. Additionally, the retention time increases with increasing writing time, shown in Figure 14 b). The decay time is defined as the time required to reach the inflection point in the fast decay region (see Figure 14 b), right). Therefore, the data are fitted with the function

$$f(x) = a \times \arctan(b \times (c - x)) + d \times (c - x) + e,$$

which does not have any physical meaning, but is a useful method to extract lifetimes of the observed decay process. For short writing times (2 s) a relaxation time of several seconds is thereby observed. This dependence supports the conclusions drawn for the I-V curves, where relaxation processes during cycling compete with the field induced switching mechanism, which affects the switching curves. It shows, that a short write pulse, similar to the stimulation time in the I-V curves results in a relaxation for few seconds. This is therefore suggested to be responsible for the overshoot behavior in the I-V cycle. More precisely, when the applied voltage during cycling goes below the threshold voltage, the resistance state starts to relax and still relaxes while the voltage cycling proceeds. Accordingly, the resistance state, which is written during the negative applied voltage, has not relaxed back before the polarity has changed. Therefore, the current is still high for small applied positive bias, but decreases for increasing voltages upon relaxation, whereas the increasing field pro-
4.3 The Switching Mechanism in NRAs

The Switching Mechanism in NRAs

4.3. The Switching Mechanism in NRAs

Switching in metal oxides is mostly explained by the motion of $O_{\text{vac}}$ [125, 126, 195, 195], which can be either moved by an electrical potential gradient (drift) [196], a temperature gradient (Soret diffusion) [134], or a concentration gradient (Ficks diffusion) [34, 122, 197], as introduced in Section 2.2. The $O_{\text{vac}}$ movement causes a change in the valence of the
metal oxide [34] making the device more conductive when those vacancies accumulate at the electrode to lower the bulk resistance or interface barrier, or build conductive filaments. Furthermore, local heating effects can make the device more conductive by either pushing additional electrons into the conduction band, or by inducing a redistribution of oxygen ions, which move away from the hot part, leaving n-type $O_{\text{vac}}$ behind [198, 199]. The migration of $O_{\text{vac}}$ only happens on few nanometer length scales [38], so that a growth of filaments through the $\sim 1\mu m$ long nanowire can be excluded. Therefore, either an accumulation of $O_{\text{vac}}$ at interfaces, in the bulk, or along conductive filaments through the high resistive part of the nanowire, reducing the resistance, is suggested. The resistance change has to happen along the highest resistance part of the device, since this is limiting the current. Besides STEM images, which show the most stoichiometric part to be at the bottom of the nanowires, also the diode behavior indicates the highest resistance to be at the bottom part of the NRAs. STEM images show an increased amount of grain boundaries in the upper part of the nanowire, which contain an excess of n-type $O_{\text{vac}}$ [133]. This is schematically shown in Figure 15 (pristine state, without applied bias, left). Futhermore, the asymmetric I-V curve and the different decay behavior for different applied polarities indicate two independent switching mechanisms for a negative or positive applied voltage. When a negative voltage is applied (Figure 15, middle), electrons move from the top towards the FTO, encountering a low interface barrier at the top part of the nanowire. At the high resistive parts, which starts at the ends of the grain boundaries, local Joule heating effects and an electric field gradient induce oxygen ions to move away from the grain boundary part, leaving additional $O_{\text{vac}}$ behind (dark green). Furthermore, positively charged $O_{\text{vac}}$ are repelled from the positive electrode by the electric field towards the top of the nanowire. Therefore, the length of the

![Figure 15: Schematic of the oxygen vacancy rearrangement upon resistive switching. The schematic shows the oxygen vacancy accumulation at the ends of the v-shaped defect structure for a positive biased bottom electrode and an accumulation at the bottom for a negative biased bottom electrode. Adapted with permission from [173]. Copyright (2021) American Chemical Society.](image)
highest resistant part of the nanowire is reduced, reducing the overall resistance. On the other hand, when a field with opposite direction is applied (Figure 15, right), the accumulation of O\textsubscript{vac} happens at the FTO interface. The oxygen ions are pushed away from the bottom electrode by the electrical field, leaving O\textsubscript{vac} behind, which lower the interface and bulk resistance of the device.

However, a retention loss in memristive devices is explained by the spontaneous, random motion of O\textsubscript{vac} [38, 53, 200] leading to a diffusive redistribution of accumulated O\textsubscript{vac}. After applying a negative bias, the O\textsubscript{vac} accumulate at the defective grain boundary part, where it is known that O\textsubscript{vac} can move more easily [132, 133]. Therefore, the redistribution of O\textsubscript{vac} is faster for a negative writing pulse compared to a positive writing pulse. Furthermore, the concentration gradient is already high in the upper part of the nanowire in the equilibrium state, which competes the electric field and temperature gradient driving force during the writing process and hence, leads to fewer oxygen vacancy migration. Additionally, a higher concentration gradient supports the fast redistribution process, which altogether leads to a fast decay of the current after the stimulation with a negative bias is removed. When a positive bias is applied during writing, O\textsubscript{vac} accumulate at the bottom part of the nanowire. Thereby, the concentration gradient, competing the two other driving forces during the write process, is small, so that O\textsubscript{vac} can accumulate at the bottom electrode. This leads on the one hand, to a larger on/off ration between the LRS and the HRS and, on the other hand, to a slower relaxation of the resistance state. This is even supported by slow moving O\textsubscript{vac}, compared to the mobile vacancies along the grain boundaries. Moreover, Figure 14 a) shows the saturated lifetime of the IRS, i.e. when a negative write bias was applied, the highly defective part of the top nanowire is saturated with O\textsubscript{vac}, whereas for a positive write bias, a great change in the quite defect-free bottom part is possible, which then takes longer to relax.

**4.3.1. Impact of the Growth Temperature**

The two main differences of the three devices are the change of the contact area upon a higher nanowire density for larger growth temperatures, as well as the higher defect density for decreasing growth temperatures. To figure out the influence of the contact area, two Au tips with different contact areas are used on the NRAs grown at 220\degree C. The results are shown in Figure 16. The I-V curves show a clear decrease in current for Tip 2 with a smaller contact area. Several tests have been made until the same decay lifetime is observed for both tips. A higher positive voltage is needed to be applied for the smaller contact area, which then results in the same decay lifetime. As the current of Tip 2 is smaller, it is concluded, that the current density has to have the greatest impact on the lifetime of the resistance states. Not only the I-V characteristics (Figure 11), but also the writing process (Figure 12) show similar current levels for all growth temperatures. Therefore, the highest
current density is observed for lower growth temperatures, which have the smallest contact area, since they exhibit the smallest nanowire density. Especially, the current in the beginning of the decay measurements (Figure 13) is similar for all growth temperatures, indicating a higher current density for decreasing growth temperatures. The better conductivity of the NRAs grown at lower temperatures is related to a higher n-type O$_{\text{vac}}$ concentration within those devices (Figure 11 e)). Furthermore, the lifetime of the resistance state is observed to increase with increasing growth temperature, where on the opposite, the different contact area measurements show a dependence of the lifetime on the current density. As the current density decreases with increasing growth temperature, the change of the stoichiometry of the nanowires for different growth temperatures has to be the main impact factor on the lifetime of the memristive states, rather than the contact area. From STEM it is known that the stoichiometry increases for increasing growth temperatures, so that a higher stoichiometry results in a longer lifetime of the memristive state. On the one hand, a better stoichiometry results in a slower O$_{\text{vac}}$ movement due to less defects [201, 202], which results in a slower relaxation process. It has been shown that O$_{\text{vac}}$ can move more easily along defective parts (especially grain boundaries) [130, 133, 167]. Since the NRAs grown at lower temperatures contain more defects and grain boundaries, the faster redistribution of O$_{\text{vac}}$ along those defects can result in a faster decay. On the other hand, the higher defect density for the lower growth temperature leads to a faster saturation of the accumulated O$_{\text{vac}}$. This is supported by the fact that the decay is much faster when a negative bias is applied before. Less O$_{\text{vac}}$
can accumulate at the grain boundary part, due to the high defect concentration in the top part of the nanowire. In the more stoichiometric part of the TiO$_2$, the resistance can change more easily due to a higher possibility of O$_{vac}$ accumulation, which results in a longer lifetime of the respective state. Repetition of the decay measurements for several cycles (Figure 14 a)) shows, that the lifetime of the LRS increases with cycling for the NRAs grown at 220°C, whereas for the IRS it remains always the same. For the NRAs grown at 150°C, the LRS is saturated already after the first cycle and for the NRAs grown at 180°C, it is saturated after the second cycle. The increase of the retention time for the NRAs grown at 220°C also saturates slightly with increasing cycle number. As long as it does not saturate completely, some of the O$_{vac}$ remain at the accumulated part after each measurement, so that the amount of already accumulated O$_{vac}$ is higher for the increasing cycle number. Since more O$_{vac}$ have to redistribute, the retention time increases for each cycle. This indicates, that the decay is faster for lower growth temperatures due to a saturation of the accumulated O$_{vac}$ and the 'faster' vacancy motion along defective parts. Additionally, measurements with even longer writing times (Figure 14 b)) show, that for lower growth temperatures the decay time is similar for writing times of 300 s and 400 s, whereas for the 220°C grown devices the decay time is increasing with increasing writing pulse duration. Thus, at smaller growth temperatures the accumulation of O$_{vac}$ is saturated due to the high defect density. However, higher growth temperatures lead to more stoichiometric nanowires, so that the accumulation of O$_{vac}$ can still increase with each cycle and by applying longer writing pulses since the device is not saturated.

Therefore, longer retention times for higher growth temperatures and positive applied bias are a result of two points: one is the slower oxygen vacancy migration due to less grain boundaries and the second is the smaller defect density which reduces the saturation effect being present for the high defective NRAs grown at low temperatures. These results indicate already the possibility utilizing hydrothermally grown NRAs as biological synapse emulators. The change between a short- and long-term memory with lifetimes from milliseconds up to several minutes is herein realized by changing the oxygen vacancy density of the device and two different write voltages. However, to confirm the short- and long-term memory transition, further studies are performed and, as biological synapses have many more functions like the spike-rate dependent plasticity, paired-pulsed-facilitation, and more, further investigations are necessary to proof the possibility using NRAs as artificial synapses, which is demonstrated in the next section.

4.4. Summary

In summary, we developed a physical picture describing the observed metastable memristive switching behavior in hydrothermally grown TiO$_2$ nanowire devices. The change of the resistance has to happen at the part with the highest resistance, which appears to be at the
bottom part of the nanowire. Therefore, the O\textsubscript{vac} accumulate at either the nanowire/FTO interface or at the ends of the V-shaped grain boundaries. This leads then to a change of the resistance, due to an interface barrier lowering and an overall shortening of the high resistive bulk part of the NRAs.

Time-dependent write/probe measurements show a volatile behavior for the nanowire memristors, which is tested for two different write voltages for each samples. The volatility is related to a redistribution of O\textsubscript{vac} over time due to a concentration gradient. NRAs grown at higher temperatures show the highest lifetime of 20 min, which is related to decreased defect density within those nanowires. A high defect density results in a better O\textsubscript{vac} mobility along defective sites in the nanowires, reducing the lifetime of the resistance states. Furthermore, as for lower growth temperatures the retention time could not be increased by longer writing times, a saturation effect due to the high defect concentration limits the O\textsubscript{vac} accumulation.

Moreover, the volatility of the resistance states is visible in the I-V behavior. At small voltages, the resistance states can relax, whereas when the voltage is increased with an opposite voltage, the write process starts again, competing, or additionally supporting the relaxation of the previous state. This leads in a metastable resistive switching behavior, which has been observed for all growth temperatures.
5. Emulation of Synaptic Functions with TiO$_2$ Nanorod Arrays

According to the previous chapter, the TiO$_2$ nanorod arrays are now investigated regarding their artificial synaptic function behavior. The previously described switching mechanism is now used to emulate biological synaptic functions to demonstrate the possibility for neuromorphic computing applications with hydrothermally TiO$_2$ NRAs. Spike-rate dependent plasticity, excitatory postsynaptic currents, paired-pulse facilitation, as well as high endurance and short-term to long-term memory transitions are functions of biological synapses, which could be emulated with the presented artificial synapse. The decays of the memory loss are fitted with the Kohlrausch equation to extract the lifetime of resistance states of different stimulation pulse amplitudes and durations. The lifetimes range from few milliseconds, up to several hundred seconds which mimics to short- to long-term memory transition of a biological synapse. The results are published as part of my dissertation in the paper *TiO$_2$ Nanowire Array Memristive Devices Emulating Functionalities of Biological Synapses* [203], which I have written. Parts of this section are resumed with permission from [203] and John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021, license number: 4992540955032.
5.1 Introduction into Biological Synapses

Many human brain mechanisms are already understood quite well, whereas human learning and forgetting is related to the chemical synapses [204–206]. A synapse is the connection between two neurons and is responsible for the signal transfer between them. A schematic representation of the signal transfer process is shown in Figure 17. In the first neuron an action potential along the membrane is sent to the endings of the neuron, called axon. The increased potential leads to an opening of Calcium-ion (Ca\(^{2+}\)) channels, so that for a short time, Ca\(^{2+}\) ions can diffuse into the neuron. The increased calcium concentration leads to a release of neurotransmitters into the synaptic gap, where they diffuse to the postsynaptic region to the second neuron, the dendrite. The membrane of the dendrite contains suit-

![Figure 17: Schematic of the signal transfer of a chemical synapse. The axon is the end of the pre-synapse, where an action potential arrives. The signal is transferred via neurotransmitters to the dendrite of the post synapse.](image)

able receptors to which the respective transmitters bind. Ion channels are opened, and an increased concentration of the respective ions, like Na\(^{+}\) ions, is observed in the dendrite, leading to an increase or depression of the postsynaptic potential. This again results in a change of the membrane potential of the second neuron. If the change of the membrane potential is large enough (beyond a threshold potential) the signal is transmitted to the cell nucleus [207]. Meanwhile, the calcium concentration of the presynaptic region relaxes back to equilibrium [61]. However, if another action potential reaches the dendrite before the calcium concentration could relax back, the amount of released neurotransmitters is larger compared to the first stimulus, resulting in an increased postsynaptic potential, since more Na\(^{+}\) channels are opened and the Na\(^{+}\) concentration in the dendrite is increased. The postsynaptic signal is therefore dependent on the action potential amplitude and frequency, called the spike-rate and -amplitude dependent plasticity [208–210]. High frequencies or large stimulation amplitudes can lead to a persistent durable structural and functional change of the synapse, so that even after a long time, a similar action potential results in a higher postsynaptic potential than for the first stimulus [211, 212].

Memristive devices have found to be able to emulate those synaptic functions, which can pave the way for neuromorphic computing [8, 22, 52, 53, 200, 213, 214]. Above all, metal oxides
[144, 149, 215, 216] and nitrides [217–221] are the most investigated memristive material, but also organic polymer based materials [41], as well as hybrid perovskite materials [43] have shown to be promising memristive device candidates. Besides, the memristive behavior of TiO$_x$ based devices is found to be modifiable by the manufacturing procedure, the electrode configuration and material, but also by the measurement procedure [144, 146, 222, 223]. In the following, the influence of the asymmetric structure of the nanowires on synaptic functionalities, such as endurance, spike-timing dependent plasticity (STDP), short-term plasticity (STP), paired pulse facilitation (PPF), and post-tetanic potentiation (PTP) is demonstrated. It is found, that the polarity has a great influence on the behavior of the different resistance states due to the asymmetry of the TiO$_2$ nanowires. The decay for a negative applied voltage perfectly follow Kohlrausch’s law, whereas an exponential growth equation has to be added to Kohlrausch’s equation to fit the postsynaptic current for positively biased stimulation pulses.

5.2. Current-Voltage and Endurance Characteristics

Hydrothermally grown nanorod arrays, shown in Figure 18 a), are investigated using the two electrode system introduced in Section 3.2.3 and shown in Figure 18 b) (inset). A FTO substrate is used as bottom electrode, whereas a gold tip contacts the nanowires from the top. Multiple nanowires are contacted by the mm-sized gold electrode tip, which act then as parallel resistors. The current-voltage (I-V) characteristics is shown in Figure 18 b) on a logarithmic scale. The curve shows an asymmetric behavior with a higher conductivity for a negative applied potential. The previous chapter describes the origin of the asymmetry originating from the asymmetry of the nanowires itself. The difference in the resistance can be clearly seen at a voltage of 0.1 V as highlighted in Figure 18 b). Therefore, the read-out and probe voltage is chosen to be 0.1 V, which is too small to induce switching, so that no resistive switching effects during readout is expected. However, this leads to three different distinct resistance states in total: an intermediate resistance state (IRS) with a current around $10^{-3}$ to $10^{-4}$ mA, and a low resistance state (LRS) with a current around $10^{-2}$ mA, both read at 0.1 V (see markers in Figure 18 b)). The highest resistance state (HRS), which is the state where no current is measured anymore, is not observed in the I-V curve, but in the time dependent measurements, discussed later on. There, the IRS and LRS relax into the HRS over time, with the current dropping to around $10^{-8}$ mA (see also Figure 14a)). However, a change of the resistance state in TiO$_x$ is mostly related to an accumulation and/or formation of filaments consisting of n-type dopants like oxygen vacancies [125, 126, 183, 224]. In Section 4.3 the switching mechanism of hydrothermally grown TiO$_x$ NRAs has also been attributed to the field and temperature driven accumulation of oxygen vacancies at either the top or bottom of the nanowire, dependent on the applied polarity. A retention loss after several minutes has been attributed to a redistribution of oxygen vacancies due to a
5.2 Current-Voltage and Endurance Characteristics

Figure 18: **SEM cross-section, I-V behavior, and endurance of TiO$_2$ NRAs.** a) SEM cross-section image of the hydrothermally grown nanowires on top of a FTO substrate. b) I-V characteristics with a scan speed of 0.14 V/s, measured with the electrode system shown in the inset. c) and d) shows the endurance over 1000 I-V cycles with a readout voltage of 0.1 V for a small and large top electrode, respectively. Reprinted and adapted with permission from [203], John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021.
concentration gradient, which was additionally demonstrated by Strukov et al. [134]. Due to the asymmetry of the nanowires, the redistribution of the oxygen vacancies happens on different timescales for the two different polarities. Endurance measurements of 1000 and 100 cycles are shown in Figure 18 c) and d), respectively. In addition to Section 4.3.1 the endurance is measured with two different tip sizes (small in c) and large in d)), which do show a similar trend, so that the endurance is independent of the contact area. However, the conductivity of both intermediate and low resistance states increases within the first 10-50 cycles, followed by a quite stabilized value for both the LRS and the IRS. Within the first cycles, the amount of accumulated oxygen vacancies at each electrode increases, lowering the interface barrier and hence, leading to a higher conductivity. The redistribution is slower than the cycling speed, so that the amount of accumulated vacancies increases per cycle. Slower cycling speeds lead to similar I-V characteristics, since the redistribution also takes longer. At some point, an equilibrium between the two competing effects, the redistribution versus the accumulation due to the electric field of the next cycle, is reached and a stabilized value for both resistance states is observed. By combining the previous results with the presented findings, the emulation of biological synapses by hydrothermally grown TiO$_2$ memristors are discussed.

5.3. Spike-rate Dependent Plasticity

The spike-rate dependent plasticity (SRDP) signal is shown in Figure 19 a) for a negative applied pulse potential, as well as a positive pulse bias in b) (further frequencies and voltages can be found in Appendix A). Ten voltage pulses of 1 s duration at frequencies of 0.17 Hz to 0.67 Hz are applied to the memristors (a schematic of the pulse trains is shown in Figure 20 a)). The excitatory postsynaptic current (EPSC) between each voltage pulse is recorded at 0.1 V. An example for the EPSC decay for both polarities is given in Figure 19 c) and d) for a frequency of 0.25 Hz. After each pulse train (one pulse train contains 10 voltage pulses) the transient current is probed at 0.1 V for 60 s, so that the device can relax back to equilibrium before the next pulse train starts. However, for a stimulation amplitude of 3.3 V and frequencies of ≤0.25 Hz, the 60 s are too short to let the device relax back to the equilibrium, so that the current of the first voltage pulse of the next pulse train is already higher than the current height of the initial voltage pulse. Anyhow, this indicates the possibility of a short-term to long-term memory transition for short pulse intervals and large voltage negative/positive amplitudes, respectively. Beside that, the EPSC decay for a negative stimulation potential perfectly follows a single stretched exponential decay (Kohlrausch’s law) as introduced in Section 2.3.3 and [58, 158, 225, 226]

$$I(t) = I_{0,K} \exp(-t/\tau^\beta).$$

(17)
5.3 Spike-rate Dependent Plasticity

Figure 19: Spike-rate dependent plasticity (SRDP) signal for TiO$_2$ NRAs. a/b) SRDP for pulse voltages of -2 and 3.3 V for different frequencies. c/d) EPSC decays measured at 0.25 Hz for both polarities. e) Evolution of the transient current after stimuli. The growth of the current becomes more dominant with increasing pulse number until no decay is visible anymore within the pulse interval. Reprinted with permission from [203], John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021.
$I_{0,K}$ is the thereby the amplitude, $\tau$ is the lifetime of the decay process and $\beta$ the stretching factor of the exponential decay. The fits for the negative pulse trains are shown in Figure 19 c) and e), whereas in e) all ten decays after the pulse at a frequency of 0.25 Hz are shown. The Kohlrausch relaxation is based on a stochastic nature of relaxation processes [58, 59, 227] and is mostly used for relaxation processes based on oxygen redistribution [21, 161, 200, 228]. This fits very well to the previous findings in Section 2.3.3, where the retention loss could be attributed to the oxygen vacancy redistribution. The excellent agreement of the stretched exponential fit (SEF) with the experimentally recorded decays additionally support the conclusions from Section 4 of the oxygen vacancy redistribution model. Moreover, the decay curves for a positive applied pulse bias show an additional exponential growth in the beginning, followed by a retention loss according to Kohlrausch’s law. The fitting equation then is given by

$$I(t) = -I_0 \exp\left(-\frac{t}{\lambda}\right) + I_{0,K} \exp\left(-\frac{t}{\tau}\beta\right)$$ (18)

where $I_0$ is the amplitude of the growth and $\lambda$ is the growth time. In Figure 19 d) and f) the very well fitting of the measured data to the fitted curve is visible. f) shows thereby again the ten postsynaptic currents for a positive applied stimulation pulse at a frequency of 0.25 Hz. In Figure 19 f) however, it is already obvious that the growth time is increasing with pulse number and becomes even larger than the pulse interval, so that the decay is not seen anymore. This can also be seen in the fitting parameters, shown in Figure 20 b) and c), where the decay lifetimes, the growth time for positive stimulation pulses, as well as the beta fitting parameter are presented with respect to the pulse number and frequency. It is observed, that the decay lifetime, as well as the growth time for positive pulse biases, increase for increasing pulse numbers and frequencies, which is in accordance with the behavior of biological synapses. The stretching parameter beta is 0.5 for a negative applied bias and $\sim 0.2$ for a positive applied bias, both laying in the permitted region for a stretched exponential decay. For a positive bias, large pulse numbers and high frequencies lead to a vanishing of the decay within the pulse interval, so that the lifetime value becomes insignificant. Especially at a frequency of $\leq 0.5$ Hz the growth time outlasts the pulse interval completely. The lifetime values range from milliseconds to seconds for a negative pulse voltage and up to 100 s for a positive pulse voltage and increase per pulse number similar to biological synapses. The increase of the SEF lifetime, which is observed for both polarities, is related to an increased amount of accumulated oxygen vacancies at the top or bottom interface for large enough frequencies. A maximum lifetime for the present memristive devices has been observed in the previous chapter to be around 20 min, which is due to a saturation of accumulated oxygen vacancies. However, we observe lifetimes of smaller than 100 s for the SRDP measurements, which is in a similar range to the short-term plasticity (STP) observed in human brains [229]. Furthermore, an exponential growth of the current has been seen in previous studies on nanobatteries [119]. It has been related to a contamination of adsorbed species at the interface to the electrode. Indeed, the exponential growth is only observed, when oxygen vacancies
5.3 Spike-rate Dependent Plasticity

Figure 20: **Pulse number and frequency dependent lifetime of the HRS and IRS.** a) Schematic of the measurement protocol, where f is the frequency. b) Fitting parameters for voltage stimuli of −2 V amplitude and c) for stimuli voltage of 3.3 V. Reprinted with permission from [203], John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021.

accumulated at the bottom FTO interface (at positive bias). It is therefore suggested, that reactions of the oxygen ions from the FTO and the accumulated oxygen vacancies in the TiO$_x$ are taking place. It is likely, that oxygen vacancies migrate into the FTO upon applying the electric field. Upon removal of the field, the oxygen vacancies redistribute throughout the nanowire, increasing its conductivity. As this effect is even more pronounced for higher frequencies (Figure 19 e) and Figure 20 c)), it is concluded that the oxidation at the bottom nanowire could not relax back to equilibrium before the next voltage pulse, so that the growth time increases with each pulse number. It has to be mentioned, that is was not possible to fit the EPSC signals for a frequency of 0.67 Hz since the source meter did not record enough data to fit the curve properly. Another way to compare the SRDP of

Figure 21: **PPF and PTP** Current difference between first and second, and first and tenth pulse, indicating PPF and PTP, respectively, for the two polarities. Adapted with permission from [203], John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021.
TiO$_x$ nanowire emulators to biological synapses is to calculate the PTP and the PPF of the SRDP measurements. Therefore, the maximum current height difference between the first and tenth (PTP), as well as the first and second pulse (PPF), is calculated and shown in Figure 21. The lines are added only as a guide to the eye. For increasing intervals (smaller frequencies), the difference of the currents is small. However, for high enough frequencies, the transient current decay overlaps with the following stimulus, increasing the conductivity of the memristor. This means, that the redistribution of the oxygen vacancies competes with the following stimulation pulse, similar to the biological counterpart, where the action potential induces an influx of calcium ions into the presynaptic end. This leads to a release of neurotransmitters, inducing a synaptic potential at the postsynaptic region. If the next action potential reaches the presynaptic end before the synapse relaxed back to equilibrium, the resulting postsynaptic response is larger than the one before [200, 230]. Therefore, the presented results are in accordance with previous results on artificial synapses [42, 231–234], as well as its biological counterpart.

5.4. Stimulation Pulse Amplitude Dependent Plasticity

![Figure 22: Amplitude dependent Lifetime.](image)

The strong dependence of the postsynaptic response to the action potential is schematically shown in Figure 22 a). The respective dependence of the lifetime of the postsynaptic current of the TiO$_x$ memristors on the pulse amplitude is presented in Figure 22 b) and c). The respective SRDP measurements can be found in Appendix A. A threshold voltage is observed for both polarities, where at a frequency of 0.5 Hz switching starts at $-1\,\text{V}$/$-1.5\,\text{V}$ for negative bias and at $2\,\text{V}$/$3\,\text{V}$ for positive applied bias. The threshold behavior is also observed in chemical synapses, which affirms the possibility of bio-realistic memristive TiO$_x$ NRA devices, where a large enough action potential is also necessary to transfer signals from one cell.
to another in biological systems [61]. Furthermore, the lifetime, as well as the growth time, increase with larger stimulation amplitudes, similar again to chemical synapse functions. The dependence in NRAs is related to the stronger field, making the oxygen vacancies more mobile and increasing the number of accumulated oxygen vacancies. Again, a larger amount of oxygen vacancies accumulates at the interfaces, requiring more time to redistribute and hence, leading to a longer lifetime of the postsynaptic signal. The beta fitting parameter is again $\sim 0.5$ for negative applied biases and $\sim 0.2$ for positive applied bias, both lying in the region for stretched exponential functions ($0 < \beta < 1$) [59]. As a last verification for the NRAs being possibly implemented as artificial synapse, 150 identical voltage pulses (with either -2 and 3.3 V amplitude) at a frequency of 0.5 Hz are applied to the memristor. The transient current between each single pulses and after the whole pulse train is probed at 0.1 V and results are shown in Figure 23. The current increases with increasing pulse number until a steady state is reached. The transient current is probed afterwards at 0.1 V, leading to a retention time of $\sim 100$ s for a negative applied potential and a lifetime larger than 300 s for the positive applied potential, indicating the transition to a long term memory (LTM). This brings us back to the observations of Section 4, where the LTM states are observed, for long writing times with similar decay behaviors. Altogether, those results show the possibility to emulate important functionalities of biological synapsis by using TiO$_2$ nanorod arrays. However, for device application as artificial synapsis in physical neuronal networks, the device architecture and the structures dimensions need to be adjusted. Previous work already shows the possibility of position controlled growth and the impact of the growth parameters on the resulting structure of the nanowire [163, 235], which can be used in further device engineering work on building physical neuronal networks based on TiO$_2$ nanowires.

Figure 23: **Sum of PPF with 150 voltage pulses.** PPF of 150 identical voltage pulses for -2 and 3.3 V amplitude, with a probe voltage of 0.1 V on a logarithmic scale, whereas the inset shows the measurement procedure. Reprinted with permission from [203], John Wiley and Sons. Copyright from Advanced Electronic Materials, Jan. 19, 2021.

### 5.5. Summary

The hydrothermally grown TiO$_2$ NRAs show a great potential in being a candidate as artificial synapses for neuromorphic computing. Beside a high endurance, switching between
a short- and long-term memory state is demonstrated by using different stimulation pulse duration or amplitudes. By combining the results from the previous chapter (Section 4) to the recent finding, the physical mechanism behind the switching process is attributed to an oxygen vacancy migration and accumulation upon an temperature and electric field gradient. Furthermore, the spontaneous relaxation of the resistance states is related to a concentration gradient driven redistribution of oxygen vacancies. In addition, the decay dynamic could be perfectly fitted with Kohlrausch’s law, which is commonly used for stochastic redistribution processes and supports therefore the suggested switching mechanism. However, an increase of the decay dynamic for positively applied voltages is detected and ascribed to an interaction of the oxygen vacancies within the nanowires and the oxygen ions of the FTO, which could further be responsible for the very slow decay time for positive stimulation pulses. Nevertheless, other important synaptic functionalities, such as PTP and PPF, as well as a sum of PPF with 150 voltages pulses has been demonstrated, making the nanowires a promising memristive system applicant.
6. Complementary Switching in
Single Nb$_3$O$_7$(OH) Nanowires

In order to investigate the influence of the device material and architecture on the switching mechanism, Nb$_3$O$_7$(OH) nanowires are utilized and compared to the TiO$_2$ switching behavior. Single nanowires, grown by the same hydrothermal method as the TiO$_2$ nanowires are prepared as described in Section 3.1.2. A complementary resistive switching (CRS) mechanism is attributed to a migration of oxygen vacancies in a similar approach to the previous results. Using an oxygen plasma treatment increases the oxygen content, which lowers the conductivity due to a lack of n-type oxygen vacancies. Furthermore, this affirms the suggestions about the impact of oxygen vacancies on the resistive switching mechanism. Besides, the conventional destruction of the resistance state due to the readout procedure is investigated and dependencies of the readout voltage amplitude and duration on the readout behavior are presented. The results are published in the paper *Complementary Switching in Single Nb$_3$O$_7$(OH) Nanowires* [236], which I have written as part of my PhD in cooperation with T. Gänsler from the group of C. Scheu at the *Max-Planck-Institut* in Düsseldorf.
6.1 Structural Analysis

The single Nb$_3$O$_7$(OH) nanowire devices are shown in Figure 24 a), where the nanowire lays on top of two gold electrodes, left and right. A schematic of the device architecture is shown in below. An EtOH/Nb$_3$O$_7$(OH) nanowire solution is dropped on the fingerelectrode sub-

![Figure 24: SEM, STEM images, schematic device architecture, and crystal structure of the Nb$_3$O$_7$(OH) nanowire. a) SEM image from the top with the nanowires laying on top of the electrodes (left and right), b) STEM image revealing the defects within the single crystal, inset: SAED pattern with associated lattice planes, c) crystal structure, with Nb = blue, O = red, and H = green sphere (Reprinted with permission from [169]. Copyright (2021) American Chemical Society), and d) schematic of the device architecture.](image)

strate, as described in Section 3.1.2. Single nanowires are found by chance laying on top of two gold electrodes. Previous results of our cooperation partners form Düsseldorf [169] have shown, that the hydrothermal growth method results in single crystalline nanowires with a orthorhombic crystal structure as shown in Figure 24 c). Slight lattice plane dislocations and oxygen vacancy defects are present in the pristine devices, as shown by STEM investigations in Figure 24 b). EDX spectroscopy is used to investigate the impact of an oxygen plasma treatment on the O to Nb ratio of the Nb$_3$O$_7$(OH) structures. Therefore, large Nb$_3$O$_7$(OH) structures on top of 1 µm thick SiO$_2$ are used for investigations, shown in Figure 25 a). The samples are placed for 420 s in the oxygen plasma. However, for electronic measurements, the impact of an oxygen plasma treatment is investigated by placing the single nanowire/finger electrode device for 30 s into an oxygen plasma. As the Au line of the EDX signal has a similar energy to the K-line of Nb, it would not be possible to distinguish between those two. Therefore, SiO$_2$ is used as a substrate for EDX spectroscopy. Furthermore, due to the smaller surface to bulk ratio for the large structures, a longer treatment is used for the EDX samples to ensure a sufficient oxygen incorporation.

However, with this method, it is possible to observe reasonable EDX signals, as shown in Figure 25 b). Additional peaks from C and F are suggested to be a result from the growth
6 COMPLEMENTARY SWITCHING IN SINGLE NB$_3$O$_7$(OH) NANOWIRES

process and sediments from the surrounding. To calculate the O/Nb ratio the oxygen signal has to be reduced by two times of the Si signal, as the substrate is detected in the signal, even for the large structures. A comparison of multiple oxygen/niobium ratios is given in Figure 25:

Figure 25: **EDX results.** a) Position of the EDX measurement, b) typical EDX signal, and c) calculated O/Nb ratio for sample with and without plasma treatment for different positions and samples.

It is observed, that the signal for different positions and different structures of the untreated, pristine samples scatter quite a bit. Therefore, multiple measurements are done to get a better statistic about the O/Nb ratio. The big scattering is related to an inhomogeneously distributed defect density within the large, untreated structures. However, the ratio of the plasma treated sample scatters only a bit, since the defects are reduced, making the crystal structure more stoichiometric and thus, overall more homogeneous. During the plasma treatment, highly reactive oxygen ions diffuse into the nanowire and occupy free defect locations, which leads to the reduction of oxygen vacancy defects [107, 237, 238]. In average, a higher oxygen/niobium ratio for the untreated samples is observed, which results from oxygen incorporation into the crystal during the plasma treatment. Oxygen vacancies act as n-type dopant in Nb$_3$O$_7$(OH) materials by adding electron states below the conduction band [69, 169]. The treatment reduces therefore the Fermi level, making the device less conductivity, which will be discussed in the next section.
6.2 Current-Voltage Characteristics and Endurance

Figure 26: Current-voltage (I-V) characteristics of Nb$_3$O$_7$(OH). a) Electroforming process, b) complementary switching curve, c) and d) I-V curve for a negative and positive polarity bias, respectively. The black line is always the first measurement, with gradually increases by cycle number to light green.

After mounting the device into the measurement setup as described in Section 3.2.3, an electroforming process (Section 2.3) is necessary, to switch the device from a non-conductive to a conductive state, shown in Figure 26 a). Therefore, a bias of 20 V is applied for 300 s. Afterwards, standard current-voltage (I-V) measurements are performed, to investigate the switching behavior of the nanowires. The color specifies the cycle number, whereas the first cycle is shown in black and the last in bright green. Within the first four to five measurements, the current height increases and a saturation to a stable switching behavior after the first five cycles. However, the devices show a complementary switching behavior, which has been observed for niobium oxide materials before [72]. The resistance decreases by increasing the voltage up to $\sim$12 V and afterwards increases again for even higher voltages. During backcycling, the device remains in its low conductive state. However, the resistance starts to decrease again after the polarity change up to a voltage of $\sim$−15 V, followed again by a current drop. Figure 26 c) and d) show ten I-V cycles for negative and positive applied
voltage regime, respectively. It shows, that the hysteresis behavior is not present, when only one polarity is applied. Therefore, a polarity change is necessary to observe switching, while it otherwise remains in its low conductive state. Therefore, the switching mechanism is attributed to an electric field driven mechanism as described in Section 2.3.1.

Figure 27: Endurance results of Nb$_3$O$_7$(OH). a) and b) are endurance results of two different Nb$_3$O$_7$(OH) single nanowires with the same preparation process and device architecture, but different endurance behaviors.

shows the endurance results of two different single Nb$_3$O$_7$(OH) nanowires, which are prepared under the same conditions. The readout voltage is 10 V for both devices. An on/off ratio of about one order of magnitude is observed for each device. However, the long-term behavior differs for different samples. After $\sim$100 cycles, the current starts to increase for the sample shown in a), whereas the device in b) show a quite constant behavior up to a rupture of the current after $\sim$700 cycles. Although the two devices show a similar complementary switching behavior during cycling the differences within the endurance measurements are important when thinking about long-term application. An extensive statistical study is necessary to find a reasonable explanation for the difference within the endurance measurements, as a low sample-to-sample variation over a large timescale is significant for application purposes.

However, as a second step, the devices are oxygen plasma treated for 10 s. As found in Section 6.1 the plasma treatment results in a diffusion of ionized, radical oxygen species into the nanowire, leading to a reduction of the oxygen vacancy concentration. As oxygen vacancies are electron donor defects [169], a reduction of the oxygen vacancy concentration due to the oxygen plasma treatment results in a lower conductivity of the nanowire and an increased metal/MO interface barrier due to a Fermi level lowering. Figure 28 shows the I-V behavior of an oxygen plasma treated sample in comparison to an untreated sample. It is observed, that the device has lost its conductivity completely even though SEM investigations do not show any visible change of the nanowire position, the morphology, or the surface of the nanowire itself. However, EDX results confirm the increase of the oxygen content, which make the devices less conductive. Moreover, it is observed, that the oxygen plasma treatment is only slightly reversible. A long electroforming process of at least 1 h at 20 V could not bring the device back to its initial conductive state. At some point, however, a current could be
6.3 The Memristive Switching Mechanism

Figure 28: **Influence of plasma treatment on the conductivity.** The green curve shows the I-V behavior of the untreated sample. After plasma treatment (red), the device is not conductive any more. A long electroforming process (at least 1 h) lead to an increased conductivity, whereas the initial conductivity could not be reached back.

measured again, which results in a CRS with smaller currents than before, seen in Figure 28 (second forming). Even longer forming processes could not bring back the initial conduction state of the device. However, during electroforming a small current flows through the device, gradually heating the surrounding of the localized current flow by Joule heating. This leads to a reduction of the oxygen content, creating n-type oxygen vacancies. This indicates the importance of oxygen vacancies for resistive switching in single Nb$_3$O$_7$(OH) nanowires, which will be discussed in the following part.

6.3. The Memristive Switching Mechanism

CRS is usually explained by the migration of oxygen vacancies under the influence of an electric field, which can be supported by a temperature gradient, as explained in Section 2.3. Based on the previous findings combined with discoveries found in literature [72, 239, 240] a schematic of the expected switching process within the single Nb$_3$O$_7$(OH) nanowires is developed and shown in Figure 29. During electroforming heat induced oxidation within the nanowires lead to formation of a conductive path within the device [34, 125, 150]. Local Joule heating effects lead to redox processes within the nanowire, increasing the oxygen vacancy concentration [126]. The I-V curves afterwards show an increase in current during cycling within the first five cycles. An unbalanced accumulation of oxygen vacancies is suggested, as the ions will most likely accumulate already at one electrode due to the electric field during electroforming, which is then balanced out during cycling. At some point, the migration of oxygen vacancies stabilizes to an equilibrium switching state, so that no current increase during cycling is observed anymore. The first five I-V cycles can therefor be seen as part of the electroforming process, until a stabilized switching state is reached. The device can then be switched between different resistance states upon cycling, following a CRS behavior.
Figure 29: Schematic of the switching mechanism in Nb$_3$O$_7$(OH) nanowires. A conductive channel is formed in 1 by increasing the voltage, which decreases the resistance of the device. At a specific voltage, the current decreases, although the voltage is increased further, due to the repulsion of the positively charged oxygen vacancies (O$_{\text{vac}}$) at the electrode, shown in 2. In 3, the conductive channel is formed again due to the polarity change, whereas the high conductive state is lost, if the voltage is again too large (4).
However, within the equilibrium state, oxygen vacancies are expected to be uniformly distributed with the nanowire. Therefore, the device is in a high conductive state when 0 V is applied, which even increases the voltage is increased from zero to higher bias, as shown in Figure 29 (1). By increasing the voltage further the positively charged oxygen vacancies are more and more repelled at the positive electrode and even further attracted at the negatively charged electrode, as illustrated in Figure 29 (2). This results in a disruption of the conductive path, as well as an increased interface barrier for electrons and hence, a lower bulk and interface conductivity, respectively. A change of the polarity of the applied field in (3) leads to a backward redistribution of the oxygen vacancies upon the field and the before arisen concentration gradient. At some point, a conductive channel is gained back, so that the device is set back to a LRS. If the voltage goes further to even large negative values, the oxygen vacancies get repelled at the opposite electrode (4) and the high conductivity is lost. The complementary switching behavior is therefore suggested to mainly happen at the interfaces, which has been described before [122]. It has to be mentioned, that oxygen vacancy migration can be supported by a temperature gradient, as Joule heating effects will be present due to the current flow, see Section 2.3 for further information.

Other reports on metal oxide single nanowire memristive systems visualized the oxygen vacancy accumulation at the electrode interface visible by in-situ electron loss spectroscopy [186, 241–248]. Although their devices show mostly bipolar or unipolar switching mechanism, the underlying mechanism of oxygen vacancy migration affirm our conclusions. Jeong et al. [146] reported the coexistence of URS and BRS mechanism within TiO$_2$ thin-films and Nallagatla et al. [185] showed shift from BRS to CRS by applying different electroforming processes. Therefore, the different switching mechanism compared to the previous references is related to a different electroforming process, resulting in a different defect structure and oxygen vacancy amount within the devices. It underlays the great impact of the crystal defects on the resulting switching mechanism.

6.3.1. The Destructive Readout Process

Upon probing the resistance state of the device, a readout voltage is applied, which is typically small enough to prevent switching effects during readout, but large enough for a high on/off ratio. Within CRS devices, the readout process usually leads to a destruction of the resistance state, which needs to be rewritten afterwards [55, 114, 154, 198]. The destructive readout process of the Nb$_3$O$_7$(OH) nanowire devices show a readout voltage amplitude and polarity dependence as shown in Figure 30.

Eight different readout amplitudes (12, -12, 10, -10, 8, -8, 6, -6 V) are applied after a 20 and -20 V write pulse of 5 s. The opposite voltage polarity has been chosen to probe the resistance state, which is then comparable to a time resolved I-V curve. With this method, only the time-dependent destruction of the HRS for different amplitudes is investigated.
Figure 30: Analyzation of the destructive readout current. The destruction of the readout current is investigated by time-dependent measurements, with different readout voltage amplitudes, shown above. The write process is done for 20 V and −20 V for 5 s.
During the 'write' process, the system is set into a HRS. During readout, the resistance decreases in the beginning, followed by a current drop, bringing the device back to a HRS. This process is similar to the schematic, shown in Figure 29. There, the oxygen vacancies are repelled at the positive electrode for a large voltage potential. Upon switching the polarity, the oxygen vacancies migrate opposite the previous direction upon the field direction change and additionally driven by the concentration gradient. However, if the readout process takes long enough, oxygen vacancies of the now positive electrode are pushed away, increasing the interface barrier for electrons, hence, increasing the resistance of the device again. This effect is much slower for smaller potentials, whereas at 6 V the difference of the current in the beginning to the current after the readout is quite small, so that the on/off ratio is too small and a voltage $\leq 6$ V is necessary for reasonable on/off ratios. For negative write operations, the device is in condition (2) after the write process (Figure 29).

The readout operation leads to a migration of oxygen vacancies to the negative electrode and a reduction at the positive electrode, until a conductive path is formed (3). However, the oxygen vacancies are further repelled from the positive electrode over time, increasing the interface barrier for electrons and reducing the conductivity again (4).

It has to be mentioned, that for application purposes, the readout voltage to probe the resistance state of the device is always the same. Here, a study about the temporal behavior of the destructive readout current in regard to the I-V curves is demonstrated. It shows, that it can be useful to make studies to find an appropriate readout voltage, since the destruction is not only dependent on the voltage amplitude, but also on the polarity for the Nb$_3$O$_7$(OH) nanowire device. A slow destruction is therefore possible for smaller positive voltages and less energy needs to be consumed to rewrite the resistance state again. It is furthermore suggested, that with short readout pulses, the readout process is possible for several pulses, without destroying the resistance state and a re-write is not needed after every readout procedure. This could reduce the total energy consumption of the CRS, as the re-write process is only necessary after several readout processes. This however, needs to be investigated further by pulsed readout process with different frequencies.

6.4. Summary

Single Nb$_3$O$_7$(OH) nanowires are shown to be a promising memristive candidate for neuromorphic computing. Atomic resolution images show a orthorhombic crystal structure with planar and point defects within the $\sim 3\mu$m nanowire. Single Nb$_3$O$_7$(OH) nanowires are successfully contacted by dropping an EtOH/Nb$_3$O$_7$(OH) solution on top of fingerelectrode substrates. By applying a high voltage for 300s, the current is increased, by increasing the defect density during the electroforming process. Local Joule heating effects lead to an outward diffusion of oxygen ions, leaving n-type conductive oxygen vacancies behind. Afterwards, the device can be switched between a high and a low resistance state, showing a
CRS behavior. The influence of the oxygen vacancies on the switching performance is further supported by treating the devices with oxygen plasma for few seconds. EDX investigations show a reduction of the oxygen vacancy concentration and hence, a less-defective and more perfect Nb$_3$O$_7$(OH) crystal structure. Consequentially, a total insulating behavior due to the lack of charge carrier ions and reduction of the valence band transport is observed. However, an electroforming process of at least 1 h could bring back the device conductivity, whereas the initial current height could never be reached again. A schematic based on the previous results shows the suggested switching mechanism of moving oxygen vacancies due to the applied electric field. Nevertheless, complementary switching devices show a destruction of the low resistance state during readout. This happens on different time-scales for different applied bias. Interestingly, the readout behavior is different for the same amplitude, but different polarities, which could be a result from the asymmetric electroforming procedure. However, it is an important factor to be considered when finding the appropriate readout voltage.
7. Conclusion and Outlook

Conclusion

In summary, the memristive behavior of metal oxide nanowires has been shown to be controllable by targeted defect engineering and regulated electronic stimulation processes. This makes them promising candidates for artificial synapses to be implemented in neuromorphic computing systems. Two material systems, TiO\textsubscript{2} NRAs and Nb\textsubscript{3}O\textsubscript{7}(OH) single nanowires, are therefore presented as model example for metal oxide nanowire memristors.

TiO\textsubscript{2} nanorod arrays are grown directly on the bottom FTO electrode substrate by a hydrothermal growth method. Multiple nanowires are contacted simultaneously by a mm-sized gold tip electrode from the top. With this method, the conductive and memristive behavior of nanorod arrays with a manufacturing growth temperature of 150°C, 180°C, and 220°C are investigated. The nanowires show a V-shaped grain boundary defect structure, with oxygen vacancies accumulating along those grain boundaries. With increasing growth temperature, the grain boundary distance becomes larger, so that the nanowires are more stoichiometric for higher growth temperatures and the defect density decreases with increasing growth temperature. However, all NRA devices show a metastable resistive switching behavior, i.e. resistance states are unstable and decay into the initial, equilibrium resistance state over time. Thereby, the grain boundary and defect density arrangement has shown to impact the metastable resistive switching behavior greatly. The high oxygen vacancy mobility along grain boundaries in combination with the increased oxygen vacancy concentration leads to a faster decay of resistance states within NRAs grown at 150°C. Furthermore, local Joule heating effects play an even larger role for the low conductive devices, which leads to oxygen reduction processes inside the nanowire. This cause a slower relaxation of the system back to its equilibrium state. Therefore, the low oxygen vacancy density for larger growth temperatures is shown to be responsible for the long lifetime of the low resistance state.

Based on those findings, the possibility for biological synapse emulation is studied. Therefore, transitions from short- to long-term memories are enabled by choosing the appropriate stimulation voltage duration and amplitude. Furthermore, by applying voltage pulse trains with different frequencies and amplitudes, the spike-rate dependent plasticity function of biological synapses has been demonstrated. The signal is probed between each pulse and after each pulse train by a small voltage, which is too low to induce resistive switching. The decay of the current (the excitatory post-synaptic current) has been shown to follow...
perfectly Kohlrausch’s stretched exponential function. It describes relaxation processes with stochastically distributed rearrangements in disordered systems, which fits perfectly to the redistribution model of the oxygen vacancies.

Additionally, single Nb$_3$O$_7$(OH) nanowire memristive properties are compared to the previous findings. It is shown, that the oxygen vacancy migration model can be adapted from TiO$_2$ switching model. The Nb$_3$O$_7$(OH) memristive systems show a CRS behavior, whereas the difference to the TiO$_2$ is suggested to result from the different defect structure in the device. However, in CRS devices it is known, that the physical switching happens close to the electrode interfaces, which could be perfectly adapted to our system. Furthermore, the devices show a destruction of the resistance state during a readout process, whereas it is found, that the destruction time can be reduced by choosing the appropriate readout voltage and polarity.

**Outlook**

The great impact of the defect structure on the memristive switching mechanism is further supported by the work of Xiao et al. [249]. They observe a different switching behavior for a similar TiO$_2$ NRA system, which is related to the different defect structure. Therefore, the transfer of the mechanism model between different metal oxides should be used with caution and requires a complete knowledge of the material system, atomic arrangement, and defect nature of the memristive material. Those findings are quite important for application purposes, where precise device performance is necessary and only small device-to-device variations are allowed [37]. A targeted manipulation and control of the inner structure of the nanowires is required, which could be presented in this work by a precise manufacturing process.

Furthermore, to compete with recent neuromorphic computing systems based on complementary metal-oxide-semiconductor (CMOS) devices, position controlled growth and scaling down the devices to several nanometers is required [37]. The scalability of the our devices is reached by adjusting the hydrothermal growth parameters, whereas it needs to be studies, whether the memristive behavior can be received. A position controlled growth of TiO$_2$ has been successfully demonstrated by Kalb et al. [235]. By combining these two methods a controlled growth of single standing nanowires in a 3D crossbar array structure is conceivable, whereby further research is necessary to find solutions for the commercial use.

Besides, our finding on Nb$_3$O$_7$(OH) single nanowires raise further questions about the possibilities to implement Nb$_3$O$_7$(OH) as artificial synapse. To the best of our knowledge, no position controlled growth technique for Nb$_3$O$_7$(OH) nanowires exist so far. Additionally, a detailed study about the impact of the growth parameters on the defect structure is required, to optimize the sample-to-sample variation in nanometer sized Nb$_3$O$_7$(OH). However, based on the promising results of this work, research on this topic should definitely be continued.
Nevertheless, information about the defect structures and their influence on the electronic properties can further be used in various application and research fields, like e.g. in solar cells. The high surface to volume ratio of nanowires has thereby shown to improve the hybrid solar cell performance considerably [87, 250]. However, the defect structure of the nanostructures play a crucial role in the performance of the solar cells. As we showed in previous works, the growth temperature of the presented TiO$_2$ nanowire arrays impacts the solar cell performance, which is summarized in [103, 104].

This is only one example which shows the importance of understanding and controlling the defect structure in metal oxide nanostructures, besides memristive devices. Such examples can be found in many research and application fields, like photocatalysts, sensors, lab-on-a-chip devices, and many more [75]. Therefore, the findings of the present work do not only advance the memristive research field, but can additionally be applied in all kinds of metal oxide research.
A. Appendix - Emulation of Synaptic Functions with TiO$_2$ Nanorod Arrays

Figure 31: STDP for different voltages. The frequency is 0.5 Hz.

Figure 32: STDP for different frequencies. Left: A small negative bias of $-1\,\text{V}$ and right: Pulse bias of $3.3\,\text{V}$ with small frequencies.
References


References


[30] Henry Markram, Karlheinz Meier, Thomas Lippert, Sten Grillner, Richard Frackowiak, Stanislas Dehaene, Alois Knoll, Haim Sompolinsky, Kris Verstreken, Javier DeFelipe,
References


References


References


References


References


[161] Chao Du, Wen Ma, Ting Chang, Patrick Sheridan, and Wei D. Lu. Biorealistic Implementation of Synaptic Functions with Oxide Memristors through


References


References


References


References


References


[242] Gianluca Milano, Samuele Porro, Ilia Valov, and Carlo Ricciardi. Recent Developments and Perspectives for Memristive Devices Based on Metal Oxide


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Publications, Conferences, Teaching, and Supervision

Publications


Conferences

2020

2019
European Materials Research Society (EMRS) Spring Meeting in Warsaw, Poland: Memristive Functionalities of Hydrothermally Grown TiO$_2$ Nanorod Arrays - **oral presentation**

2019

2019
Deutsche Physikalische Gesellschaft in Regensburg, Germany: Investigating the Memristive Behavior of Hydrothermally Grown TiO$_2$ Nanorod Arrays - **oral presentation**

2018
International Workshop on Hybrid Perovskite Photovoltaic and Optoelectronic Devices in Islamabad, Pakistan: Titanium Dioxide (TiO$_2$) Nanostructures: Application, Fabrication, and Characterization - **oral presentation**

2018
Deutsche Physikalische Gesellschaft in Berlin, Germany: Controlling and Analyzing the Conductivity of TiO$_2$ Nanorod Arrays - **oral presentation**

2017
Statusworkshop 2017 des Kompetenznetzes „Funktionelle Nanostrukturen“ in Bad Herrenalb, Germany: Conduction Mechanisms of Titanium Oxide Nanorod Arrays - **poster presentation**

2017
European Materials Research Society (EMRS) Fall Meeting in Strasbourg, France: Electronic properties of large grain MAPbI$_3$ perovskite films fabricated via methylamine gas healing - **oral presentation**

2017
Workshop of the Sonderforschungsbereich (SFB) in Bad Irsee, Germany: Optoelectronic properties on Interface of Metal Oxide Nanostructures - **poster presentation**
**Teaching**

SS - Sommersemester (summer term), WS - Wintersemester (winterterm)

**SS 2020**  
Tutor for the *organic photovoltaic* lecture - Master course at the Universität Konstanz

**WS 2019/20**  
Supervision of the advanced practical course, experiment: *Solar Cells*  
- Master course at the Universität Konstanz

**SS 2019**  
Tutor for the *organic photovoltaic* lecture and supervision of the advanced practical course, experiment: *Solar Cells* - Master courses at the Universität Konstanz

**WS 2018/19**  
Tutor for the *integrated course III* - Bachelor course at the Universität Konstanz

**SS 2018**  
Supervision of the beginner practical course, experiment: *Franck-Hertz* - Bachelor course at the Universität Konstanz

**WS 2017/18**  
Tutor for the *integrated course I* - Bachelor course at the Universität Konstanz

**SS 2017**  
Tutor for the integrated course II - Bachelor course at the Universität Konstanz
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<td>Characterization of FTO-sheets Using a 4-point Probe Technique</td>
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<td>Maximilian Brochnow</td>
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<td>Temperature dependent IV-characteristics of TiO₂ Nanorod Arrays</td>
<td>Domenik Vögel</td>
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I am certainly not known for being a good writer and I will hardly find the right words for how grateful I am for all the support and help I received during my PhD. However, I will try my best!

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