Transmission electron microscopy studies of ion migration in resistive switching manganite-platinum heterostructures

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Contents

1	Preface	1
2	Scientific Background - PCMO as model system for resistive switching	5
2.1	Crystallographic structure	5
2.2	Electronic Structure and doping dependent resistivity	6
2.3	Electronic transport	7
2.4	Oxygen diffusion in manganites	8
2.5	Resistive switching in PCMO sandwiched by noble metal electrodes	9
3	Developing an <i>in situ</i> environmental TEM set up for investigations of resistive switching mechanisms in Pt-Pr_{1-x}Ca_xMnO_{3-δ}-Pt sandwich structures	13
3.1	Introduction	14
3.2	Methods	16
3.3	Results and Discussion	20
3.3.1	Transport Properties	20
3.3.2	Redox reactions during <i>in situ</i> TEM experiments	20
3.3.3	Resistive Switching	26
3.4	Conclusions	32
3.5	Supplemental Material	33
3.5.1	<i>In situ</i> resistive switching experiments with nano-tip	33
3.5.2	Onset for non-volatile resistive switching in micro-pillars	34
3.5.3	Evolution of remanent resistance and manganese valence during the <i>in situ</i> resistive switching experiment with fixed contacts	35
3.5.4	Recrystallisation under electron beam irradiation	39
3.5.5	Integration of EELS oxygen K edge intensity and determining of O K A/B ratio	41
4	Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO₃	43
4.1	Introduction	44
4.2	Materials and Methods	46
4.2.1	Sample preparation	46
4.2.2	Charge Attachment Induced Transport	46

4.2.3	Depth profiling	47
4.2.4	Electron microscopy	47
4.3	Results	48
4.3.1	ToF-SIMS analysis - data processing and interpretation	48
4.3.2	Electron microscopy	50
4.3.3	Diffusion of potassium in the PMO	50
4.4	Discussion	56
4.5	Summary	57
4.6	Supplemental Material	58
5	Role of oxygen vacancies for resistive switching in noble metal sandwiched $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$	61
5.1	Introduction	62
5.2	Methods and Materials	63
5.3	Results and Discussion	64
5.4	Summary	69
5.5	Supplemental Material	70
5.5.1	PCMO phase decomposition due to vacuum annealing	70
5.5.2	XRD analysis of as-grown and post-treated PCMO	70
5.5.3	Manganese valence maps near the surface	70
5.5.4	Electric characterization of the micro-pillars	70
6	General Discussion and Summary	77
	Author Contributions	94
	Curriculum Vitae	96

List of Figures

1.1	Schematic Flash- and oxide-memory cells	2
2.1	Crystal Structure of PCMO	6
2.2	Self-diffusion constant of Pr, Mn and O in LaMnO ₃ obtained by tracer-diffusion experiments	9
2.3	Model of oxygen vancancy migration induced resisistive switching	11
3.1	Sample geometry for <i>in situ</i> TEM cross-plane biasing	17
3.2	Sample geometry and experimental set up for resistive switching experiments on micro-pillars in SEM	18
3.3	Electric characterization of the Pt/PCMO/Pt TEM lamella	21
3.4	Correlation of Oxygen K-edge properties with Mn valence	23
3.5	Oxidation of PCMO induced by electron beam illumination in oxygen environment	24
3.6	Redox reactions of PCMO during electric-stimulation	27
3.7	Oxygen redistribution before and during resistive switching	29
3.8	Electric field- and beam-induced resistive switching	30
3.9	Oxygen electromigration	31
3.10	<i>In situ</i> TEM switching experiments with nano-tip	33
3.11	Representative $R - V$ -characteristics of micro-pillar devices in order to determine switching-onset	34
3.12	Overview of resistance changes during <i>in situ</i> resistive switching experiment	37
3.13	Manganese valence maps after applied voltages	38
3.14	Details of cycle 24 ($V_{exc,max} = -1.5$ V)	39
3.15	HR-TEM images of the top left corner of a lamella before a) before and b) after the <i>in situ</i> resistive switching experiment	40
3.16	Integration and Gaussian fitting of the O K-edge	41
4.1	An illustration of the diffusion of potassium through the bulk and along the grain boundaries of PMO.	44
4.2	Concentration profile of the bombarded PrMnO ₃	49
4.3	TEM,STEM-EDX analysis of PMO after CAIT	51
4.4	TEM twin boundary analysis	52

4.5	Simulated concentration distributions using Fisher's model	53
4.6	Normalized concentration along the thickness of the film from ToF-SIMS, simulated mixed pathway diffusion and simulated sole bulk diffusion with no grain boundary	54
4.7	ToF-SIMS raw data of the normalized data shown in Figure 4.2	59
4.8	ToF-SIMS-Analysis of a PMO reference without K^+ -BIIT	59
4.9	Illustration of the correlation between K^+ and Pr^+ signals	60
5.1	SEM cross-section image of a micro-pillar	64
5.2	Mn valence of the three different films in virgin state	66
5.3	Resistive switching behavior of differently post-treated heterostructures . .	68
5.4	TEM investigation of an annealed PCMO film grown on STO	71
5.5	X-ray diffraction pattern of differently post-treated PCMO films on Pt/MgO	72
5.6	Representative manganese valence maps obtained by STEM-EELS near the top electrodes	73
5.7	Calculated relative resistances resulting from the Mn valence maps of Fig. 5.6	74
5.8	Electric characterization of micro-pillars	75

CHAPTER 1

Preface

With the digital revolution, an increasing volume of nonvolatile electronic data storage is required, which is fast, small and cheap. The current development in this field is that *Solid State Drives (SSD)* complement or even replace conventional on magnetization based *Hard Disc Drives (HDD)*. *SSDs* are assemblies of integrated transistors. They provide higher data-transfer rates, lower latency and access times, higher storage density, lower power consumption and higher reliability [1–3]. Additionally, they do not need mechanic parts like the magnetic head of a *HDD* making them more shock resistant.

The basic devices of state-of-the-art *SSDs* are based on the *Flash*-technology developed in the early 1980s by *Toshiba* (see figure 1.1 a)). In these devices, voltage pulses between control gate and source/drain change the charge of the floating gate, which, in turn, influence the conductivity between source and drain. In this way, it is possible to switch the required two different states (conducting, insulating) using solely voltage pulses. The main downsides of *Flash*-memory are its high cost, limitations in scalability and its limited life-time due to the returning high voltages applied on the insulating layers surrounding the floating gate [4–6].

As an alternative, devices based on resistive switching oxides have come into focus in the last years [5, 7]. These materials are characterized by their intrinsic non-volatile resistance change induced by electric pulses [8–11]. As a consequence, the structure of such devices is simpler (see figure 1.1 b)) and has therefore the potential to be scaled down to very small structure sizes [7]. Additionally, most oxides are very cheap, the remanent resistive switching process is fast [12] and the required voltages are an order of magnitude lower than in *Flash*-devices [13]. These properties make them also highly interesting for resistive switching random access memory (ReRAM) applications [5, 14].

Consequently, *Sharp Laboratories Of America Inc.* intensively researched on ReRAM devices consisting of a $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin-film sandwiched by metal electrodes in the early 2000s (e.g. [15]). Although this particular approach was finally not realized due to lack of long-term stability, in general, oxides remain promising candidates for a new generation of storage, especially in the field of ReRAM [16–19].

Resistive switching oxides also could play a crucial role in the research field of neuromorphic computing [20], i.e. emulation of the biological neural system by artificial synapses and neurons. Conventional computers are based on the *von Neumann*-principle, i.e. the

Figure 1.1: Schematic memory cells: a) Flash: The device consists of differently doped semiconductors. The floating gate is enclosed by an insulating layer (mostly silicon oxide). b) ReRAM: A thin layer of a oxide is sandwiched by metal contacts.

separation of processing and storage. This approach has the disadvantage of the so called *von Neumann-bottleneck*, i.e. the connection between processor and storage limits the data processing.

Neuromorphic computing avoids this problem, because processing and storage are performed at the same location. There are already great advances in the field of emulated neural networks (e.g. [21, 22]), however, commonly these networks are simulated on conventional *von Neumann*-based platforms and are thus limited in efficiency.

The next step would be a direct emulation of the synapses and neurons by electronic elements. Redox-based resistive switching materials are promising materials for this approach. They can modulate the electric signal by a changed resistance state in order to get similar results as biochemical synapses. Furthermore, the above mentioned advantages of easy scalability and lower energy requirements to change their state, complemented by the ability to store multiple bits of information per element (by different resistances [23]) strongly favors oxides for these applications [24–27].

The basic mechanisms of resistive switching in oxides vary strongly with the used material system [5, 14] (see also chapter 2.5). An universal review of all possible systems is therefore beyond the scope of this work. Instead, the focus is on $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO), which serves as a model system. PCMO was one of the first investigated resistive switching oxides [28] and also considered for industrial application as mentioned above.

Besides the oxide itself, the material of the electrodes plays an important role for the switching characteristic of a device. Usually, unnoble metals such as Cu, Ti, W or the noble metals Ag, Au and Pt are used. These two categories provide different polarities of bipolar switching [29]. The foundation of the switching effect in PCMO devices with electrodes made of unnoble metals has been identified as redox-reactions at the interface between the electrode and the oxide leading to oxygen deficient and high resistive areas of PCMO near the interface [30]. However, noble-metal-PCMO devices also show a bipolar resistive switching effect [13, 29]. Thus, the underlying mechanism is either different for noble and unnoble metals or there is one unique switching mechanism within the oxide

which is only modified by the different degree of redox-activity of the electrode-oxide interfaces. Following the second hypothesis, it is consequent to concentrate on the process within PCMO and use noble-metal electrodes as contacts, in this work made of platinum.

The electric transport and resistive switching properties of this material system have been electrically analyzed in detail by M. Scherff [31]. In summary, his results point to a model of oxygen ion migration in electric field as basic mechanism.

The following thesis is divided in three chapters, consisting of the publications

- Chapter 3: Developing an *in situ* environmental TEM set up for investigations of resistive switching mechanisms in Pt-Pr_{1-x}Ca_xMnO_{3-δ}-Pt sandwich structures
- Chapter 4: Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO₃
- Chapter 5: Role of oxygen vacancies for resistive switching in noble metal sandwiched Pr_{1-x}Ca_xMnO_{3-δ}

Chapter 3 aims to give evidences for the model suggested by M. Scherff by measuring the spatial redistribution of oxygen after different stages of applied voltages in an *in situ* environmental transmission electron microscopy (ETEM) experiment. The development of a novel measurement geometry with fixed contacts is described as well as the influence of contact resistance, electron beam and gas environment. Subsequently, the spatial oxygen distribution within the film, measured by electron energy loss spectroscopy in scanning mode (STEM-EELS) is correlated to previously applied voltage pulses. The chapter establishes the first *in situ* resistive switching experiments in oxygen atmospheres and confirms that such a controlled environment is necessary for mechanistic studies of switching in the transmission electron microscope (TEM). The reason is that otherwise oxygen losses in high vacuum would strongly influence the observations.

Chapter 4 is concerned with the determination of the ionic conductivity of K⁺-ions in PrMnO₃ at room temperature. This study is based on the combined analysis of charge attachment induced transport (CAIT), secondary ion mass spectroscopy, transmission electron microscopy (TEM) and theoretical simulations according to Fisher's model. Findings are, among others, enhanced grain boundary diffusion and thus unavoidable easy diffusion pathways even in epitaxial PMO due to twin boundaries. The experiments demonstrate the applicability of CAIT to systems with mixed conductivity and thus has a huge potential to be a basis for future studies of oxygen migration in PCMO.

In chapter 5 the interplay of oxygen deficient areas at the interface to the top electrode and their influence on the initial resistance and resistive switching characteristics is analyzed. As a result, a model is presented, where switching is based on an oxygen vacancy induced metal-insulator transition. This contrasts strongly with the well-understood doping-mechanism in e.g. SrTiO₃ [32] or HfO₂ [33], where oxygen vacancies cause an enhanced electric conductivity.

In the general discussion (chapter 6) the recurring theme of all chapters is addressed, condensed in the following questions:

Firstly, does the resistive switching effect in PCMO involve a redistribution of atoms? If so, what atoms are redistributed and does the redistribution take place along with valence changes (redistribution of oxygen ions) or in charge neutrality (additional redistribution of the cations)?

On the basis of this knowledge, the issue of the exact correlation of anion and/or cation redistribution and resistance change arises. An important point in this context is the fact that oxygen vacancies act as electron donors in PCMO, which counteracts the Ca-hole doping. So, this issue includes the need for investigations if oxygen vacancies mainly reduce doping level or can also induce other effects like a metal-insulator transition.

Furthermore, a major question is what driving force is responsible for the potential redistributions. Especially, it is interesting to clarify in what way the applied electric field, the temperature and the potential concentration gradient influences the ion migration.

Last, but not least, an important point is the question where the switching is located: at the oxide-electrode interface or in the bulk. If the switching takes mainly place at the interfaces, additionally, the question arises about the impact of the electrode material on the interface ion migration or redox process.

CHAPTER 2

Scientific Background - PCMO as model system for resistive switching

2.1 Crystallographic structure

The crystallographic structure of the perovskite manganite $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is at room temperature characterized by the mismatch of the ionic radii causing a tilting of the MnO_6 octahedra. These tilts are slightly different within the unit cell, so an orthorhombic structure arises. The lattice parameters vary with the doping level x in a range of $a = 5.300(3) - 5.442(2) \text{ \AA}$, $b = 5.300(3) - 5.617(3) \text{ \AA}$ and $c = 7.495(5) - 7.635(3) \text{ \AA}$ (in $Pbnm$ space group) [34] (see figure 2.1). PCMO thin films usually provide a large variety of twin domains, due to the fact, that these differences are only induced by small changes in the octahedral tilt system [35]. At temperatures above ca. 1000 K the octahedral tilt vanishes and the structure changes to the cubic $R\bar{3}C$ space group [36]. The thin-films investigated in this work are deposited at ca. 1100 K and are subsequently cooled down to room temperature at a rate of about 30 K per minute. Therefore, the phase transition $R\bar{3}C$ to $Pbnm$ probably has significant influence on the stress-strain state. Vice-versa it is plausible that the stress-strain state of the thin-film, e.g. by the lattice mismatch to the substrate, has influence on the creation of twin boundaries.

Figure 2.1: Crystal Structure of PCMO. Blue: Praseodymium/ Calcium, purple: Manganese, red: Oxygen. The size of the atoms is not scaled for the sake of clarity.

2.2 Electronic Structure and doping dependent resistivity

In the orthorhombic structure, investigated in this work, the Mn-O-Mn bonding angle varies in the range of $149\text{-}160^\circ$. It strongly affects the orbital overlap of the manganese and the oxygen sites and, thus, influence the electronic structure and the transport properties [37].

The electronic structure near the Fermi energy is dominated by Mn $3d$ and O $2p$ hybrid states. The octahedral Mn-O configuration leads to crystal-field splitting of the five Mn $3d$ states into three t_{2g} and two e_g states, which are all in high-spin configuration because of strong Hunds coupling. As a result, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ has three t_{2g} and $(1-x)$ e_g electrons with parallel spin per MnO_6 -site. For $x = 0$, the oxidation state of the Mn-sites is $+3$ and each MnO_6 unit contains one e_g electron suggesting a metallic state. However, due to ordered static Jahn-Teller distortion the e_g -band splits into e_g^1 and e_g^2 with an energy band gap of about 1.3 eV forming a Mott-like insulator [30, 38]. Increasing x by Ca^{2+} -doping leads to weaker Jahn-Teller distortion and mobile hot polarons resulting in a smaller band gap [38]. Consequently, the conductivity increases with x .

A similar situation arises, when Ca-doped PCMO is reduced to $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$. For each oxygen vacancy two electron holes are annihilated, resulting in similar effects on the electronic band structure as a reduction of the Ca-doping [39, 40]. This behavior is in contrast to the commonly observed systems like SrTiO_3 or HfO_2 , where oxygen vacancies act as electron donors, so oxygen vacancies increase conductivity [32, 33]. According to Lee et al., even the insulating PMO-configuration can be reached at $\delta = x/2$ leading to

an oxygen vacancy induced metal-insulator transition [30]. Such a transition would have dramatic consequences for ReRAM systems based on PCMO as described in chapter 5.

2.3 Electronic transport

The electronic transport in PCMO in the here observed temperature regime above the half Debye temperature (≈ 150 K) is explained by thermally activated hopping of small polarons (TAP) along the Mn-O-Mn bonds in the so-called “Two-site model” [41–43]. Assuming adiabatic polaron movement, it is valid for the conductivity in this model:

$$\sigma_h(T) = \frac{\sigma_0}{T} \exp\left(\frac{-E_a}{k_B T}\right), \quad \sigma_0 = \frac{n_0 e^2 a^2 \nu_0}{2\pi k_b} \quad (2.1)$$

with adiabatic carrier density n_0 ($n_0 = 2.2 \times 10^{27} \frac{1}{\text{m}^3}$ for $x = 0.3$), knock-on-frequency $\nu_0 = 1.4 \times 10^{13} \frac{1}{\text{s}}$, hopping distance (= Mn distance) $a \approx 3.86 \text{ \AA}$ and typical activation energy $\approx 140 \text{ meV}$ [44]. $\sigma_h(T)$ has to be corrected by two terms for large electric fields $\frac{2k_B T}{ea} < E \ll \frac{4E_a}{ea}$ [45]:

$$\sigma(E, T) = \sigma_h(T) \times \frac{\sinh(\frac{eEa}{2k_B T})}{\frac{eEa}{2k_B T}} \times \exp\left(\frac{-(eEa)^2}{16E_a k_B T}\right) \quad (2.2)$$

The formulas take into account the gradient in the potential between the two sites due to the external field and the probability for tunneling. The model is valid for electric fields below $E = \frac{4E_a}{ea}$, i.e. for PCMO $E_{max} \approx 10^6 \text{ V/cm}$. The usually applied fields in this work are below $E \approx 1 \text{ V}/250 \text{ nm} \approx 4 \times 10^5 \text{ V/cm}$.

At high electric fields, temperature has a large influence on the resistance. As can be seen in equations 2.1 and 2.2, the conductivity exponentially decreases with increasing temperature. The resulting increased current, in turn, further increases temperature. This run-away-effect can even result in a negative differential resistance [46]. Therefore, experiments on devices with limited heat dissipation such as thin TEM lamellae as described in chapter 3 have to be conducted very carefully.

Due to the hopping along the Mn-O-Mn bonds, in general, the resistance is affected by changes in the Mn-O-Mn bonding angle and in turn changes in the respective orbital overlapp. Such changes can be, for example, inflicted by doping [34] or strain [35, 47]. Oxygen vacancies could thus change the electric transport via

- introducing a disorder potential giving rise to partial localization of polarons. However, measurements of the disorder potential in PCMO thin films give only a small contribution of about 10 meV to the activation energy of a hole polaron of the order of 140 meV [44].
- changing the carrier concentration and thus the electron ground state of the manganite. For doping levels with an orbitally ordered ground state, such as PrMnO_3 , a bandgap of about 1.3 eV separates the valence bond and conduction bond and thus leads to a metal-insulator-transition as described in section 2.2 and chapter 5.

2.4 Oxygen diffusion in manganites

Oxygen diffusion (driven by applied electric field) plays a major role in many models explaining resistive switching. Therefore, in addition to the overview of diffusion of potassium in PrMnO_3 in chapter 4, in the following section a short overview of oxygen diffusion in PCMO is given.

For the diffusion coefficient $D_{self,free}^O$ of oxygen diffusion in a 3D lattice without further limitations, it is valid [48]:

$$D_{self,free}^O = \frac{Z}{6} \omega a^2 \quad (2.3)$$

with the number of next neighbours Z , the hopping frequency ω and the hopping distance a .

In a crystal lattice, ω consists of the product of two possibilities, the one to hop to the next site ν_{hop} and the one of the existence of a vacancy at this site ν_{V_O} . Both values are based on thermally activated processes and can be expressed proportional to $\exp\left(\frac{-\Delta H}{kT} + \frac{-S}{k}\right)$, with the total enthalpy H , the Boltzmann constant k and the entropy S . Additionally, a correlation factor f has to be considered and represents a preferred hopping back due to the already distorted lattice on the way to the previous occupied site. As a consequence, it is valid for oxygen self diffusion in the crystal lattice:

$$D_{self}^O = \frac{Z}{6} \nu_{V_O} \nu_{hop} f a^2 \quad (2.4)$$

$$= \frac{Z}{6} \nu_0 f a^2 \exp\left(\frac{-\Delta S^{V_0}}{k} + \frac{-\Delta H^{V_0}}{kT}\right) \exp\left(\frac{-\Delta S^{hop}}{k} + \frac{-\Delta H^{hop}}{kT}\right) \quad (2.5)$$

$$= D_{0,self} \exp\left(-\frac{\Delta H^{V_0} + \Delta H^{hop}}{kT}\right) \quad (2.6)$$

Assuming there is no isotopic effect, the self diffusion coefficient is measurable in tracer diffusion experiments, e.g. diffusion of O^{18} in an O^{16} matrix. A comparison of self-diffusion constants for Pr [49], Mn [50, 51] and O [52] in LaMnO_3 is shown in figure 2.2. Roughly, the one of oxygen is one order of magnitude higher than the one of Mn and two orders of magnitude higher than the one of Pr in the observed temperature range above 1300 K.

In the complex perovskite structure, several further circumstances have to be taken into account for a deep understanding of the the diffusion processes. Obviously, chemical diffusion of oxygen into oxygen deficient volumes is an important process. Bak et al. [53] show that the chemical diffusion coefficient is in the same order of magnitude as the self-diffusion coefficient.

Besides the interaction with vacancies, also the microstructure is important for the diffusion kinetics. E.g. the oxygen diffusion along grain boundaries is three orders of magnitude larger than bulk diffusion [52, 54]. Moreover, the kinetics for oxidation and reduction can differ, depending on which defects are involved into the transport, oxygen vacancies (reduction) or cation vacancies (oxidation) [53].

Figure 2.2: Self-diffusion constant of Pr, Mn and O in LaMnO_3 obtained by tracer-diffusion experiments. The dashed line is an extrapolation of the obtained oxygen data to high temperatures.

2.5 Resistive switching in PCMO sandwiched by noble metal electrodes

Exceeding certain onset voltages, PCMO devices sandwiched by metal electrodes show a non-volatile resistive switching effect [28]. This means electric pulses can switch the electric resistance from a low resistance state (LRS) to a high resistance state (HRS) and vice versa. This switching is bipolar, i.e. switching from HRS to LRS requires electric pulses with opposite polarity to switching from LRS to HRS [13,29,31,55]. In Pt-PCMO-Pt thin-film devices, as investigated in chapter 3 and 5, two different bipolar switching regimes are present: At low voltages or short pulses, switching from LRS to HRS takes place with positive bias at the top electrode, defined as *Positive* or *Clockwise Switching*. Further increase of the excitation pulse voltage or duration results in a reversed switching behavior, i.e. a transition from HRS to LRS by positive bias at the top electrode, called *Negative* or *Counter-Clockwise Switching*.

In general, resistive switching can be classified by two criteria, the location (bulk or at interface) and the type of the dominating physical mechanism (thermal, electronic or ionic) [14].

Switching induced by thermal effects is mostly unipolar, i.e the switching direction is dependent of the applied voltage level instead of the polarity. An example is a voltage-induced dielectric breakdown forming a conducting filament. Further increase of the

voltage results in increasing Joule heating and finally melting and disruption of the filament, e.g. in NiO [56, 57] or TiO₂ [58].

Electronic effects are the modification of the electronic structure by charge injection. For example, charge-trapping at defects [59] or metal-insulator transitions on the principle of charge injection counteracting doping [30, 60–62].

The third category describes systems where either anion migration within the oxide results in redox-reactions with the electrodes or the electrochemically active electrode material (e.g. Ag) is ionized at the electrode, drifts into the oxide and is neutralized at the counterelectrode forming conducting filaments [63].

According to [46] switching in PCMO probably bases on electronic and ionic transport processes and is located near the interfaces. It is suggested that the applied electric field leads to oxygen vacancy migration and, as a result, to an accumulation of the positive charged oxygen vacancies near the electrode with the negative bias (see figure 2.3). Areas with significantly higher oxygen vacancy concentration are affected by a metal-insulator-transition and do not contribute to the measured overall resistance. As a result, the following equation describes the relation of interface resistance R_{IF} , the total contact area A , the specific resistivity of the conducting PCMO $\rho(T)$, the width of the insulating layer d and the conducting area A_{eff} :

$$R_{IF} \times A = \rho(T) \frac{d}{A_{eff}} \times A \quad (2.7)$$

The emergence of HRS and LRS is based on the size of the conductive area A_{eff} . If it is large, the resistance is low and the system in LRS; respectively, if it is small, in HRS. The appearance of the two switching regimes is explained by the same mechanism taking place at the two electrodes. The asymmetry in the switching behavior of the two regimes is probably caused by different properties of the two Pt-PCMO interfaces at the top and the bottom electrode. The interface to the bottom electrode is coherent due to epitaxial growth. In contrast, the top electrode is deposited by ion beam sputter deposition at room temperature and therefore incoherent and additionally more affected by defects. Consequently, the interface resistance of the two interfaces and thus the local electric field may be different. Furthermore, different defect densities may influence the onset of oxygen migration.

Figure 2.3: Model of oxygen vancancy migration induced resisistive switching according to [46]. In the two images the area near the top interface is shown. The polarity of the applied voltage, is marked within the Pt-electrode. The electric field-driven migration of positive oxygen vacancies indicated by black arrows result in larger or smaller areas of oxygen deficient regions with high resistivity.

CHAPTER 3

Developing an *in situ* environmental TEM set up for investigations of resistive switching mechanisms in Pt- $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ -Pt sandwich structures

This whole chapter is a complete reproduction of the original publication

Developing an *in situ* environmental TEM set up for investigations of resistive switching mechanisms in Pt- $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ -Pt sandwich structures

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Abstract

Non-volatile resistance change under electric stimulation in many metal-oxides is a promising path to next generation memory devices. However, the underlying mechanisms are still not fully understood. *in situ* transmission electron microscopy experiments provide a powerful tool to elucidate these mechanisms. In this contribution, we demonstrate a TEM lamella geometry for *in situ* biasing with two fixed electrode contacts ensuring low and stable contact resistances. We use $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ sandwiched by Pt electrodes as model system. The evolution of manganese valence state during electric stimulation in different environments is mapped by means of electron energy loss spectroscopy with high spatial resolution in STEM. Correlation of Mn valence with local oxygen content is found. In addition to electrically driven switching, beam-induced redox reactions in oxygen environment are observed. This effect might be restricted to thin lamellae. In general, our results support that bulk oxygen electromigration is the relevant mechanism for non-volatile resistive switching in PCMO.

3.1 Introduction

The effect of a non-volatile resistance change due to applied electric pulses is observed in many metal-oxide-sandwich structures [10, 28, 64]. Resistive random access memory based on the resistive switching phenomenon is emerging as a strong candidate for next generation of non-volatile memories. Although there are already first steps into applications, the underlying mechanisms are still not fully understood.

Sawa [5] classifies switching processes by their macroscopic appearance as filament- or interface-type. In filament-type switching, a conductive filament in an insulating matrix is created and disrupted. In interface-type switching, a small insulating layer formed at the interface between the oxide and the electrode is responsible for the resistance change. For clarification of the proposed mechanisms, cross-section investigations of the change of atomic and electronic structure during the resistance change are highly desired. Consequently, in the last years several *in situ* transmission electron microscopy (TEM) studies were performed, mostly on binary metal oxides [65–74], but also on the perovskite LSTO [75], showing filament-type switching. Investigations of the perovskite $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) point to interface-type switching [76–79].

However, the high benefit of *in situ* TEM investigations is accompanied by serious challenges concerning preparation and experimental conditions. According to our experience, e.g. in TEM experiments with piezo-controlled nano-tips, the contribution of the tip contact resistance strongly varies between 1-100 k Ω (see supplemental material sec. 3.5.1). Large or unreliable contact resistances can preclude meaningful electric measurements and can even lead to device behavior quite different from switching in macroscopic devices. Furthermore, macroscopic devices and electron transparent cross section lamellae strongly differ with respect to thermal boundary conditions, the aspect ratio and the exchange with the gas environment. In addition, beam-induced electro-chemical effects even far below the threshold for knock-on damage have to be taken into account in TEM-based experiments.

Generally, the effect of the environment such as ambient condition or high vacuum on the oxygen vacancy concentration and distribution has to be considered. Resistive switching in TiO_2 , e.g., is suppressed in oxygen environment [65, 70]. However, as far as we know, there are no *in situ* environmental TEM or X-ray resistive switching investigations in ambient conditions or different gas atmospheres yet.

We use p-doped $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO), $x \approx 0.35$, sandwiched by Pt electrodes as model system for ex situ and *in situ* TEM switching studies. The electric conductivity in PCMO below the switching threshold is governed by hopping transport of small polarons [42]. A volatile resistance drop caused by applied electric fields is an intrinsic property of such small polaron systems and has been studied both in bulk single crystals [60] as well as in lateral thin films geometry [43]. The small polaron mobility is thermally activated. Higher temperatures, e.g. due to Joule heating, can therefore significantly reduce the resistance. During electric stimulation above the switching threshold, the resistance drop due to the combined effect of electric field and Joule heating can thus give rise to a thermal instability. A temperature increase of several hundred Kelvin can easily be induced during resistive switching [31], posing huge stability challenges for *in situ* TEM experiments.

Although thermal effects are very crucial for the resistivity, a primarily thermally induced resistive switching in PCMO is unlikely. Such a mechanism typically results in unipolar resistive switching [14], whereas bipolar switching is observed in PCMO [31, 55]. Following the classification of Waser et al. [14], PCMO is rather affected by electrical or ion migration related mechanisms. There is, indeed, evidence for a charge-injected insulator-metal transition [30, 60–62], or for an electric-field-induced oxygen vacancy migration process [78, 79].

Besides the oxide itself, the electrode material plays an important role for the switching mechanism. Typically for non-precious metal electrodes, the formation of an insulating interface layer is caused by a redox reaction at the electrode, as demonstrated by *in situ* X-ray photoelectron spectroscopy measurements [30, 80]. This results in a bipolar resistive switching of the I-V-characteristics. However, for precious metal electrodes no redox reactions at the electrode have been observed [31]. Pt-PCMO-Pt devices show bipolar switching characterized by the appearance of two polarities of resistive switching [29, 31, 81] probably due to one active switching regime for each of the two interfaces with the electrodes [82].

In this contribution, we show an *in situ* TEM method for cross-plane electric stimulation and measurement of lamella devices with fixed electric contacts. This method ensures mechanically stable electric contacts and minimizes the active area in switching, hence allowing for controlled current pathways and high-resolution TEM studies. We compare the electric transport properties of the Pt-PCMO-Pt heterostructure below the switching threshold of TEM lamellae and micro-pillar devices. Furthermore, we point out the influence of electron beam irradiation and heat-generation induced by the electric stimulation. We analyze especially the influence of different gas atmospheres and the interaction with the electron beam in combination with electric stimulation of PCMO. Spatial mapping of the Mn valence state by means of electron energy loss spectroscopy (EELS) across the entire PCMO cross section reflects subtle changes of the oxygen concentration. In our *in situ* studies, we correlate the measured resistance change with structural, chemical and electronic changes in the manganite. Bulk oxygen electromigration in the PCMO lamella is shown to be the relevant switching mechanism. The switching is superposed by beam-induced oxidation of the thin lamellae in oxygen environment.

3.2 Methods

The thin film Pt/PCMO/Pt sandwich structures are subsequently deposited by ion beam sputtering on 10×10 mm MgO (001) single crystal substrates. About 750 nm of Pt as bottom electrode followed by 250 nm of PCMO are deposited at 1023 K at a partial pressure of 1.4×10^{-4} mbar O_2 , 1.0×10^{-4} mbar Xe (sputter gas) and 1.0×10^{-4} mbar Ar (neutralizer plasma). One of the samples is additionally annealed for 20 h at 1170 K in atmosphere prior to the deposition of the top electrode. All PCMO films reveal the orthorhombic crystal structure with dominating twinned [001]/[110] orientations perpendicular to the substrate with up to 25 % of [112] misorientations. However, all TEM lamellae are cut from areas of [001]/[110] growth. The top electrode consists of 150 nm Pt followed by a 150 nm Au film, both deposited at room temperature. The additional Au layer improves the electric contact to the nano-tip in the micro-pillar-experiments.

The electron transparent lamellae are fabricated by Focused Ion Beam (FIB) FEI Nova Nanolab 600 dual beam system. We cut a $40 \mu\text{m} \times 3 \mu\text{m}$ cross-section-lamella out of the MgO/Pt/PCMO/Pt/Au stack and transfer it to a carrier grid. The grids base on commercial SiN TEM membranes (Plano GmbH). Two Pt contact lines (Fig. 3.1 a)) are deposited on top of the grid by ion beam sputtering and patterned via electron beam lithography. The electrical contact between the lamella and the Pt leads is established by Gallium ion- and electron-beam assisted deposition of a carbon-platinum mixture, in the following called FIB-Pt. Two copper clamps connected to the supply lines within a custom-made single-tilt TEM holder provide the electric contact to the external voltage source.

In order to prepare electron-transparent lamellae, a first rough ion-beam thinning step is performed down to a thickness of about $1 \mu\text{m}$. In a second step, we create a "Z-shaped" device for cross-plane measurements by etching the lamella (Fig. 3.1 b)). Thereby, surface amorphisation with a thickness of about 20 nm takes place at the etched surfaces (Fig. 3.15 of the supplemental material in sec. 3.5.4). Subsequently, the lamella is thinned to electron transparency by stepwise reduction of the power of the Ga ion-beam (down to 30 kV, 30 nA). The damaged surface layers can cause a parallel electric pathway. However, amorphous PCMO has a distinctly higher resistance and, consequently, we assume that nearly all electric current flows through the crystalline parts of the device.

We prepare Pt/PCMO/Pt micro-pillars with diameter of the order of one micrometer on the same films (Fig. 3.2). Details of FIB-preparation and measurement are described in [31]. The measurements were performed in an FEI Nova Nano SEM 650 in 10^{-6} mbar vacuum equipped with a Tungsten tip mounted on a Kleindiek micromanipulator (Fig. 3.2 b)).

We use the same electric setup for both the lamellae and the micro-pillar experiments. The voltage source is a Keithley 2430 source meter, which also performs the current measurement. The bottom electrode is grounded and during electric measurements, the electron beam is blanked. Each voltage cycle consists of 100 excitation voltage pulses with duration of 2 ms. The amplitude is increased in 50 steps up to $V_{exc,max}$ followed by a decrease to zero with the same step sequence. We apply a 2 ms "read" pulse (0.05 V-0.1 V) after each excitation pulse to determine the remanent resistance change. Micro-pillars

Figure 3.1: Sample geometry for *in situ* TEM cross-plane biasing:

- a) SEM image of the lamella on the Si-SiN-Pt-Carrier: The contact from the Pt pads to the lamella is made by FIB-Pt. The arrow marks the part thinned for the TEM observations.
- b) TEM image without contrast aperture of the thinned part of the lamella showing the PCMO layer sandwiched by Pt electrodes and on top the additional Gold and FIB-Pt layers.

Figure 3.2: Sample geometry and experimental set up for resistive switching experiments on micro-pillars in SEM:

- a) SEM image of a cross-section of the pillar-shaped sandwich structure fabricated by FIB: the FIB-Pt protection layer is necessary for the preparation of the cross section, but is not deposited on the pillars for the electric experiments.
- b) Schematic diagram of the electric circuit in two-point geometry with contact tip at the top electrode.

as well as TEM lamellae of the Pt/PCMO/Pt stack reveal ohmic behavior at such low voltages (Fig. 3.3 b)). Most cycles are followed by a STEM-EELS scan over the whole device area taking 72×24 spectra with 10 nm spatial resolution. The measurements are performed in an FEI Titan 300 kV aberration corrected ETEM with Gatan Quantum 965 ER GIF. The GIF is equipped with a dual beam deflector unit. The energy ranges -20 to 185 eV and 480 to 685 eV are measured simultaneously with a resolution of 0.1 eV per channel in order to record the zero loss peak (ZLP), the O K-edge and the Mn L-edge. The energy resolution derived from FWHM of ZLP amounts to about 1 eV, the used beam current is smaller than 10^7 e/(Å²s) and the electron dose is about 10^6 e/Å² per spectrum. During the scan, the device is disconnected from the external voltage source and both electrodes are grounded.

The Mn valence state has been extracted from the energy loss spectra by means of a C++ based LabTalk script using OriginLab's Origin. The routine subtracts the background below the L_{3,2} edges by a power-law fit within a 20 eV wide window. In the next step, the energy scale of each spectrum is calibrated by adjusting the Mn L₂ edge to 653 eV. Externally calibrated X-ray absorption spectra have demonstrated that the L₂ position is much less affected by the Mn valence state than the L₃ position [83]. Next, a Hartree-Slater cross-section step function is subtracted to account for continuum contributions [84,85]. The step function is available in Gatan's Digital Micrograph and is scaled to the data above the L₂ edge (658 - 661 eV). The resulting edge intensities are integrated from 638 to 648 eV and from 648 to 658 eV, respectively. These integrals are then used to calculate the L₃/L₂ ratio. Several analysis methods to determine this ratio have been reported [86-88]. The method chosen here is similar to the one used for Mn³⁺/Mn⁴⁺ in La_xCa_{1-x}MnO₃ by Varela et al. [86]. They observed that the ratio R of these intensities depends linearly on Mn valence V , i.e. $V = -0.73(11) \times R + 5.0(4)$. Using the same parameters for PCMO can possibly result in a significant absolute error of Mn valence determination. Nevertheless, the relative error on the same sample should be small. An error of 0.04 electrons per Mn atom has been estimated by comparing the resulting valence states from 200 spectra taken from an area of approximately homogeneous chemical composition and thickness. The error from varying the integration windows by ± 1 eV for 200 spectra with different Mn valence states is 0.05 electrons per Mn atom.

3.3 Results and Discussion

3.3.1 Transport Properties

The $R - V$ -characteristics of lamella and micro-pillars show the small polaron fingerprint of a non-linear resistance decrease with increasing applied voltage. The resistance saturates for high voltages at a constant value C (Fig. 3.3 a)). We determine C as $660(25) \Omega$ for the lamella, which is about 20 % of the zero-field resistance by applying an exponential fit $R_{exc} = C + \exp(-a \times V_{exc})$ to five different measured $R - V$ -curves. In principal, we observe the same behavior in the micro-pillars with the difference that C is only about 10 % of the zero-field resistance. We assume that both a residual resistance R_∞ of PCMO and contact resistances R_C contribute to C . In micro-pillar experiments, the contact resistance is found to be below 6Ω . Consequently, we are able to determine the contribution of R_∞ to be at least 5 % of the zero-field resistance. Assuming the same ratio for the TEM lamella with a resistance of about $3.3 \text{ k}\Omega$, we estimate R_∞ to be at least 160Ω and thus the contact resistance of the lamella to be below 500Ω . We calculate the resistance of the noble metal electrodes to about 10Ω using the specific resistivity of Pt of $\rho = 10.6 \times 10^{-6} \Omega \text{cm}$ [89] and the dimensions of the lamella. The resistance of the leads is also very small, i.e. of the order of 1Ω . Consequently, the major contribution to the contact resistance is most probably caused by the FIB-Pt contact between the noble metal electrodes of the lamella and the Pt contact lines on the SiN grids.

With the total resistance R_{exc} , the contact resistance R_C and the electric current I , we calculate the voltage drop across the PCMO device to

$$V_{PCMO} = (R_{exc} - R_C) \times I . \quad (3.1)$$

As a result, V_{PCMO} is considerably smaller than the external voltage. Replacing V_{exc} by V_{PCMO} gives rise to rather similar $I - V$ -characteristics of TEM device and micro pillars (Fig. 3.3 b)). However, contact resistances of the order of 500Ω limits the maximum voltage drop across the PCMO to about 0.6 V (Fig. 3.3 c)). Further reduction of the contact resistance by improving the electric contact of the lamella to the Pt pads of the SiN grid would be desirable. Nevertheless, resistive switching effects in the lamella should be observable because the typical onset voltage in macroscopic devices is about $0.5\text{-}0.55 \text{ V}$ [55]. The standard deviation of the determined contact contribution below 4 % indicates high stability allowing reliable interpretation of characteristics.

3.3.2 Redox reactions during *in situ* TEM experiments

Two main effects have to be considered during *in situ* TEM resistive switching experiments: i) electron irradiation, i.e. beam damage or beam-induced electro-chemistry and ii) electric stimulation, leading to Joule heating and possible space charge layers as well as electromigration. In the following, we will use the Mn valence state as a measure for redox reactions resulting from both effects.

Figure 3.3: Electric characterization of the Pt/PCMO/Pt TEM lamella:

- $R - V$ -characteristic of the lamella: Applying an exponential fit to the dynamic resistance at high voltages reveals a constant contribution of $660(25) \Omega$.
- Comparison of $I - V$ -characteristics of micro-pillar and TEM lamella with different R_C corrections of the applied voltage
- Current density and recalculated voltage drop V_{PCMO} versus excitation voltage: in order to show the influence of the contact resistance, V_{PCMO} is calculated assuming $R_C = 400$, 500 and 660Ω .

Correlation of oxygen and Mn valence

It is commonly expected for Mn-containing compounds that Praseodymium does not change its valence state [90]. This is probably also valid for Calcium due to its electron configuration. For $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_{3-\delta}$ this leads to the relation

$$\delta = 0.5 \times (3.35 - (\text{Mn valence})) \quad (3.2)$$

To crosscheck the assumption that we can use the Mn valence as measure for oxygen content, we compare the integrated intensity of the O K-edge with the corresponding calculated Mn valence during different stages of the *in situ* experiment. This provides a wide distribution of valence states. A clear trend of higher O K-edge intensity for higher calculated Mn valences is found (Fig. 3.4 a)). Additionally, we have compared the intensity ratio of the O K-edge features A (pre-edge, 530 eV) and B (536 eV) (Fig. 3.4 b), details of determination in supplemental material sec. 3.5.5)). This ratio provides a measure for the position of the Fermi-level and therefore occupation of the hybridized O 2p and Mn 3d e_g states. A low ratio represents a high occupation and thus low Mn valence.

Mn valences from 3.1 to 3.3 show a nearly linear correlation to the O $K_{A/B}$ ratio. This behavior fits to a scenario, in which oxygen vacancies give rise to a lower Mn valence. The O $K_{A/B}$ ratio is nearly constant for higher valences than 3.3, whereas the integrated O K intensity (Fig. 3.4 a)) further increases. We suppose that the reactive environment and the electron beam lead to an oxidation of the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_{3-\delta}$ even to an excess oxygen concentration. In this case, the perovskite structure can only be conserved by formation of cation vacancies or, less likely, interstitial oxygen. Compensation of Mn valence by a reduced covalence factor of the Mn-O bond due to structural disorder [91–93] could explain in both scenarios a constant O $K_{A/B}$ ratio. In summary, we conclude that the Mn valence can be used as a measure for oxygen content.

However, as described in the methods section, there can be a relatively large absolute error in determining the Mn valence, i.e. the position of $\delta = 0$ probably deviates from a Mn valence of 3.35. Consequently, we restrict ourselves to a qualitative discussion of oxygen concentration changes.

Oxidation induced by electron beam irradiation

The influence of electron beam irradiation on the Mn valence is analyzed by repeated STEM-EELS scans over the same area. No additional voltage is applied. In high vacuum, we have investigated lamellae of the annealed and non-annealed thin film showing different initial Mn valence states. Both do not change their Mn valence state within the accuracy of the measurement (Fig. 3.5 d), red dots). We observe a different behavior when applying an oxygen partial pressure of 10 μbar . Fig. 3.5 a) shows a detail of a lamella in virgin state, where the Mn valence varies from 3.05 to 3.35. The low Mn valence at the surface is probably due to oxygen vacancies formed during sputter deposition of the top electrode.

Figure 3.4: Correlation of Oxygen K-edge properties with Mn valence: a) Integrated intensity of O K-edge versus Mn valence: the data are obtained from one single Pt-PCMO-Pt TEM lamella in different stages of the resistive switching experiment. b) Intensity ratio of O K-edge feature A (pre-edge) and B versus Mn valence for the same set of data

Figure 3.5: Oxidation of PCMO induced by electron beam illumination in oxygen environment: a) Mn valence map of a PCMO area at the interface to the Pt top electrode at the start of the electric experiments: In the bottom left corner the subsequently measured remanent resistance is shown. b) The same area after a subsequent second scan: In the bottom left corner the subsequently measured remanent resistance is shown. c) STEM ADF image of the observed area. d) Changes of Mn valence under electron beam irradiation: The data in 10 μbar oxygen pressure are a selection of the acquired Mn valences in a) and b).

The Mn valence is strongly increased after a second scan over the same area, especially in regions with an initially low Mn valence (Fig. 3.5 b)). Plotting Mn oxidation versus the initial valence state (Fig. 3.5 d)) shows a clear linear relation. In other words, beam-induced oxidation in oxygen environment completely oxidizes the PCMO to a Mn valence of about 3.38, independent of the initial oxidation state.

It is interesting to correlate the beam-induced oxidation to the non-volatile electric resistance change. The oxidation shown in Fig. 3.5 a) and b) is accompanied by a decrease of the total electric resistance of about 30 %. In addition to the detail of the interface presented in Fig. 3.5, the whole PCMO layer has been illuminated by electron beam in the course of a STEM-EELS-scan as described in the method section. Consequently, we assume we can expand the observed oxidation of an oxygen deficient area near the top electrode to the whole interface.

Resistive switching is often attributed to redox reactions with non-precious metal electrodes [5, 14]. In contrast, such processes are not expected with Pt electrodes [29, 81]. However, in contrast to macroscopic devices, the large surface of the about 100 nm thin TEM lamella enables a strong interaction with the vacuum or gas environment. Thus electron beam irradiation can have more influence.

Generally, inelastic collisions of the high-energy electrons and the sample can lead to atomic displacements. The probability for an atomic displacement is a function of the atomic mass and the energy of the primary electrons [94]. Point defect generation sets in above a threshold value of the primary electron energy depending on the sample material. The displacement energy E_d for oxygen atoms in perovskites is in the range of 45-55 eV [95–97]. The threshold energy for oxygen displacement is thus estimated at 260-320 keV for the primary electrons using Eq. (2) in [94]. Extensive studies of fully oxidized PCMO without FIB damage show high stability for 300 keV electrons in high vacuum, even at electron fluxes as high as $10^{10} \text{ e}/(\text{\AA}^2\text{s})$ in STEM/EELS. Consequently, we conclude no major impact of point defect generation in our experiments with three orders lower electron fluxes. Instead, we suppose an oxidation based on the emission of secondary electrons, which induces an electrochemical relevant positive local potential [98, 99]. This potential could favor the oxidation of PCMO by oxygen from the atmosphere or from neighboring sites with higher oxygen content. In contrast to most other oxides, the electric conductivity of PCMO is based on hole doping, so healing of oxygen vacancies should increase the conductivity, which we observe.

Redox reactions induced by electric stimulation

We analyze the global evolution of oxidation state within a PCMO lamella under electric stimulation by spatially averaging the Mn valence of the whole lamella. Local variations, e.g. induced by electromigration of oxygen ions in the switching regime, are eliminated in this way. We examine lamellae in high vacuum experiments ($p < 10^{-6}$ mbar), as well as in 10 μbar and 3 mbar oxygen pressure. We use a lamella from the annealed thin film, providing a slightly higher initial Mn valence for electric stimulation in vacuum. An overall Mn reduction arises after several electric cycles (Fig. 3.6, black squares). Mn valence maps before and after the stimulation (Fig. 3.6 a) and b)) show a stronger oxygen depletion

in the center of the PCMO than near the electrodes. This is probably caused by the poor thermal conductivity of PCMO ($\sigma_{PCMO}/\sigma_{Pt} \approx 0.02$ [100, 101] in combination with the orders of magnitude higher electrical resistance compared to the Pt electrodes. We therefore expect significant Joule heating, leading to higher temperature in the center than at the interfaces to the thermally well conductive electrodes. Finite Element simulations by Scherff et al. [31] show similar results on macroscopic devices.

Electric stimulation of nearly stoichiometric lamellae in oxygen atmosphere leads to no reduction, but instead to slight oxidation (Fig. 3.6, red dots/ green triangles). However, electron beam-induced oxidation as described above has to be taken into account, because of the electron irradiation during EELS measurements. A possible mechanism could be beam-induced oxidation compensating the reduction by Joule heating.

Additional hints for this hypothesis are provided by a lamella, which is examined twice at an oxygen partial pressure of 3 mbar. Firstly, the average oxygen content at the beginning of the experiment is nearly stoichiometric and only slight changes within 2 % of the initial Mn valence are observed after electric stimulation (Fig. 3.6, green triangles). Before the second experiment, the sample has been exposed to an undefined high voltage pulse leading to Joule heating and massive oxygen depletion of the PCMO layer. The lamella now strongly oxidizes at the same oxygen pressure and applied voltages as in previous experiments, even at zero electric potential (Fig. 3.6, blue triangles). Respecting the significantly decreased initial Mn valence, this behavior fits perfectly to beam-induced oxidation as described above. We observe saturation of the oxidation state in the course of the experiment, possibly resulting from weaker beam-induced oxidation due to the higher average Mn valence. Additionally, we expect an increased reduction by Joule heating due to higher excitation voltages.

3.3.3 Resistive Switching

Redox signature of resistance change

We examine *in situ* resistive switching experiments in oxygen partial pressure of 10 μ bar. We have performed 23 electric stimulation cycles, in which the maximum applied voltage is increased in irregular steps (details in the supplemental material sec. 3.5.3).

The lamella exhibits a homogeneous oxygen distribution in the virgin state (Fig. 3.7 a)). However, an inhomogeneous oxygen distribution is formed already at excitation voltages of 0.1 V (Fig. 3.7 b)). We observe a stronger oxidation in thinner areas. This is clearly visible on the thin edges of the lamella, but stronger oxidation also correlates to the increasing thickness from top to bottom electrode. We conclude that this first forming of inhomogeneous oxygen distribution is not generated by the electric stimulation but most probably caused by the thickness gradient and the related change in surface to volume ratio.

We observe first signs of voltage-induced non-volatile switching at excitation voltages of 0.6 V. A clear remanent resistance drop arises at excitation voltages of 0.9 V. This implies an onset voltage of about 0.47-0.57 V by taking the determined contact resistance into account (Fig. 3.3 c)). This is slightly lower than the switching threshold of 0.55 V measured

Figure 3.6: Redox reactions of PCMO during electric-stimulation: a) Mn valence map of an annealed PCMO sample in initial state b) The same lamella after seven cycles with applied $V_{exc,max}$ between 0.4 V and 0.9 V c) TEM image without contrast aperture of the observed area d) Evolution of the spatially averaged Mn valence of the PCMO layer during electric stimulation at different oxygen partial pressures: The maximum applied excitation voltage of each previously measured cycle is assigned to the x-axis. The initial state of the lamellae varies: The annealed PCMO shown in a) and b) is plotted as black squares. The other lamellae are cut from a non-annealed thin film. Blue triangles represent a second measurement of lamella "B: 3 mbar" after massive oxygen depletion, due to Joule heating in vacuum. The error bars represent the standard deviation within the sample. The dashed square marks a measurement in zero-electric potential.

in micro-pillars (see supplemental material Fig. 3.11). At excitation voltages above 0.9 V, V_{PCMO} remains almost constant. Nevertheless, the remanent resistance further decreases with increasing V_{exc} (Fig. 3.8), clearly indicating, that current and power also play a role.

Fig. 3.8 shows the voltage dependence of the remanent resistance of different subsequent cycles (full data in supplemental material sec. 3.5.3). The first cycle (black squares) to a maximum negative voltage of -1.2 V causes a crossover from a high resistance state (HRS) to a low resistance state (LRS), starting at about -0.9 V. The second cycle (red circles) to a maximum positive voltage of +1.2 V does not change the resistance, i.e. the device remains in the LRS state. Performing a third cycle (green up-triangles) to a maximum negative voltage of -1.3 V results in a further decrease of resistance that starts at -1.2 V. After this cycle, we perform an EELS analysis. The electron illumination causes a crossover to a HRS. Applying now a cycle (blue down-triangles) to a maximum positive voltage of +1.3 V sets the sample state back to the LRS of the preceding negative voltage sweep.

It is worthwhile to note that all performed voltage cycles only result in a polarity-independent crossover to LR states. Switching back to HRS always takes place during an electron beam scan. In contrast to the beam-induced oxidation, the formation of LRS does not depend on the oxygen environment: Performing a cycle to maximum negative voltage of -1.1 V under high-vacuum conditions, a crossover to LRS also starts at -0.9 V and polarity inversion does not cause a HRS. A consecutive EELS scan in the presence of 10 μ bar oxygen partial pressure sets the device back in HRS.

Simultaneously, formation of filament-like structures of high oxygen content also in thicker areas of the lamella is observed in the Mn valence maps (Fig. 3.7 c)). We suppose, these filaments constitute conductive paths within the PCMO formed by electromigration of oxygen ions during the excitation pulses. Large-area beam-induced oxidation could weaken these structures because of stronger oxidation of low valence area, resulting in an overall homogenization of oxygen content.

The difference in the aspect ratios is most probably the main reason for completely different behavior in macroscopic and TEM-based switching experiments. While in TEM lamellae all atoms are within 50 nm to the surface, only 7 % of atoms are that close to the surface in the micro-pillars. Additionally, the TEM lamella is illuminated by 300 kV electrons in a reactive oxygen environment in the *in situ* switching experiment, while the micro-pillars are examined in high vacuum ($\approx 10^{-6}$ mbar) and the PCMO is not influenced by electron beam irradiation. Therefore, it is plausible that surface-related redox processes play a minor role in the micro-pillars, whereas they represent the major effects in the lamellae.

We suppose that the thin regions at the edges of the lamella can serve as a probe for surface effects. Here, we observe the strongest changes in oxygen content and a recrystallization of FIB damaged regions (see supplemental material Fig. 3.13 and 3.15 for details). This hints at an increased activity near the surfaces, because capture of gas oxygen and loss of lattice oxygen in beam induced and electric pulse induced redox processes always starts at lamella surfaces.

Figure 3.7: Oxygen redistribution before and during resistive switching: a) Mn valence map before any electric pulse: the missing values in the middle are caused by malfunctions of the camera. b) Mn valence map after the second cycle with a maximum excitation voltage of 0.1 V. c) Mn valence map after resistive switching to LRS (cycle 20): the box marks an area with additional electron beam irradiation caused by repeated laterally higher resolved EELS scans and thus increased oxygen content. d) STEM ADF image of the observed area.

Figure 3.8: Electric field- and beam-induced resistive switching: The arrows indicate the sequence of a set of representative cycles in the switching regime. The dashed arrow marks an EELS scan, recorded after cycle 20.

Electromigration

Mn valence gradient profiles are created by horizontal binning (perpendicular to the electric field) of the valence maps after electric cycles, where switching is observed. We subtract the respective average Mn valence of the whole map in order to neglect global oxidation. The inhomogeneous oxygen distribution causes a high variance of the data. Nevertheless, linear fits reveal global gradients, which change systematically with polarity of voltage, especially in the center of the PCMO layer (Fig. 3.9). Applying a positive bias at the top electrode increases the negative gradient from top to bottom and vice versa. This supports a simple model of oxygen electromigration, where the negatively charged oxygen ions migrate towards a positive potential. As described in section 3.3.2, we expect higher temperatures to enhance diffusion in the center. This behavior furthermore illustrates that thermal conditions have to be considered for more detailed modeling of the electric field-driven diffusion in thin lamellae.

Figure 3.9: Oxygen electromigration: a) Horizontally binned data of the center of Mn valence maps in the switching regime: The data are linearly fitted. The direction of the previously applied electric field is marked at the ends of the fitting windows. The arrows on the right additionally illustrate the change of slope when the electric field is inverted. b) Mn valence gradient obtained by linear fitting of the mid-section and the whole data: The indicated voltages are the maximum excitation voltage of the respective previous cycle.

3.4 Conclusions

We conclude that our TEM lamella geometry is a useful tool to study resistive switching phenomena. Fixed electrode contacts provide a low and, in particular, stable contact resistance for cross-plane *in situ* electric stimulation and measurement of thin film sandwich structures. This allows a clear and reproducible correlation of resistance changes to observed changes in the structure and redox state of the TEM lamella. Current-voltage-characteristics are similar to micro-pillar-devices, showing the transport properties in thin lamellae are comparable to macroscopic devices.

Our investigations clearly show that the effects of sample geometry, electron beam, electric stimulation and oxygen or vacuum environment have to be analyzed carefully. In high vacuum, usually present in most *in situ* TEM switching experiments, we have found a significant Mn reduction in PCMO by electrical stimulation due to loss of oxygen to the vacuum during Joule heating. However, this reduction can be prevented by using an oxygen gas environment in a mbar range.

We conclude that the chosen in-situ TEM approach allows for studying switching mechanisms, which are characteristic for oxide/noble metal devices. However, the large surface-to-volume-ratio in thin TEM lamella geometries as well as beam-induced redox processes can modify the general mechanisms. PCMO/Pt-devices are characterized by switching to LRS via polarity-independent electric stimulation and to HRS via electron beam-induced oxidation. Besides these special characteristics, the observed correlation of oxygen distribution and applied electric field suggests that oxygen electromigration is the relevant mechanism for resistive switching in noble metal manganite sandwich structures.

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3.5 Supplemental Material

3.5.1 *In situ* resistive switching experiments with nano-tip

Figure 3.10: *in situ* TEM switching experiments with nano-tip: a) STEM ADF image of the lamella. On the left a segment is seen with previously applied voltages up to 1.1 V. A crystallization of the FIB Pt and melting of the gold layer is observed. On the right a segment is contacted by the nano-tip. b) $R_{ref} - V_{exc}$ characteristics of representative subsequently measured cycles in the tip set up.

We have made additional experiments with a nanofactory STM-TEM holder equipped with a Pt-Ir nano-tip. The specimen is prepared by Focused Ion Beam. The lamella has been cut into several cross plane segments to allow several experiments (Fig. 3.10 a)). The experiments are done at the same FEI TITAN 80-300 ETEM in high vacuum mode. The electric set up is nearly the same as described in the methods section with the difference that the bias is applied to the lamella (bottom electrode) and the nano-tip (top electrode) is grounded.

Representative R-V-characteristics are presented in Fig. 3.10 b), which show on the one hand a resistive switching behavior similar to the SEM reference devices (cycles 30 and 31), but on the other hand atypical behavior (cycle 32). A resistance increase sets in at lower excitation voltages than in the previous cycle and the resistance increase is more linear than expected. In general, the regime of measured LRS-resistances varies from the expected value of several kΩ up to 100 kΩ. This hints to an unstable contact resistance. Potential reasons could be changing resistivity in the electrode material or the loss of mechanical contact between tip and lamella. In Fig. 3.10 a) two sections of the lamella are shown, one examined by several electric cycles, the other in original state. A clear change appears in the form of the gold electrode, probably caused by deformation due

Figure 3.11: Representative $R - V$ -characteristics of micro-pillar devices in order to determine switching-onset: The characteristics of the as-prepared thin-film is shown as well as that of the additional annealed thin film (20 h at 1170 K in air). The vertical lines indicate the switching onset.

to the high temperatures during the electric experiments. Even melting of the electrodes occurs in some experiments of high voltages and grain coarsening is observed in the FIB-Pt layer. During the electrical experiments many changes in strain contrast are observed, probably also induced by the high temperatures. This suggests a changing mechanical contact of the tip to the lamella, probably resulting in an unstable electrical contact.

3.5.2 Onset for non-volatile resistive switching in micro-pillars

We have performed electric stimulation on micro-pillars as described in [55] of the same samples used for the lamellae. We average the results of four micro-pillars to determine the onset of non-volatile resistive switching. Micro-pillars of the as-prepared thin film exhibit an onset of 0.56(4) V. The onset for micro-pillars of the annealed thin film is slightly lower at 0.45(3) V. An example for $R - V$ -characteristics is shown in Fig. 3.11.

3.5.3 Evolution of remanent resistance and manganese valence during the *in situ* resistive switching experiment with fixed contacts

In the following, we present the details of the *in situ* switching experiment discussed in the main text in section 3.3.2 and 3.3.3. The parameters of the complete sequence of cycles are described in Tab. 3.1. The respective evolution of the remanent resistance is shown in Fig. 3.12 a). The corresponding manganese valence maps are shown in Fig. 3.13.

- **Cycles 0-5:** Regime below the switching threshold: the resistance drop from cycle 1 to 2 is described in detail in section 3.3.2 (Fig. 3.5) of the main text. Already at low voltages a forming of inhomogeneities of high oxygen content on the left edge of the lamella is observed.
- **Cycles 6:** Slight switching from HRS to LRS sets in at $V_{exc,max} = -0.6$ V or $V_{PCMO} \approx 0.42$ V.
- **Cycles 7-15:** Resistive switching occurs, but only from HRS to LRS. A STEM-EELS scan for acquiring a manganese valence map comes in hand with a resistive switching back to HRS.
- **Cycles 16-17:** Pumping to high vacuum increases the resistance at the start of cycle 16, although the contact resistance derived from $R_{exc} - V_{exc}$ -characteristics is unchanged (Fig. 3.11 b)). A significant drop of the overall valence and thus oxygen content is observable in the Mn valence map of cycle 17, especially on the right half of the device. However, a simple dependency of resistance and oxygen content cannot be found taking the other cycles into account. Maybe subtle surface effects play an important role, which are not measurable with our STEM-EELS method. Despite of the higher resistance at low voltages the switching threshold and ratio do not change.
- **Cycles 18-23:** The switching ratio increases with higher excitation voltage and overall a relaxation to a lower resistance is observed. The $R - V$ -characteristics of cycles 18-21 are presented in the main text (Fig. 3.8).
- **Cycle 24:** (Fig. 3.14): After a huge resistance drop of about $1\text{ k}\Omega$, a sudden and temporarily increase of resistance up to $8\text{ k}\Omega$ occurs in the cycle, followed by a return to the previous $2\text{ k}\Omega$. However, it emerges that during the electric cycle the FIB-Pt on the top electrode was seriously damaged (Fig. 3.14 b)) and so the electric features are probably mainly evoked by a change in the contact resistance. Also the creation of a parallel parasitic circuit cannot be excluded.

Cycle	$V_{exc,max}$ [V]	V_{PCMO} [V]	EELS scan	p_{O_2} [μ bar]
0	-0.05; +0.05	-0.04; +0.04	x	8
1	-0.1	-0.09	x	8.2
2	-0.3	-0.25	x	9.1
3	-0.5	-0.4	x	9.8
4	+0.5	+0.4	x	10.3
5	-0.6	-0.47	x	10.3
6	+0.6	+0.47		10.3
7	-0.7	-0.52	x	10.5
8	-0.8	-0.55	x	10.5
9	-0.9	-0.57	x	10.5
10	+0.9	+0.57		10.5
11	-1	-0.57	x	10.5
12	+1	+0.57		10.5
13	-1; +1	-0.57; +0.57		10.5
14	-1.1	-0.55		10.5
15	+1.1	+0.55	x	10.5
16	-1.1	-0.55		0.008
17	+1.1	+0.55	x	0.006
18	-1.2	-0.55		13.8
19	+1.2	+0.55		20
20	-1.3	-0.52	x	23.8
21	+1.3	+0.52	x	26.8
22	-1.4	-0.53		26.8
23	+1.4	+0.53		26.8
24	-1.5	-0.47	x	26.8

Table 3.1: Sequence of the applied cycles: The maximum applied voltage $V_{exc,max}$, the respecting voltage applied at the PCMO layer assuming a contact resistance of $500\ \Omega$, the existence of a manganese valence map and the prevailing oxygen pressure at the beginning of the STEM EELS scan is shown for each cycle. In cycle 0 and cycle 13, the voltage has been increased to $-V_{exc,max}$ and subsequently to $+V_{exc,max}$. The EELS scan are always performed measured after the electric stimulation with the exception of cycle 0.

Figure 3.12: Overview of resistance changes during *in situ* resistive switching experiment: a) Evolution of the remanent resistance: If no switching is observed, the resistance is averaged over the whole characteristic. In case of an apparent resistive switching in cycle x HRS and LRS are separately averaged and plotted as $x.0$ (HRS) and $x.5$ (LRS). The error bar is the statistical error of the averaging (in most cases within dots). Cycles with a negative $V_{exc,max}$ are plotted as black squares, cycles with a positive $V_{exc,max}$ as red circles. The vertical lines indicate STEM-EELS scans after the respective electric measurement. Aside the cycles within the red square ($p = 10^{-6}$ mbar), all measurements were executed at oxygen partial pressure of about $10 \mu\text{bar}$ (see also Tab 3.1). b) $R_{exc} - V_{exc}$ characteristics of cycles 15 and 17.

Figure 3.13: Manganese valence maps after applied voltages: The data are obtained from STEM EELS scans with 10 nm spatial resolution as described in the methods section. In x-direction the data is binned by three. The last map (cycle 24: -1.5 V) implies serious changes in the top electrode, after switching to LRS, so additional effects cannot be excluded. The STEM ADF image shows the location of the maps.

Figure 3.14: Details of cycle 24 ($V_{exc,max} = -1.5$ V):

- a) $R - V_{exc}$ characteristic of cycle 24. The dynamic resistance $R_{exc}(V_{exc})$ is plotted as well as the remanent resistance $R(V_{exc} = -0.1$ V). b) STEM ADF image of the device and the deformed top electrode after cycle 24.

3.5.4 Recrystallisation under electron beam irradiation

We want to illustrate in this section the effect of recrystallization during the *in situ* resistive switching experiment by a study of the FIB damaged edge of the lamella. The damaged region on the left and right edges is thicker than the usual preparation induced layer of a few nanometers, because of the etching procedure to form the device. Before the experiment the width of this region is about 20 nm (Fig. 3.15 a). The same area has changed its structure after the experiment of 24 electric cycles and 15 STEM-EELS mappings (Fig. 3.15 b)). Now the damaged region is diminished to 4 nm thickness. In this particular area the recrystallized region even has the same structure as the film on the right. Polycrystalline recrystallization is also observed in other areas. We obtain a homogenous carbon contamination on the lamella before *in situ* experiments in oxygen environment, which vanishes after a few EELS scans in oxygen environment. This is probably why in general the lattice fringes after the experiment are seen more clearly than in the as prepared state.

Figure 3.15: HR-TEM images of the top left corner of a lamella before a) before and b) after the *in situ* resistive switching experiment, described in section 3.5.3. The FFT of the marked area is shown as inset. The width of the area, where no lattice fringes are observable, is illustrated by a double arrow.

3.5.5 Integration of EELS oxygen K edge intensity and determining of O K A/B ratio

Figure 3.16: Integration and Gaussian fitting of the O K-edge: The grey area marks the range for the intensity integration. The red and green curves are the results of a two-peak Gaussian fit within the range marked by the dashed lines.

For determining the integrated oxygen intensity, we firstly subtract the background below the O K-edge by a power-law fit within a 15 eV wide window. Then we integrate the area of onset to third local minimum of the oxygen K edge (Fig. 3.16). The error is estimated by a variation of the position of the energy interval used for background subtraction by 0.2 eV.

For determining intensity of O K_A and K_B feature we use a simultaneous fit of two Gaussians within the range of the onset of O K_A and the second local minimum of the O K-edge. Including more features to the fit (and using more Gaussians) leads to the same trends, but entails a higher error.

CHAPTER 4

Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO_3

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Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO_3

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Abstract

The transport of potassium through praseodymium-manganese oxide (PrMnO_3 ; PMO) has been investigated by means of the charge attachment induced transport (CAIT) technique. To this end, potassium ions have been attached to the front side of a 250 nm thick sample of PMO. The majority of the potassium ions become neutralized at the surface of the PMO, while some of the potassium ions diffuse through. Ex situ analysis of the sample by time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveals pronounced concentration profiles of the potassium, which is indicative of diffusion. Two diffusion coefficients have been obtained, namely, the bulk diffusion coefficient and the diffusion coefficient associated with the grain boundaries. The latter conclusion is supported by transmission electron microscopy of thin lamella cut out from the sample, which reveals twin grain boundaries reaching throughout the entire sample as well as model calculations.

Figure 4.1: An illustration of the diffusion of potassium through the bulk and along the grain boundaries of PMO.

4.1 Introduction

Perovskite-oxide based materials with the composition ABO_3 have promising potential for new innovations and technologies including solid oxide fuel cells (SOFC) [102], water electrolysis [103–106] and resistive random access memory (RRAM) [5, 19]. Operating temperatures for these devices can range from room temperature (e.g., water electrolysis electrodes [103, 107] to high temperatures (e.g., SOFC and RRAM). Therefore, an understanding of ionic mobility and diffusion over a wide temperature range is necessary.

The perovskite oxide ABO_3 structure consists of a network of corner sharing BO_6 octahedra, while A-site cations exhibit dodecahedral environments to next neighbor oxygen. The large A-site cations stabilize the crystal structure of perovskite oxides, enabling the accommodation of high point defect concentrations, e.g. in $La_{1-x}Sr_xCoO_{3-\delta}$ [108] and $La_{1-x}Sr_xMnO_{3-\delta}$ [109]. These high defect concentrations give rise to a large variety of physical effects including conduction phenomena connected to electron and hole doping, e.g. in $La_{1-x}A_xMnO_3$ ($A = Ca$ or Ce) [110], and the colossal magneto resistance in hole doped manganites [111]. High temperature tracer diffusion data compiled by Miyoshi et al. for cations in $LaMnO_3$ and by Ishigaki et al. for anions in strontium doped $LaMnO_3$, show a trend in which the diffusion of oxygen is faster than that of manganese, which is in turn faster than that of praseodymium [51, 112]. The relative value of diffusion coefficients of A-site and B-site cations can differ by many orders of magnitude and, as a result, significantly influence the surface and interface chemistry and dopant concentrations under operation. Thus, it is particularly important to obtain information about the relative values, but there seems to be no general trend. One important contribution to a better understanding is extending diffusion data of different cation and anion species to

room temperature. For manganites, which represent mixed ionic- electronic conductors, this requires a highly sensitive and reliable method.

In a series of papers published in this journal we have described the development and selected applications of the “Bombardment Induced Ion Transport” technique [113–117]. That work was based on attaching an alkali ion beam of well-defined energy to a sample of interest. If the sample has a low conductivity, attachment of ions will lead to charging the surface. This in turn generates gradients of the electric potential and the concentration towards a backside electrode. Measurements of current-voltage data then provides direct access to the conductivity. When the bombarder ion is different from the native conducting ion, concentration profiles evolve, which are classified as electrodiffusion profiles, since they contain contributions from migration and diffusion [118, 119].

In this work, we present an extension of the approach described above to investigate potassium diffusion in a praseodymium-manganese oxide with the composition PrMnO_3 (PMO). To this end, a low-energy K^+ beam is aimed at a PMO sample in contact with a single platinum electrode. Since the PMO exhibits a relatively low electrical resistivity ($\rho = 100 \Omega\text{cm}$) due to negative charge carriers, the sample surface will not become charged in this case. However, pronounced concentration gradients will develop and induce diffusion. This constitutes Charge Attachment Induced Transport (CAIT) in the sample. Ultimately, the transport of potassium through the PMO gives rise to concentration profiles characteristic of diffusion. The concentration profiles will be quantitatively determined by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and rationalized by theoretical modeling. A high-resolution transmission electron microscope (TEM) and an energy-dispersive X-ray spectroscopy (EDX) are used to support the central findings of the ToF-SIMS analysis. The perovskite structure of the PMO is maintained, even near the interface of the potassium surface layer.

4.2 Materials and Methods

4.2.1 Sample preparation

The samples were deposited by ion beam sputtering technique on 10 x 10 mm MgO [001] single crystal substrates. Firstly, about 600 nm of Pt as bottom electrode followed by 250 nm of PMO are deposited at 1023 K under 1.4×10^{-4} mbar O_2 , 1.0×10^{-4} mbar Xe (sputter gas) and 1.0×10^{-4} mbar Ar (neutralizer plasma) background pressure. In order to have a well-defined area for the charge attachment experiment, a ring of 8 mm diameter Allresist AR_N 7520.18 negative lacquer was prepared on the PMO by electron beam lithography. The sample was glued to a copper electrode by using thermally and electrically conductive glue (Polytech EC 101). The platinum layer and the copper electrode were short-circuited by means of a copper mesh glued on both materials.

4.2.2 Charge Attachment Induced Transport

The basic concept of the experimental approach has been described in previous reports [114,119,120]. Only a brief summary of the important key features is given in this section. The setup can be divided into three parts: (i) the generation of ions, (ii) the guiding of ions and (iii) the sample region. Alkali containing tectosilicates with the common composition $MA\text{Si}_2\text{O}_6$ (here M: K) were synthesized in the lab and used to generate these M^+ ions via the thermionic emission. The synthesis and properties of these ion sources have been presented elsewhere [121]. To guarantee a collision free path of the K^+ ion to the sample, the working pressure was set to a value below 2×10^{-6} mbar. The ion source was operated at a working temperature of about 1148 K and a fixed potential of 10 V, applied at the repeller lens to accelerate the ions towards the sample. The potential applied to the abstraction lens was -1.90 kV, so that the electric field relevant for thermionic emission was 2 kV/cm. The current of the ion beam I_{Ref} was ≥ 200 nA. The potassium ions were guided and focused towards the sample via ion optics consisting of a system of electrostatic lenses. The ions were passed through a grounded aperture with three 95 %-transmission meshes inside. The middle mesh was used to record the reference current, while the two outer meshes guaranteed homogeneous electric fields in front of the middle mesh and in front of the sample, respectively. After passing the aperture, the ions reach the sample surface. The bombarded area was determined by a steel mask placed 1 mm from the surface of the PMO (and thus not in contact). This setup is similar to that described in Ref. [120], with the exception that the mask was in contact with the sample in that work. Since the PMO is a good electrical conductor [122,123] for negative charge carriers (electrons and possibly O^{2-} ions), the ions were neutralized upon adsorption at its surface. The deposition of potassium leads to a concentration gradient at the front interface of the sample such that transport in the sample was induced. The current through the PMO, I_{back} , was recorded with a homemade transimpedance-amplifier, A/D converted, and processed in a computer. The measurement was completed when the incorporated amount of ions reached a charge of 10 mC. The sample temperature was set to 308.15 K and kept constant to ± 0.1 K via a resistance heating device equipped with a Pt100

thermometer and a temperature controller (Series 3216, Eurotherm).

4.2.3 Depth profiling

Concentration profiles arising from diffusion of potassium through the sample are analyzed by ToF-SIMS (IONTOF GmbH, Münster, Germany). For analysis of positive ions, the Bi⁺-LMIG (liquid metal ion gun) is used in the high current bunched mode (25 keV Bi⁺-ions, pulsed target current 0.50 pA). A Cs⁺ ion gun (30 nA; 3 kV) and an O₂⁺ ion gun (150 nA; 3 kV) are used for the sputtering process. The reason for using two different sputter guns will be discussed in the results section. All ion guns are oriented at a 45° angle to the sample surface. The area analyzed by the LMIG is 100 μm x 100 μm with a resolution of (128 x 128) pixels in the interlaced mode. The sputtered area was 300 μm x 300 μm. Mass spectra were collected within the mass range up to the mass to charge ratio of $m/z = 800$ with a mass resolution of $m/\Delta m = 6000-8000$. The SIMS spectra are calibrated using the peaks with a well-known mass to charge ratio, e.g., potassium (³⁹K⁺, ⁴¹K⁺), manganese (Mn⁺) or praseodymium (Pr⁺). With this technique, about 10⁷ mass spectra are recorded per crater, giving access to concentration profiles. The integrated area of the investigated ion peaks is obtained as a function of sputter time. The crater depth is determined post-analysis with a surface profilometer (SLOAN Dektak3ST, Veeco Instruments) and TEM to translate the sputter time into a sputter depth.

4.2.4 Electron microscopy

Changes of the microstructure and chemical structure due to ion incorporation on the nm scale are studied by transmission electron microscopy (TEM). We have used an aberration corrected FEI TITAN ETEM 80-300 with 300 kV acceleration voltage and a Philips CM 12 with 120 kV acceleration voltage, both equipped with an energy dispersive x-ray (EDX) detection system (X-Max provided by Oxford instruments with 130 eV energy resolution). EDX line scans were measured in scanning mode (STEM) with a spatial resolution of about 5 nm (CM12) or about 1 nm (TITAN). For the preparation of electron transparent thin lamellae, a focused ion beam (FIB) system (FEI Nova NanoLab 600; dual beam) is used. It is equipped with a gas injection system that enables chemical vapor deposition of carbon-platinum protection layers (hereafter termed FIB-Pt) using a carbon-platinum precursor. In addition, scanning electron microscope (SEM) images of the sample surfaces after ion incorporation are acquired by this system. Before every TEM lamella preparation, a protection layer of about 1 μm FIB-Pt is deposited in two steps in the respective area, cracking the precursor first with a 5 kV/1.6 nA electron beam and then a 30 kV/300 pA Ga⁺-ion beam. For the lamella cut out and thinning we have used a 30 kV Ga⁺-beam with beam currents between 30 pA and 7 nA.

4.3 Results

The diffusion of potassium through PMO has been investigated by the CAIT approach. A low energy K^+ ion beam ($E_{kin} = 10$ eV) was incident on the PMO sample for 28.3 hours, inducing the attachment of K^+ corresponding to a charge of 10 mC. During the bombardment, the measured backside current was constant (about $98 \text{ nA} \pm 7 \text{ nA}$) and the estimated reference current, I_{Ref} , obtained from a current measurement at the 95% transmission mesh was $\geq 200 \text{ nA}$. The sample temperature was kept constant at $T = 308.15 \text{ K}$. Directly after finishing the CAIT experiment, the sample was transferred to a ToF-SIMS machine where a depth profiling was performed. These concentration profiles clearly exhibited a pronounced diffusion profile of the potassium in the PMO sample. These concentration profiles will be analyzed and discussed below. Subsequent to the ToF-SIMS analysis, the sample was also analyzed by means of SEM and TEM.

4.3.1 ToF-SIMS analysis - data processing and interpretation

In ToF-SIMS, the raw data (provided as supplemental material in sec. 4.6) are affected by different detection efficiencies for distinct elements [117]. For quantitative analysis, the raw data must be normalized to take into account such variation as well as the stoichiometry of the sample. Inside the bulk of the PMO, the molar fractions x_i^0 of O^+ , Mn^+ and Pr^+ are well known. The averaged ion signal between the depth of 100 nm and 200 nm is related to the molar fraction of the corresponding ion by using equation 4.1,

$$x_i^0 = \frac{n_i^0}{n_{O^+}^0 + n_{Mn^+}^0 + n_{Pr^+}^0} = a_i \times I_i, \text{ with } i = O^+, Mn^+, Pr^+ \quad (4.1)$$

where n is the amount of substance, a is a proportionality constant, and I is the ToF-SIMS signal. The averaged platinum ion signal in its bulk between the depth of 400 nm and 420 nm and the highest potassium ion signal at the onset of the PMO are set to be one. It should be noted that the potassium ion signal in the vicinity of the surface (first 3 nm) is ignored due to the transient effect in SIMS [124, 125]. Finally, for graphical presentation, the concentration profiles for oxygen and platinum have been averaged over five data points in the depth domain. The final concentration profiles derived from this ToF-SIMS analysis of the PMO bombarded with potassium ions is shown in Figure 4.2. The Cs^+ gun has been used for sputtering in this analysis. Within the first nm, only the potassium signal (red crosses) and the oxygen signal (black circles) are observed. Subsequently the manganese signal (green squares) and the praseodymium signal (blue diamonds) increases. The front edge of the PMO is determined by the inflection point of the manganese signal marked by the grey solid line at 25 nm. The cesium sputtering causes a signal at $m/z (Cs_2O^{++}) = 140.905$, which interferes with the praseodymium ion signal at $m/z (Pr^+ = 140.908)$. Therefore, for the data displayed in Figure 4.2, we have used the PrO^+ ion signal instead of the Pr^+ signal to represent the praseodymium concentration profile. This procedure has been validated by performing ToF-SIMS depth profiling on a reference PMO sample employing an O^{2+} sputter gun. These studies demonstrate that

Figure 4.2: Concentration profile of the bombarded PrMnO_3 . The ion signals are normalized to their molar fraction.

an apparent Pr^+ peak observable in the raw data at the PMO-platinum interface for Cs^+ sputtering does not occur for O^{2+} sputtering (for further details see supplemental material 4.6). It is therefore justified to label the PrO^+ trace “ Pr^+ ”. Furthermore, the intensity of the $^{39}\text{K}^+$ -ion signal is often so strong that it saturates the detector. We therefore use the $^{41}\text{K}^+$ -ion signal to represent the potassium concentration instead.

The potassium ion signal as well as the oxygen ion signal show a local maximum in the intensity around 17 nm. Additionally it is observed that, inside the PMO matrix, the oxygen ion signal decreases. It is well known that the oxygen ions are mobile, due to the oxygen vacancy-related transport mechanism in perovskite typed materials [126–128]. Consequently, one might expect that oxygen ions diffuse in the direction of the PMO surface due to the chemical potential that is generated by the adsorbed potassium ions. In doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ $^{18}\text{O}/^{16}\text{O}$ isotope exchange depth profile experiments at a sample temperature of 700°C have shown that the diffusion coefficient for oxygen ions is $3.1 \times 10^{-16} \text{ cm}^2/\text{s}$ [129]. In our experiment the undoped PrMnO_3 has less oxygen vacancies and the sample temperature was set to 35°C ; therefore the oxygen diffusion coefficient is expected to be orders of magnitudes lower. Within the short attachment time of 28.3 h, oxygen diffusion would not be observed. It is more likely that potassium ions are neutralized at the PMO surface, due to its good electronic conductivity. Later upon transferring the sample to the ToF-SIMS machine, the potassium can possibly react with oxygen to form K_2O or with air humidity to form KOH . Since the profiling is conducted immediately after transferring the sample, this will not affect the concentration profiles inside the PMO region. Figure 4.2 illustrates that the potassium is not only deposited at the PMO surface, but also transported into the PMO matrix. One can observe that the potassium signal is decreasing exponentially. Since the potassium is able to occupy praseodymium-sites [122], the observed behavior could be explained by the substitution

of praseodymium by the incorporated potassium. A more detailed analysis shows that the Pr^+ signal slightly increases from the front to the back side of the sample. The effect is small but appears to be reproducible, suggesting that praseodymium is depleted towards the back side and possibly replaced by potassium. This is further supported by the observation that the sum of the normalized Pr^+ and K^+ signals is constant in the bulk region (see data provided in the supplemental material sec. 4.6). However, further studies are required to better understand which sites are involved in the transport of potassium.

4.3.2 Electron microscopy

In addition to the SIMS characterization, the sample was examined by electron microscopy. A cross sectional TEM lamella reveals a layer deposited in front of the PMO by the charge attachment experiment (Figure 4.3 a)). The average thickness of this layer is about 30 nm. Figure 4.3 a) also shows that this layer has turned into an agglomeration in one location. An EDX line scan recorded at the position of an agglomerate reveals that this agglomerate consists of potassium and oxygen - as does the entire front layer - (Figure 4.3 b)), which is in good agreement with the SIMS results. The exact stoichiometry of the front layer cannot be determined because of an intermixing with the FIB-platinum protection layer required for the preparation. Most likely, this is also the origin of an unexpected potassium signal within the protection layer. The offset between manganese and praseodymium in Figure 4.3 b) is a systematic error of the EDX analysis. The expected 1:1 ratio, however, is measured in the SIMS analysis (Figure 4.2). Apart from this discrepancy, the EDX analysis matches well to the SIMS measurements. Figure 4.3 c) and 4.3 d) show STEM images of the $\text{PMO-K}_x\text{O}_y$ interface being very smooth. STEM-EDX line scans across this interface reveal diffusion of the potassium into the PMO sample (Figure 4.3 e)). For a quantitative analysis of the potassium diffusion profile, we will focus on the ToF-SIMS data that have the advantage of sampling over a macroscopic region. Furthermore, this was recorded directly after the transport experiment.

The agglomerations observed in the TEM images (Figure 4.3 a)) are on the average $2\text{ }\mu\text{m}$ wide. At the time of the TEM investigation they covered about 10 % of the surface. Most likely, they have formed after the ToF-SIMS analysis. Evidence for this comes from a thorough analysis of the ToF-SIMS data. Since ToF-SIMS is a surface conformal technique, any relevant agglomerate sitting on the top of the sample would inevitably lead to a shift in the signal characterizing the beginning of the sample, here praseodymium and manganese. No shift is observed in the analysis. The normalized signals of praseodymium, of manganese as well as of potassium are independent of the local position on the ToF-SIMS crater. We further point out, that the TEM data show no positional correlation between the agglomerates and the grain boundaries discussed below.

4.3.3 Diffusion of potassium in the PMO

The concentration profiles shown in Figure 4.2 demonstrate that potassium has been transported into the PMO sample. In the following, we analyze this potassium concentration profile in more detail. Figure 4.6 shows the ToF-SIMS signal of potassium

Figure 4.3: a) Cross section TEM image without contrast aperture. The arrows marks the position of the STEM-EDX line scan presented in b). b) EDX concentration profile over an agglomeration and the underlying PMO film. The position of the interface of potassium compound and PMO is derived from the manganese signal and set to zero. x is the direction orthogonal to the sample surface. c), d) STEM HAADF images of the interface of PMO to K_xO_y . The arrows mark the location of the EDX potassium profiles presented in e). e) STEM-EDX intensity of potassium K_{α} at the interface of PMO to K_xO_y .

Figure 4.4: a) TEM Bright field image of the PMO film with representative density of twin boundaries. b) HRTEM image of a section of a twin boundary close to the surface.

(normalized at ≈ 15 nm) as a function of the depth, x , into the PMO. This ToF-SIMS signal is averaged over an area of $100\ \mu\text{m} \times 100\ \mu\text{m}$, in contrast to the EDX line scans shown in Figure 4.3. We take cautions in interpreting the ToF-SIMS signals in the first 10 nm due to limitations of the technique. Beyond a depth of about 15 nm we assume the potassium ion signal to be proportional to the ion concentration. The obtained ToF-SIMS profile represents a concentration profile that can be compared to theoretical models.

From comparison with previous BIIT work [118,119] it is evident that this profile is not an electrodiffusion profile. One might expect that the potassium profile can be rationalized by a solution of Fick's second representing bulk diffusion. Here, we are constantly shining a potassium ion beam at the sample surface constituting in good approximation a constant source. As we will further elucidate below the experimental concentration profiles cannot be rationalized by assuming a single pathway of bulk diffusion. This raised the question of whether two different transport pathways may be operative.

To shed further light on this question, we have recorded additional high-resolution TEM images. The TEM-data (Figure 4.4) reveal that the film has a columnar structure, which is caused by the existence of twin boundaries between (001) and (110) oriented twin domains. Here, the columns are separated by twin boundaries with an average distance of about 140 nm. The reason for this structure may be from a ferroelastic transition from cubic to orthorhombic narrowly below the deposition temperature [36] which leads to different twin orientations. This suggests two possible pathways for the potassium ion transport: (i) the bulk diffusion path and (ii) the diffusion along the twin boundaries. Generally, diffusion along the grain boundary is much faster than the bulk diffusion [130]. It has not been possible to observe concentration profiles along the grain boundaries in STEM-EDX, possibly due to the relatively high diffusion coefficient in combination with the time of several months between bombardment, lamella preparation, and increased

Figure 4.5: Simulated concentration distributions using Fisher's model for a) mixed pathway diffusion with enhanced grain boundary diffusion where $D_b = 1.5 \times 10^{-17} \frac{\text{cm}^2}{\text{s}}$ and $D_{gb} = 2.5 \times 10^{-14} \frac{\text{cm}^2}{\text{s}}$ and b) bulk diffusion only where $D_b = 1.5 \times 10^{-17} \frac{\text{cm}^2}{\text{s}}$.

temperatures during the latter. However, the STEM-EDX data (Figure 4.3 e) in the bulk shows profiles as expected according to Figure 4.6 for bulk diffusion.

The experimental concentration profile of potassium can be approximated by Fisher's model and lends support to the conclusion that the transport is dominated by the concentration gradient of potassium. In our theoretical modeling we examine the free diffusion of potassium in PMO from $\approx 15\text{nm}$ (of the sputter depth) using a simulation configuration similar to that used by Fisher [131]. The equations for bulk and grain boundary diffusion are discretized using the finite difference method as described in Ref. [132]. The computational domain contains 141×245 grid points in the x and y directions, respectively, which is bisected vertically with a straight grain boundary. These dimensions represent the average distance between grain boundaries and free diffusion distance, respectively. For the boundary conditions, constant values of one and zero are imposed at $y = 0$ and $y = 246$, respectively. This is assuming a constant source of potassium and that the opposite face is far from the deposited surface. We impose periodic boundary conditions on the remaining two edges. This configuration represents the experimental sample where twin boundaries are an average distance of 140 nm apart. Figure 4.5 compares the concentration profile between mixed pathway transport with enhanced grain boundary diffusion (Figure 4.5 a) and uniform diffusion in the bulk only (Figure 4.5 b) at $t=102,000$ seconds (28.4 hours). Figure 4.6 plots the average concentration along the film thickness for both simulation configurations along with the experimental ToF-SIMS data.

This diffusion model demonstrates K^+ diffusion through PMO via mixed pathways. A good fit is achieved using diffusion coefficients of $D_b = 1.5 \times 10^{-17} \frac{\text{cm}^2}{\text{s}}$ and $D_{gb} = 2.5 \times 10^{-14} \frac{\text{cm}^2}{\text{s}}$ for bulk and grain boundary diffusion, respectively. Sole bulk diffusion is also simulated using $D_b = 1.5 \times 10^{-17} \frac{\text{cm}^2}{\text{s}}$ for comparison. Both Figures 4.5 and 4.6

Figure 4.6: Normalized concentration along the thickness of the film from ToF-SIMS (black), simulated mixed pathway diffusion (green), and simulated sole bulk diffusion with no grain boundary (red). The surface of the sample is at $x = 0$ nm.

clearly illustrate the increased depth of penetration with high grain boundary diffusivities. It should be noted that in these simulations, the grain boundaries are placed far enough apart that their individual concentration distributions do not overlap. This may not be the case in the experimental PMO, where there may be regions with grain boundaries in close proximity. This interaction could influence the average concentration along the thickness of the film. Furthermore, our model does not consider the effects of space charge layers.

4.4 Discussion

As pointed out above the transport of potassium into the PMO occurs under the sole influence of concentration gradients. Any possible gradient of the electric potential should be small at least inside the sample, although we cannot categorially rule out the possibility of potential steps in the interface region, e.g., due to the redox pair K^+/K^O . Considering the observation that the sum of normalized signals for Pr^+ and K^+ is approximately constant in the bulk suggests that it is indeed K^+ , which diffuses through the PMO. This is not a contradiction to the remark that most of the K^+ ions are neutralized by electron conduction towards the front side of the PMO. Most likely, the overall transport of potassium involves two aspects, (i) the neutralization of K^+ at the surface of the sample and (ii) another change of the effective oxidation state at the interface K/PMO. A similar change of the effective oxidation state of iron at the interface of a perovskite/vacuum has been reported by Opitz et al. in an XPS investigation of electrochemical water splitting [133]. Since potassium and praseodymium do not exhibit the same valency, the transport described above most likely involves a compensation by electron and/or hole transport and a change in the Manganese oxidation state [134]. In fact, the material $Pr_{1-\delta}K_\delta MnO_3$ has indeed been investigated in some detail [122]. The result of our diffusion experiment corresponds to such a material, with the peculiarity that δ varies as function of depth into the material. The diffusion coefficients discussed above thus are considered effective diffusion coefficients. In the context of the classical model for grain boundary diffusion the situation operative in the current investigation most closely corresponds to Harrison's B case [135]. The HRTEM image in Figure 4.4 b) reveals that the perovskite crystal structure is preserved even in K-rich areas close to the interface. This observation supports our hypothesis that K occupies sites of the perovskite lattice. Due to its large ion radius, potassium is most likely substituting the praseodymium cations in the A site. The analysis of grain boundary diffusion and its relation to bulk diffusion has received considerable interest [49, 131, 136–140]. The finding of this work, i.e., the diffusion coefficient for grain boundary diffusion being approximately 3 orders larger than that for bulk diffusion, is in fact in line with numerous reports in the literature; for a recent review see Ref. [141]. On the other hand there are also reports of grain boundaries effectively hindering oxygen transport in yttria stabilized zirconia [142]. Ultimately, the macroscopic consequence of grain boundaries is believed to depend on many microscopic details, and therefore must most likely be examined for each sample separately.

4.5 Summary

The transport of potassium through praseodymium-manganese oxide (PMO) has been investigated by means of the charge attachment induced transport technique. Ex-situ ToF-SIMS analysis provided bimodal concentration profiles of the potassium, which were attributed with two distinct transport pathways. This conclusion is supported by electron microscopy revealing the presence of twin boundaries at average spacing of 140 nm. Based on theoretical modeling, a good fit to experimental data was achieved by assuming a bulk diffusion coefficient of $D_b = 1.5 \times 10^{-17} \frac{\text{cm}^2}{\text{s}}$ and a larger grain boundary diffusion coefficient of $D_{gb} = 2.5 \times 10^{-14} \frac{\text{cm}^2}{\text{s}}$, assuming the grain boundary density similar to the microscopy data.

4.6 Supplemental Material

In the main manuscript (section 4.3.1) we have presented the normalization procedure of the ToF-SIMS raw data, which is shown in Figure 4.7 below. In the discussion we mentioned that a cesium containing mass fragment (Cs_2O^{++} , $m/z = 140.9052$) interferes with the Pr^+ -signal ($m/z = 140.9077$). Since we use a ToF-SIMS (ION TOF GmbH, Münster, Germany) with a mass resolution of about $m/\Delta m = 8000$, we are not able to distinguish between the Pr^+ and Cs_2O^{++} -ion signal ($\Delta m_{\text{max}}(141) = 0.0176$). As a consequence, we have compared the concentration profiles obtained by cesium and by oxygen sputtering (see Figure 4.8).

In Figure 4.8 a) it is observed, that at the PMO-Pt-interface the Cs^+ and the Pr^+ -ion signal are increasing. As it is not expected, that the praseodymium is accumulated at the PMO-Pt-interface, we assume that this peak in the signal is caused by the Cs_2O^+ fragment. In Figure 4.8 b) there are no cesium ions used for sputtering and the accumulation of praseodymium at the PMO-Pt-interface was not observed. Furthermore the Pr^+ and PrO^+ trace show a similar behavior.

We have further commented in the main text that the sum of normalized K^+ and Pr^+ signals is constant inside the PMO bulk. To demonstrate this, we have normalized K^+ trace to the local intensity maximum around 17 nm and the Pr^+ trace to the local maximum at the interface between the PMO and the Pt electrode around 260 nm. These traces are shown in Figure 4.9.

Figure 4.9 also shows the sum of these two normalized traces K^+ and Pr^+ . Evidently the sum has a constant value of about 0.9 between 40 nm and 240 nm. This lends support to the interpretation that the K^+ ions indeed enter into the Pr^+ sites and consequently replace the latter.

Figure 4.7: ToF-SIMS raw data of the normalized data shown in Figure 4.2.

Figure 4.8: ToF-SIMS-Analysis of a PMO reference without K^+ -BIIT. The investigated PMO sample and its reference have been synthesized simultaneously. For yielding the concentration profile in a) we used the Cs^+ -sputter gun and for b) the O_2^+ -sputter gun was used.

Figure 4.9: Illustration of the correlation between K^+ and Pr^+ signals. K^+ and Pr^+ traces have been normalized at 17 nm and 260 nm respectively. Also shown is the sum of the normalized traces K^+ and Pr^+ as well as a line at intensity 1 to guide the eye.

CHAPTER 5

Role of oxygen vacancies for resistive switching in noble metal sandwiched $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$

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Role of oxygen vacancies for resistive switching in noble metal sandwiched $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$

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Abstract

Non-volatile resistance change under electric stimulation in oxides is a promising path to next generation memory devices. However, the underlying mechanisms are still not fully understood. We report here on the study of switching in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$ (PCMO) films sandwiched by noble metal Pt electrodes, where electrode oxidation can be excluded. In order to develop an understanding of the switching induced oxygen migration, its initial concentration is modified by post-annealing of the deposited PCMO films. The oxygen distribution is obtained by manganese valence determination using spatially resolved electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy mode (STEM). We observe correlations between virgin state resistance, resistive switching properties, oxygen vacancy distribution and stress/strain state of the PCMO films and propose a simplified interface resistance model based on the measured valence distribution. It assumes a linear correlation of oxygen vacancy concentration with conductivity and a metal to insulator transition above a critical vacancy concentration threshold. Our results suggest that resistance changes can take place at both interfaces of symmetric devices and only requires small changes in oxygen vacancy concentration.

5.1 Introduction

Since the discovery of non-volatile resistive switching in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) sandwiched by metal electrodes by Liu et al. [28], many investigations have been performed to understand the underlying mechanisms. A well-known model, based on redox reactions between PCMO and non-precious electrode materials, is the formation of an interfacial oxide layer with variable size and oxidation state [30, 80, 143, 144].

Switching also occurs in PCMO devices sandwiched by precious metal electrodes. The polarity of this switching is inversed with respect to the redox-based switching [29, 81], and frequently interpreted as an oxygen migration based mechanisms within the PCMO film. Since oxygen vacancies act as electron donors in p-doped PCMO [5], redistribution of oxygen vacancies within the PCMO should have significant impact on the electric properties, even leading to a vacancy-induced metal-insulator transition [30]. Evidence for such migration processes has been observed in diffusion [145] as well as in *in situ* TEM investigations [79].

However, assignment of switching polarities to single mechanisms is challenging because noble metal-PCMO heterostructures reveal two switching regimes [13]. Applying positive potential to the top electrode (PS: positive switching), small excitation voltages and/or short-term pulses cause a crossover from low-resistance state (LRS) to high-resistance state (HRS). In voltage cycling, the PS regime is superimposed by a "negative switching" regime (NS) where the HRS is formed at high negative top electrode potentials. Since electrode oxidation does not take place at noble metal/PCMO interfaces, the appearance of two switching polarities in one type of devices may point to two different migration-based mechanisms or to a single mechanism, which takes place at different interfaces. Experimentally, Scherff et al. [31] show that NS takes place near the top electrode. However, the active area for PS has not been unambiguously clarified.

The oxygen content of PCMO thin film samples can be altered by post-annealing, strongly influencing switching properties [146, 147]. Theoretical simulations by Rozenberg et al. [82] suggest that mainly the interface regions are affected by oxygen ion migration and are thus relevant for switching. Post-annealing can not only alter the oxygen vacancy concentration in this region, but can also change the strain state and thus affect the inhomogeneity of vacancy migration or networks of fast diffusion paths formed by extended defects like twin domains.

In this contribution, we focus on moderate post-annealing of PCMO in Pt-PCMO-Pt sandwich structures, where the crystal structure and phase composition is preserved and only point-like defects and nano-sized twin domains are affected. We study the influence on the virgin state resistance and resistive switching properties. The electric characterization is combined with measurement of the Mn valence state by means of electron energy loss spectroscopy (EELS) in scanning transmission electron microscopy (STEM) allowing to correlate oxygen content to resistivity changes.

5.2 Methods and Materials

Pt/PCMO/Pt thin film heterostructures have been deposited by means of ion beam sputtering on MgO (001) single crystal substrates. Using a deposition temperature T_{Dep} of 1073 K and partial pressures of 1.4×10^{-4} mbar O_2 , 1.0×10^{-4} mbar Xe (sputter gas) and 1.0×10^{-4} mbar Ar (neutralizer plasma), about 750 nm thick Pt films are deposited as bottom electrodes, followed by deposition of 250 nm thick PCMO layers. One of these samples ("air-annealed") is post-annealed in air at 1170 K for 20 h. This procedure should result in stoichiometric oxygen concentration of the PCMO. A second sample ("vacuum-annealed") is post-annealed at 1020 K for 2 h at a pressure of about 10^{-6} mbar. This treatment preserves the crystalline structure of the films. In contrast, vacuum post-annealing for 4 h at 1070 K causes phase decomposition of PCMO (see supplemental material sec. 5.5.1). As top electrodes, Pt layers, and, subsequently, Au layers of about 200 nm thickness are deposited at room temperature on all samples after the annealing, resulting in a symmetric Pt/PCMO/Pt heterostructure. The symmetry, however, is slightly cancelled by the epitaxial interface to the bottom electrode in contrast to the non-epitaxial one to the top interface.

The different heterostructures are characterized by means of X-ray diffraction performed in a Bruker D8 Discovery diffractometer and by transmission electron microscopy (TEM) in a FEI Titan 80-300 aberration corrected environmental TEM (ETEM) operated at 300 kV and in high vacuum. The oxygen content of the samples is determined with a Gatan Quantum 965 ER GIF for electron energy loss spectroscopy (EELS) in STEM mode. The GIF is equipped with a dual beam deflector unit. In order to record the zero loss peak (ZLP) and the Mn L-edge the energy ranges from -20 to 185 eV and from 480 to 685 eV are measured simultaneously with a resolution of 0.1 eV per channel. The energy resolution derived from full-width-half-maximum (FWHM) of the ZLP amounts to about 1 eV, and the electron dose has been about 10^6 to 10^7 e/ $\text{\AA}^2$ per spectrum.

The Mn L3/L2 intensity ratio is a measure of the Mn valence state [86, 87], and also qualitatively describes the oxygen content, as shown in detail in section 3.3.2. Assuming that the formation of an oxygen vacancy creates two electrons, the oxygen deficiency δ in $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_{3-\delta}$ can be deduced from the Mn valence Z_{Mn} according to $\delta = 0.5 \times (3.35 - Z_{Mn})$. Consequently, we interpret a decrease of the Mn valence state as a decrease of the oxygen content.

Micro-pillar devices (Fig. 5.1) with diameter of $1.5 \mu\text{m}$ have been prepared by means of a focused-ion-beam (FIB) based technique [55] for electric measurements in an FEI Nova Nano SEM 650 system. The bottom electrodes of the devices are grounded and the potential is applied to the top electrode by a Tungsten tip mounted on a Kleindiek micromanipulator. A Keithley 2430 source meter serves as voltage source and for current detection. Voltage cycles ($0 \Rightarrow V_{max} \Rightarrow 0 \Rightarrow -V_{max} \Rightarrow 0$) of 2 ms pulses with different maximum voltages are performed. The number of the equidistant excitation pulses is fixed to 400. Each excitation pulse is followed by a 2 ms "read pulse" of 0.05 V in order to determine the remanent resistance change. During the electric measurements the electron beam of the SEM is blanked.

Figure 5.1: SEM cross-section image of a micro-pillar. Electric characterizations are performed without additional FIB-platinum protection layers. Inset: Electrical connection.

5.3 Results and Discussion

Independently from additional post-treatment steps, X-ray diffraction inspections as well as TEM analysis exclude the presence of impurity phases or PCMO phase decomposition. All PCMO films on Pt/MgO reveal preferred [001] growth direction perpendicular to the substrate accompanied by different amounts of [110] twins which inevitably exist because of the cubic-orthorhombic phase transition [36]. In addition, significant fractions of [020]/[112] misorientations are present. Consequently, we prepared the micro-pillar devices for electric characterization in sample areas with [001]/[110] growth direction. Additional post-annealing steps mainly affect the strain state of the PCMO thin films. Using a bulk lattice parameter of $c = 7.67 \text{ \AA}$ [34], as-grown PCMO films on Pt/MgO reveal an out-of-plane strain of $\varepsilon_{oop} = 1.03(6) \%$. Post-annealing reduces this strain by $\varepsilon_{oop} = -0.213(1) \%$ for the air-annealed samples and by $\varepsilon_{oop} = -0.154(1) \%$ for the vacuum-annealed samples (see supplemental material sec. 5.5.2).

In order to investigate the influence of post-treatments on the oxygen content of PCMO, we have performed STEM-EELS scans from top to bottom electrode (Fig. 5.2 a). Each of these measurements has been recorded in areas, which are not electrically stimulated. As-grown, the Mn valence decreases from about 3.3 to 3.15 within the first 100 nm and then remains almost constant near the bottom electrode. We expect that ion-beam sputtering is accompanied by formation of oxygen-deficient films. Most probably, the increasing oxygen content towards the top area is formed due to additional oxidation during cooling from deposition temperature down to room temperature at an oxygen partial pressure of about $1 \times 10^{-4} \text{ mbar}$. Post-annealing in vacuum mainly reduces this gradient, i.e. the oxygen content near the bottom electrode is almost unaffected. In contrast, long-term

annealing at atmospheric pressure increases the oxygen content. The absolute values of the Mn valence probably include a systematic error, as discussed in detail in 3.3.2. Assuming that air-annealing completely removes the oxygen deficit δ in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$ the difference in Mn valence implies a preparation-induced average oxygen deficit of $\delta \approx 0.04$ in as-grown samples, which is preserved during vacuum-annealing.

The contribution of the interfaces and the PCMO bulk to the resistance are comparable in as-grown films [55]. Changing the mean oxygen content and the oxygen distribution near the interface should therefore strongly affect the resistance. Indeed, the virgin state resistances of the three heterostructures are quite different (see Tab. 5.1). To estimate changes of interface resistance, we analyze the Mn valence distribution in at least three separate areas near the top interface of each lamella. The total analyzed area per lamella is ca. $500 \text{ nm} \times 9 \text{ nm}$. The distribution resembles an arrangement of channels, almost perpendicular to the interface (see supplemental material sec. 5.5.3). According to this structure we divided the top interface area into $1 \text{ nm} \times 3 \text{ nm}$ large segments, where for each segment the Mn valence is determined and the resistance is calculated. Thus, we assume for electric modelling a parallel circuit perpendicular to the interface, each composed of three "serial resistors" with size of $1 \text{ nm} \times 3 \text{ nm}$. Consequently, the segment of minimum Mn valence should govern the resistance of each channel in this model. The distribution of the minimum valence is shown in Fig. 5.2 b) and roughly reveals a Gaussian distribution of the Mn valence for all heterostructures. Annealing of the PCMO films mainly shifts the center of the distribution, i.e., air-annealing increases the number of high-valence channels whereas vacuum-annealing causes the opposite.

We assume that conductivity vanishes below a Mn valence of 3.0 due to metal-insulator transition [30] or polaron localization [76] and increases linearly above 3.0. Additionally, we normalize the conductivity to one for Mn valence of 3.35, the valence of the stoichiometric composition. Summing up the parallel contributions of the channels and using the as-grown virgin state as reference, this simple model implies a decrease of resistance of about 10 % due to air-annealing but an increase of about 60 % due to vacuum-annealing (see Tab. 5.1). We have additionally calculated a scenario without a metal-insulator transition assuming a vanishing conductivity at a Mn valence of 2.5. However, this results in significantly lower values for the resistance change, supporting the assumption that a metal-insulator transition at a Mn valence of 3.0 is more adequate. In general, the calculated changes are a little smaller than experimentally observed. However, the model only takes into account changes at the top electrode, neglecting resistance changes in the PCMO volume and at the bottom electrode. Nevertheless, comparison of our model with measured resistance changes show that subtle changes of the oxygen content and oxygen distribution can significantly change the interface resistance.

Voltage cycling with sufficiently high maximum voltages gives rise to a switching behavior, where both, PS and NS type of resistance changes, are present in one cycle (see Fig. 5.8 in the supplemental material sec. 5.5.4). Fig. 5.3 a) shows the coexistence of PS and NS in more detail: Starting from a low-resistance state, increasing negative excitation voltage pulses firstly cause a decrease of the remanent resistance (PS) followed by an increase, i.e. the formation of a HRS (NS). Consequently, we define the PS switching ratio $r = (R_{HRS} - R_{LRS})/R_{LRS}$ from the resistance decrease and the NS switching ratio with re-

Figure 5.2: Mn valence of the three different films in virgin state deduced from EELS as a measure of oxygen content. a) Mn valence in dependence on the distance to the top electrode. The error bars represent averaging over 500 parallel line scans recorded from different areas, each with a line distance of 1 nm (distance ≤ 10 nm) and 50 to 100 scans (distance > 10 nm), respectively. b) Mn valence distribution within the first 9 nm to the top electrode. All line scans from a) with a distance of 1 nm are subdivided into 1 nm (in-plane) $\times$ 3 nm (out-of-plane) segments and the minimum Mn valence of the out-of-plane-row is determined.

property	film	as-grown	air-annealed	vacuum-annealed
R_{VS} [Ωcm]		0.090(4)	0.072(5)	0.22(1)
$R_{VS}/R_{VS,as-grown}$		1	0.8	2.45
Calculated $R_{int}/R_{int,as-grown}$	MIT	1	0.91	1.59
	no MIT	1	0.96	1.26
V_{PS} [V]		0.55(4)	0.42(4)	0.44(4)
V_{NS} [V]		0.69(2)	0.62(2)	0.75(3)

Table 5.1: Overview of electric properties of as-grown, air-annealed and vacuum-annealed heterostructures. R_{VS} : Overall resistivity (top-to-bottom) of the virgin state. R_{int} : Interface resistance, calculated from the minimum Mn valence distribution shown in Fig. 5.2 b) assuming a metal-insulator transition (MIT) at a Mn valence of 3.0 or not (zero conductivity at a Mn valence of 2.5). V_{PS} , V_{NS} : Onset voltage of switching in the PS and NS regime.

spect to the local remanent resistance minimum as R_{LRS} (Fig. 5.3 a). The dependence of the switching ratios on excitation voltage is summarized in Fig. 5.3 b) (see supplemental material sec. 5.5.4 for full cycles and details of electric characterization). It is worthwhile to note that definition of switching ratios in such a way gives rise to very reproducible switching characteristics. The error bars in Fig. 5.3 b) represent various voltage cycles with different maximum voltages. This is remarkable, because PS is followed by a much larger NS in most cycles, indicating that PS and NS do not influence each other.

Air-annealing, i.e. increasing the oxygen content and decreasing strain of the entire PCMO layer, decreases both, the PS and the NS onset voltage hinting that both regimes are governed by the same mechanism. Vacuum-annealing also reduces the global strain, but induces an oxygen deficient layer at the top interface. This affects NS and PS differently. It hampers NS by shifting the NS-onset to higher voltages, whereas the PS onset voltage is lowered. Comparing both results leads to the conclusion that NS is located near the top electrode, whereas PS most probably takes place near the bottom electrode. Our results show that high concentration of oxygen vacancies does not necessarily reduce the switching onset or improve the switching ratio. However, even small redistributions of oxygen vacancies at the interfaces can induce pronounced resistance changes.

Figure 5.3: Resistive switching behavior of differently post-treated heterostructures: a) Negative branch of remanent resistance versus excitation voltage. The arrows indicate direction of voltage cycling. Parts of the branch attributed to PS and NS as well as the reference resistance for NS switching (magenta) are marked exemplarily at the vacuum-annealed film. b) Required excitation voltage for specified PS and NS switching ratios including linear fits of the data. The error bars indicate averaging over various voltage cycles.

5.4 Summary

In summary, we have shown that surface manipulation by post-annealing has a big impact on virgin state resistance, switching ratio and switching onset of Pt-PCMO-Pt heterostructures. We have explained this behavior in a simplified model, in which redistribution of oxygen vacancies affects the resistivity by annihilation of charge carriers. In general, we expect that the resistance change is mainly governed by the polaronic mobility which is affected by redistribution of oxygen vacancies changing the level of doping, disorder and strain.

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5.5 Supplemental Material

5.5.1 PCMO phase decomposition due to vacuum annealing

In contrast to vacuum-annealing for 2 h at 1073 K analyzed in the main text, treatment for 4 h causes phase decomposition. This is clearly visible in the recrystallized microstructure of such treated PCMO films (Fig. 5.4 a)), long-range variation of composition deduced from EDX, which implies formation of phases with different chemical compositions (Fig. 5.4 c)) and confirmed by XRD studies.

5.5.2 XRD analysis of as-grown and post-treated PCMO

In XRD, as-grown and post-treated PCMO films on Pt/MgO only reveal diffraction patterns, which correspond to the twinned (004)/(220) growth orientation and to the (020)/(112) misorientation. The latter is most probably related to (111) misorientation present in the Pt bottom electrode template (Fig. 5.5 a)). Direct comparison of the thin films before and after the post-annealing step shows that the fraction of misorientations does not strongly change. The main effect of post-treatment is strain relaxation, visible in the shift of PCMO peak positions toward the bulk peak position and reduction of FWHM indicating a better crystallinity (Fig. 5.5 b) and c)).

5.5.3 Manganese valence maps near the surface

In the main text Fig. 5.2 b) shows the distribution of the lowest Mn valence within the first 9 nm to the top electrode. These data represent averaging of several scans. Typical 2d-distributions of the Mn valence states are shown in Fig. 5.6. The scan resolution is 1 nm in x and y direction (y perpendicular to the interface). In Fig. 5.2 b) three data points in y-direction have been binned to improve signal-to-noise-ratio. As already indicated by the error bars in Fig. 5.2, the films strongly differ in their averaged Mn valence and the distribution. However, a common feature of all films is a columnar distribution perpendicular to the interface. In the vacuum annealed sample, most pronounced changes of the valence are detected close to twin boundaries, (contrast change in STEM ADF). In Fig. 5.7 we qualitatively calculate a resistance from the valence. We set the conductivity/ resistance $\sigma = 0/R = \infty$ for all valence up to 3 and $\sigma = 1/R = R_0$ for a valence of 3.35. In between, we assume a linear behavior in σ .

5.5.4 Electric characterization of the micro-pillars

Fig 5.8 a) shows the $I - V$ -characteristics of micro-pillar of the different heterostructures below the switching threshold. The different slopes at small voltages mirror the different virgin state resistances of the differently treated PCMO layers. The exponential decrease

Figure 5.4: TEM investigation of a PCMO film grown on SrTiO_3 (STO) which is annealed for 4 h at 1070 K at a pressure of 10^{-6} mbar. a) representative cross-section and selective area diffraction image of the thin film. b) STEM bright field image including the position of the STEM-EDX line scan presented in c).

of resistance at high voltages is a typical feature of polaron mobility. Increasing the excitation voltage leads to bipolar resistive switching shown in Fig 5.8 b). The small resistance changes in the PS regime are only visible by plotting the remanent resistance ($V_{exc} = 0.05$ V) versus the excitation voltage. Examples for the PS- and NS-regime for all films are presented in Fig. 5.8 c) and d). Fig. 5.8 c) shows the cycles with the highest maximum excitation voltage before NS sets in. Due to the significantly higher NS-onset voltage of the vacuum-annealed film, it is possible to apply higher voltages in the PS regime and, as a result, to achieve a higher maximum positive switching ratio.

The maximum excitation voltage of the voltage cycles has been discretely increased in 0.05 V steps. According to Tab. 5.1 the NS onsets are 0.62 V (air-annealed) and 0.75 V (vacuum-annealed). As a consequence, the voltage difference to the onset is slightly different in the shown cycles in Fig. 5.8 d) (≈ 0.13 V and ≈ 0.1 V respectively) resulting in different switching ratios.

With respect to PS, the onset voltages of the LRS to HRS transition (positive potentials) and the reverse transition (negative potentials) are very similar. Therefore, we have included data from both branches in our analysis. In the NS-regime, small differences between the branches occur, especially in the vacuum-annealed film. Consequently, we have only used data from the negative branch, i.e. LRS to HRS transition.

Figure 5.5: X-ray diffraction pattern of differently post-treated PCMO films on Pt/MgO. a) Overview. b) and c) detailed scans in the vicinity of the (020)/(112) and (004)/(220) pattern, respectively. The Au peak corresponds to top electrode material for electrical characterization. Dashed lines in b) and c) indicate the unstrained peak positions.

Figure 5.6: (Right) Representative manganese valence maps obtained by STEM-EELS near the top electrodes. y is the distance to the top electrode. (Left) STEM ADF images of the analyzed regions.

Figure 5.7: Calculated relative resistances resulting from the Mn valence maps of Fig. 5.6. y is the distance to the top electrode.

Figure 5.8: Electric characterization of micro-pillars. The arrows indicate voltage sweep directions. a) $I - V$ -characteristics without remanent resistance change; b) $I - V$ -characteristics in the negative switching regime; c) Remanent resistance versus excitation voltage in the PS regime showing the cycle with the highest maximum excitation voltage before NS sets in. d) Remanent resistance versus excitation voltage in the NS regime. The difference of maximum excitation voltage to NS-onset slightly differ (as grown: $\approx 0.11 \text{ V}$, air-annealed $\approx 0.13 \text{ V}$, vacuum-annealed $\approx 0.1 \text{ V}$).

CHAPTER 6

General Discussion and Summary

In this work, novel experimental approaches, especially in the area of *in situ* observation in the transmission electron microscope have given deep insights in the microscopic mechanisms of resistive switching. The results give strong evidence that a redistribution of atoms is the key aspect of resistive switching in PCMO. The observed change of the manganese valence in combination with further correlations to the oxygen K-edge in the different resistance states is a strong indication that the redistributed atoms are oxygen ions.

There are two approaches in this work to correlate the amount of oxygen vacancies described by δ in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ with the resistance change using *in situ* and *ex situ* TEM investigations.

Firstly, *in situ* TEM experiments reveal the formation of conductive filaments of high oxygen content after applying voltage pulses of certain strength. As a consequence, the resistance of the whole device is decreased. The filaments can be disrupted by an electron beam-induced homogeneous oxidation.

The origin of these structures lies probably in the electric properties of PCMO. Due to the polaronic conductivity, the resistance decreases with increasing temperature [43]. Thus, more electric current flows through the hot area further increasing the temperature, giving rise to self-amplification and thus thermal instability. In such hot filament areas, preferential electro-migration of oxygen vacancies takes place, leading to non-volatile resistance changes. As a consequence, it is plausible that small variations in resistivity at the beginning of the electric pulse are amplified during electric stimulation.

The results of the diffusion experiments of potassium in PMO exhibit that there are two different diffusion channels. Besides the bulk diffusion, a three orders of magnitude faster diffusion along grain- and twin-boundaries is detected. Bak et al. [53] have found a similar relation for oxygen diffusion in LaMnO_3 , so it is reasonable that twin boundaries could be the starting point of these self-amplifying conductive channels. Nevertheless, CAIT diffusion experiments with oxygen ions are highly desired.

The main difference in switching behavior of TEM lamellae to micro-pillars is the unipolar type of switching in the $I - V$ -characteristics. This feature suggests that the observed switching is superposed by effects induced by the TEM-specific properties of the lamella: Primarily, all atoms of a TEM lamella are within 50 nm to the surface to vacuum, whereas

only about 7 % of the atoms of a micro-pillar fulfill this criterion. This, in turn, leads to completely different conditions for heat development and a stronger interaction with the environmental gas atmosphere or the vacuum. In combination, these effects evoke more exchange with the gas environment (in oxygen atmosphere) or loss of oxygen (in high vacuum) of TEM lamellae in comparison to micro-pillars. Additionally, the impact of the electron beam is higher in the thin lamella and the stress-strain is different. The substrate is assumed to be rigid in a micro-pillar, so almost the whole stress of the epitaxial interface is compensated within the PCMO. Thereby, the highest strain occurs near the epitaxial interface. With increasing distance to this interface the strain decreases [35]. In an about 50 nm thin TEM lamella, the substrate cannot be assumed as rigid so the strain-distribution is more complex and probably more homogeneous within the PCMO. The second approach investigates the properties of macroscopic devices whose oxygen content is slightly modified by different ways of annealing. It is shown that these subtle changes have large impact on the electric resistance. A basic model based on a linear correlation of oxygen deficit δ and conductivity hints to a metal-insulator-transition for $\delta = \frac{x}{2}$ as it is also proposed by Lee et al [30].

The *in situ* observations suggest the applied electric field as major driving force for the oxygen ion migration. It is probably supported by a considerable temperature-increase within the devices due to Joule heating. The exact temperature of the PCMO layer during switching has not been directly measured. However, often melting effects at the neighbored gold contacts occur. This suggests that temperatures of more than 1000 K are likely to arise in the devices. However, the results of the CAIT diffusion experiments suggest decent diffusion even at room temperature, especially at grain- and twin boundaries. The fact, that the electron-beam-induced oxidation takes also place at room temperature, is a further hint for rather low required temperature for oxygen ion movement. This is in agreement with the observation of a significant resistance relaxation of the switching states at room temperature [46].

Both, *in situ*, as well as *ex situ* annealing investigations clearly show that even subtle changes within 5 nm near the interfaces induce significant resistance changes. This fact fits well to the electric localization experiments of M. Scherff [46], which also suggest that the main effect takes place near the interface.

In contrast, the filamentary mechanism observed in the *in situ* TEM investigations is, in principle, located within the bulk instead at the interfaces to the electrodes. However, the form of the filaments in combination with the observation of a significantly higher diffusion coefficient at grain and twin boundaries in chapter 4 points in the direction that the filaments form at these boundaries, so even in this case interfaces might play an important role. Additionally, it has to be clarified in future experiments, as stated above, how far the results of the *in situ* TEM investigations can be applied to macroscopic devices.

In summary, the results support a model of oxygen electromigration as basic mechanism for resistive switching in PCMO sandwiched by noble-metal-electrodes. Especially, the emergence of oxygen deficient areas near the interfaces induces large resistance effects, probably enhanced by a metal-insulator-transition.

In the scope of application, the results present oxide based cells as a promising approach for future ReRAM. The fact, that the switching effects are located mainly at the interfaces,

combined with the low required applied voltages, suggests that it is possible to design very small devices in the order of 10 nm or less. This opens interesting perspectives to design much smaller devices than it is possible with the recent *Flash*-cells. Furthermore, this work gives hints what factors are probably crucial in such devices: The heat dissipation and interaction with the surrounding environment, for example, it will be necessary to set barriers to avoid a loss of oxygen to ensure long-term stability.

In situ TEM will probably be an important method in these processes. This work has on the one hand shown the challenges of such investigations and has on the other hand given several solution pathways to ensure *in situ* TEM observation can play a key role in further developments in the field of remanent resistive switching in oxides.

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Author Contributions

This thesis includes three published articles which present original research by the author:

Chapter 3:

Developing an *in situ* environmental TEM set up for investigations of resistive switching mechanisms in Pt-Pr_{1-x}Ca_xMnO_{3-δ}-Pt sandwich structures

Thilo Kramer, Daniel Mierwaldt, Malte Scherff, Mike Kanbach and Christian Jooss

Ultramicroscopy **2018**, 184 (A), p. 61-70

Chapter 4:

Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO₃

Johannes Martin, Melanie Gräf, Thilo Kramer, Christian Jooss, Min-Ju Choe, Katsuyo Thornton and Karl-Michael Weitzel

Physical Chemistry Chemical Physics **2017**, 19, p. 9762-9769

Chapter 5:

Role of oxygen vacancies for resistive switching in noble metal sandwiched Pr_{1-x}Ca_xMnO_{3-δ}

Thilo Kramer, Malte Scherff, Daniel Mierwaldt, Jörg Hoffmann and Christian Jooss

Applied Physics Letters **2017**, 110, 243502

The thin-films deposition and characterization as well as the TEM-lamellae preparation for all publications were made by the author. The development of SiN-grids for the *in situ* TEM investigations were done in cooperation with Dr. Daniel Mierwaldt. He also wrote the LabTalk script to automate the Mn valence determination used in chapter 3 and 5 and composed the respective paragraph in these publications.

The micropillars presented in chapter 3 and 5 were electrically characterized in cooperation with Dr. Malte Scherff. Technical help at the TEM for the experiments of all chapters was provided by Dr. Vladimir Roddatis (primarily STEM-EELS alignments) and Dr. Daniel Mierwaldt (primarily environmental experiments).

First *in situ* experiments, presented in the supplemental material of chapter 3 were performed in cooperation with Oskar Janik. All data presented in chapter 3 were analyzed by the author. The manuscript was primarily written by the author in collaboration with Prof. Dr. Christian Jooß.

Chapter 4 is derived from a close cooperation with the Research Groups of Prof. Dr. Weitzel, Philips-Universität Marburg and Prof. Dr. Thornton, University of Michigan, USA. The author deposited the films and conducted all XRD and TEM characterization. The CAIT and SIMS experiments were done in Marburg by Dr. Johannes Martin, Melanie Gräf and Prof. Dr. Karl-Michael Weitzel. They also produced the figures: 4.1, 4.2 and 4.6 in the main text as well as figures 4.7, 4.8 and 4.9 of the supplemental material. The simulations according to Fisher's model including figure 4.5 were performed by Min-Ju Choe and Prof. Dr. Katsuyo Thornton. The manuscript was written respectively to the conducted experiments, so the author wrote all paragraphs concerning preparation and

TEM characterization as well as the first part of the introduction describing PMO in collaboration with Prof. Dr. Christian Jooß.

Except the TEM-EDX characterization and analysis presented in the supplemental material (section 5.5.1), which were conducted by Dr. Stephanie Mildner, all data in chapter 5 were analyzed by the author. The manuscript was primarily written by the author in collaboration with Dr. Jörg Hoffmann and Prof. Dr. Christian Jooß.

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01/2018 „Developing an in situ environmental TEM set up for observations of resistive switching mechanisms in $\text{Pt-Pr}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ sandwich structures“
UM, 184A, 61-70

05/2017 „Role of oxygen vacancies for resistive switching in noble metal sandwiched $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$ “
Appl. Phys. Lett., 110, 243502

03/2017 „Charge Induced Transport - Bulk and Grain Boundary Diffusion of Potassium in PrMnO_3 “
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08/2016 „Mechanical stress and stress release channels in 10-350 nm palladium hydrogen thin films with different micro-structures“

Acta Materialia, 114, 116-125
01/2016 „Transport of ions in a mixed Na^+/K^+ ion conducting glass - electrodiffusion profiles and electrochemical interphase formation“
Electrochimica Acta, 191, 616-623

- 08/2015** „Influence of persistent resistance changes on structure and chemical composition of metal- $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ -metal thin film heterostructures observed *in* and *ex situ* by STEM-EELS“
Posterbeitrag auf der „MC 2015“, Göttingen
- 07/2015** „Strain driven phase decomposition in ion-beam sputtered $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ films“
in: Journal of Nanomaterials - Special issue on Functional Oxide Thin Films and Nanostructures Art. 3 (2015)
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- 09/2012** „Ferromagnetism in Lightly Doped $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ($x = 0.023, 0.036$) Nanoparticles Synthesized by Microwave Irradiation“
Chem. Mater. 24 (19), 3758-3764
- 06/2012** „Nanocomposite stability in Fe-, Co-, and Mn-based perovskite/spinel systems“
Journal of Materials Research 27 (11), 1462-1470
- 03/2012** „Thermal conductivity as sensor for defects in homoepitaxial SrTiO_3 “
Posterbeitrag auf der „DPG 2012“, Berlin
- 02/2012** „Interplay of point defects, biaxial strain, and thermal conductivity in homoepitaxial SrTiO_3 thin films “
Appl. Phys. Lett. 100, 061904 (2012)