DISS. ETH Nr. 18638

OXYGEN VACANCIES IN SrTiO₃: AN X-RAY ABSORPTION STUDY

ABHANDLUNG

zur Erlangung des Titels

DOKTOR DER WISSENSCHAFTEN der ETH ZÜRICH

vorgelegt von Björn Pererik Andreasson Fil. Mag., Göteborgs Universitet

geboren am 13 Februar 1979 aus Schweden

Angenommen auf Antrag von Prof. Dr. J. Friso van der Veen, Referent Dr. G. Ingmar Meijer, Korreferent Dr. Markus Janousch, Korreferent Dr. Urs Staub, Korreferent

2009

Summary

Oxygen vacancies have been shown to strongly influence the properties of transition metal oxides. In particular, they are very important for the control of transport properties in conducting oxides. A quantitative determination of oxygen vacancies in low concentrations, especially with spatial resolution, is generally considered very challenging. In this dissertation, X-ray absorption spectroscopy measurements on $SrTiO_3$ are presented. In these $SrTiO_3$ samples, 2‰ of the Ti has been substituted with other 3d transition metals. It is shown that the X-ray absorption spectra of the 3d transition metals change when the samples are reduced, but not the Ti X-ray absorption spectrum. Multiple scattering calculations show that this change is due to an oxygen vacancy in the first shell of the 3d transition metals. Density functional theory calculations confirm that the oxygen binding energy in the samples is lowest in the nearest neighbor shell of the Ti substituting 3d transition metals. This indicates that the 3d transition metal ions attract oxygen vacancies in $SrTiO_3$, and can be used to quantitatively calculate the oxygen vacancy concentration at values well below 1‰.

In the search for new non-volatile memories, as a replacement for the Flash technology, a resistive change memory device based on transition metal oxides has shown great potential. In the second part of this dissertation, resistive switching devices consisting of $SrTiO_3$ single crystals doped with 0.2% Cr have been studied with spatially resolved X-ray absorption spectroscopy. The induction of a resistive switching state in these devices is accompanied by the introduction of oxygen vacancies. The distribution of the oxygen vacancies in the devices was studied during the electrical conditioning of the memory devices. It was discovered that oxygen vacancies are introduced at the positively biased electrode, and percolate towards the grounded electrode to form a bifurcated conducting network. Further it is shown that the vacancies are in a confined region in the memory devices, producing a conductive path in the insulating matrix. Finally, the valence of Cr is proven not to be correlated with the resistive switching state.

Zusammenfassung

Es wurde gezeigt, dass Sauerstofffehlstellen einen starken Einfluss auf die Eigenschaften von Übergangsmetalloxiden haben, insbesondere sind sie wichtig für die Transporteigenschaften von leitenden Oxiden. Die quantitative Bestimmung von niedrigen Sauerstofffehlstellenkonzentrationen bleibt bis heute eine grosse Herausforderung und die räumliche Auflösung dieser tiefen Konzentrationen gestaltet sich als noch grössere Schwierigkeit. Im ersten Teil dieser Dissertation wird SrTiO₃ mithilfe von Röntgenabsorptionsspektroskopie studiert, wobei 2‰ von Ti mit 3*d* Übergangsmetallen ersetzt ist. Es wird gezeigt, dass sich das Röntgenabsorptionsspektrum der 3*d* Übergangsmetalle ändert, wenn die Probe reduziert wird, während das Röntgenspektrum von Ti keine Änderungen zeigt. Mehrfachstreuungsberechnungen zeigen, dass diese Änderung durch Sauerstofffehlstellen in der ersten Schale am 3*d* Übergangsmetalle erzeugt wird. Berechnungen basierend auf der Dichtefunktionaltheorie zeigen, dass die Bindungsenergie des Sauerstoffs für die nächsten Nachbarn der 3*d* Übergangsmetallionen am kleinsten ist. Das deutet darauf hin, dass die 3*d* Übergangsmetallionen in SrTiO₃ Sauerstofffehlstellen anziehen. Dieses Phänomen kann dazu verwendet werden, die Sauerstofffehlstellenkonzentration unter 1‰ quantitativ zu bestimmen.

Zur Ablösung von Flash-Speichern wird nach neuen nichtflüchtigen Speichern gesucht und Speichereinheiten aus Übergangsmetalloxiden, die auf dem Wechsel des Widerstands beruhen, zeigen grosses Potential. Im zweiten Teil dieser Dissertation wurden Speichereinheiten, die den Widerstand wechseln können, aus mit 0.2% Cr gedopten SrTiO₃ Einzelkristallen hergestellt und mit räumlich auflösender Röntgenabsorptionspektroskopie untersucht. Die Erzeugung eines Zustands, in dem der Widerstands gewechselt werden kann, ist von der Erzeugung von Sauerstofffehlstellen begleitet und die Verteilung der Sauerstofffehlstellen im Material wurde während des elektrisch leitenden Zustands der Speicherzelle untersucht. Die Sauerstofffehlstellen wurden an der positiv geladenen Elektrode erzeugt und durchdringen den Einzelkristall in Richtung der geerdeten Elektrode, indem sie ein gabelförmiges, leitendes Netzwerk bilden. Es wird gezeigt, dass die Fehlstellen sich in einer begrenzten Region der Speicherzelle befinden und einen leitenden Pfad in der isolierenden Matrix herstellen können. Desweitern wird gezeigt, dass der Valenzzustand von Cr nicht mit dem Widerstandwechselnden-Zustand korreliert werden kann.

Contents

Sı	Summary								
Zı	ısam	menfassung	v						
1 Introduction									
2	Ma	Materials and methods							
		2.0.1 Properties of $SrTiO_3$	7						
		2.0.2 Fabrication of $SrTiO_3$ samples	8						
		2.0.3 Fabrication of $Cr:SrTiO_3$ memory devices	11						
		2.0.4 Characteristics of memory devices	12						
	2.1	X-ray absorption spectroscopy	17						
		2.1.1 Heuristic derivation of the EXAFS equation	24						
	2.2 Calculating X-ray absorption spectra								
	2.3	Experimental details	34						
3	Detecting oxygen vacancies								
	3.1	X-ray absorption near edge spectroscopy							
	3.2	Extended X-ray absorption fine structure	51						
		3.2.1 Oxygen vacancy sensitivity	61						
4	Tracing oxygen vacancies								
	4.1	Tracer-ions in resistance memory devices	63						
		4.1.1 Forming model	68						
		4.1.2 Forming in H_2/Ar	71						
		4.1.3 Discussion of air and H_2/Ar as forming atmospheres	74						
	4.2	Cr valence maps	77						

$\operatorname{Contents}$

	4.3	Interaction between the X-ray beam and the memory device	80
	4.4	Extended X-ray absorption fine structure	84
	4.5	Soft X-ray spectroscopy	87
5	Cor	nclusions	91
	5.1	Oxygen vacancies in ${\rm SrTiO}_3$	91
	5.2	Oxygen vacancies in memory devices	92
6	Out	look	93
Bi	bliog	graphy	95
A	cknov	wledgments	101
Cı	ırric	ulum vitae	102

CHAPTER 1

Introduction

One of the greatest challenges in solid state physics has been the development of a satisfactory explanation of the fundamental differences between an insulator and a metal. When a few atoms of the same kind are brought together to form a molecule, the individual atomic orbitals break the degeneracy and form molecular orbitals. In a solid, where the number of atoms per cubic centimeter normally is in the order of 10^{23} , the individual atomic orbitals may form continuous bands. As explained by the nearly free electron model [1], these bands split when the electronic wave functions Bragg-scatter off the periodic lattice and give rise to regions in energy where no electrons are allowed. With this fairly simple picture, the difference between an insulator and a metal is understood as a full band and a partly filled band, respectively. In a full band, an electron has to be excited, beyond the so called "bandgap," to the next unoccupied band leaving behind a positively charged "hole." This hole moves, in an applied field, in the opposite direction of the electron and in this way no net current will flow. In a metal, where the most lightly bound electrons only partly occupy the band, the electrons directly start to move in an applied field, creating a net current. If the partly filled band is close to empty, or close to full, one normally talks about a semimetal or a semiconductor at elevated temperatures.

In the first part of the twentieth century, when the quantum theory for solids was developed, experimentalists tried to prove the nearly free electron model. It was found that wide-bandgap insulators (for example noble element crystals or diamond with bandgaps of about $\sim 5-6$ eV) and intrinsic semiconductors (for example silicon and germanium with bandgaps around 1 eV) behave fairly close to this simple model [2]. For materials with bandgaps around 2-3 eV, for example the 3*d* transition metal oxides, the behavior is not that straight forward. Many binary 3*d* transition metal oxides with partly populated 3*d* bands were found to be semiconducting and even insulating [3]. The inability of the nearly free electron model to predict the insulating behavior in the 3*d* transition metal oxides with partly filled bands has since then puzzled the scientific community. It turned out

that the localized character of the 3d orbitals was responsible for the insulating behavior. In the tightly bound 3d orbitals the coulombic interaction between the electrons cannot be neglected. The localized behavior of the 3d orbitals is in strong competition with the partly delocalized character of the hybridized oxygen 2p orbitals. Therefore, in the 3d transition metal oxides, the charge, spin, and orbital degrees of freedom, give rise to a variety of interesting properties. Many of these properties do not arise in the intrinsic 3d transition metal oxides. However, when the material has been doped, these properties are revealed. In the 3d transition metal oxides, doping can be done either by partly substituting an element for another (for example La^{3+} for Sr^{2+} in $SrTiO_3$ giving metallic conductivity[4]), or by introducing defects, such as oxygen vacancies [5]. It seems logical that a very small doping of electrons or holes would gradually induce metal-like behavior in an insulator. In practice, there is a critical doping level; normally the material remains insulating or semiconducting over a broad range of band filling. Many compounds show transitions between insulating and metallic states when different chemical or physical parameters are changed. The idea that one could controllably switch a material between an insulator and a metal originated from the nearly free electron model. The gap between the bands, formed due to the periodic potential, is controlled by the interatomic distance. Changing this distance by external pressure or other means, it would be possible to alter the bandgap. Depending on the filling of the bands, the material may switch between a metal and an insulator. Pressure dependent metal-to-insulator transitions were found in metallic Sr and Yb [6]. Several different transition metal compounds have shown metal-to-insulator transitions when other parameters were changed, for example doping or temperature [7]. The field of solid state physics, where different conductivity phenomenon are studied in the 3d transition metal oxides, belongs to the field of "strongly correlated electrons physics." A comprehensive review on early progress in this field, where the irregularities in the expected behavior of the 3d transition metal oxides is thoroughly explained, can be found in reference [8].

The solid state physics revolution induced by the discovery of the transistor by Shockley, Bardeen, and Brattain [9] in the late forties was the basis for the electronic industry. The accelerating demands on the performance of electronics refined the manufacturing processes giving a possibility to produce materials of very high purity. Increase of the quality in manufacturing has led to the miniaturization of electronic devices, where the number of transistors per chip, amount of storage space per area, roughly follows exponential growth (known as Moore's law [10]). All progress in the electronics industry since the introduction of the transistor has been based on current flow and storage of charge. Information is, in this mainly silicon based technology, processed by redirecting currents with transistors and stored by charging capacitor structures. If the limitations of this technology are reached, currents and charges would have to be determined accurately in structures smaller than a few nanometers. In such small structures, the quantum nature of the electron will become more important, making the determination of currents and charges difficult. Based on Moore's law, the industry predicts to break the 10 nm barrier in 2020 [11]. If the current electronic device development continues, ground breaking technological advances and a new perspective on current technologies will be required in order to avoid a stagnation of the market within the next few decades. Naturally, current solid state physics research is therefore trying to implement some of the recent ground breaking scientific discoveries in commercial electronic devices.

A renewed interest in transition-metal oxides and an upswing for the studies of strongly correlated systems was caused by the discovery of high temperature superconductivity in the copper oxides [12]. Since then, the temperature at which the material turns superconducting has been increasing to above 130 K [13]. Although applications such as superconducting power transmission or the generation of magnetic fields do exist, so far there has been limited impact on everyday consumer electronics.

Many of the transition metal oxides have a very large relative permittivity, making them suitable for the dielectric layer of capacitors. Especially $BaTiO_3$ [14] and later $SrTiO_3$ [15] have had many technological applications as dielectric materials. The most interesting question to ask is: How much electric field can one apply to the dielectric before the material breaks down and becomes conducting? To answer this question, and to develop new materials suitable for analog electronic devices, a lot of research effort has been spent on studying the dielectric breakdown in perovskite titanates. The phenomenon of resistance degradation has been known since the fifties, with early reports on (BeBa)TiO₃ in 1951 [16].

One phenomenon, closely related to the development of electronic devices, is the magnetoresistance effect. In recent years, this phenomenon has been detected in several manganese based oxides, where the resistivity can be changed with applied magnetic fields [17]. Due to the extreme differences in resistivity this phenomenon was termed colossal magnetoresistance. In the manganese oxide based magnetoresistance materials, when the material is close to a metal-to-insulator transition, the conductivity can be changed by several orders of magnitude with the application of a magnetic field. Possible applications for these colossal magnetoresistance compounds would be to replace the current metallic magnetoresistance materials used in the read head of computer hard-disks, if the working temperature could be raised to room temperature and above.

In several transition metal oxides, the intrinsic resistivity, as well as induced states with higher conductivity, can be switched between two or more stable states. This phenomenon was first discovered in insulating films, e.g., SiO_2 and Al_2O_3 [18, 19]. In these early measurements, oxide films were grown by oxidizing chosen regions of the material. When the fabrication methods for the

growth of oxide films were developed, there was a renewed interest in these kind of phenomena [20]. This was also boosted by the fact that the electronics industry saw possible applications with this phenomenon. If the resistivity of a material can be switched between two stable states, information can be stored.

Recently, the modern view of magnetism has been strongly challenged by the discovery of room temperature ferromagnetic order in dilutely doped semiconducting oxides. This discovery in thin films of Co-doped TiO₂ [21] has recently yielded many investigations which found these effects in many other oxides, but the causes of this effect are still under debate. Since the ferromagnetic order in TiO_2 only arises in thin films, where surface crystalline defects are more pronounced, it has been proposed to occur due to oxygen vacancies close to the surface [22]. A possible technological application for these ferromagnetic systems would be in spin-based electronics, where the spin of the electrons instead of the charge carries the information [23]. Another rather speculative phenomenon, in terms of technological applications, occurs between the two insulating perovskites $SrTiO_3$ and LaAlO₃ [24]. When at least four unit cells of LaAlO₃ are deposited on top of TiO₂ terminated $SrTiO_3$ surfaces, metallic conductivity arises at the interface. This was originally explained by a discontinuity of the polarities at the interface, leading to electrons populating the Ti conduction band [24]. One of the later proposed explanations for this conductivity are oxygen vacancies in the $SrTiO_3$ [25]. A further proposed explanation is cationic intermixing of the interface, such that a metallic sheet of a different material conducts in the interface [26]. The conductivity has been shown to vary with the oxygen pressure during growth of the LaAlO₃ film. It is a well known fact that a small amount of oxygen vacancies in $SrTiO_3$ makes the material metallic [27, 28]. Experiments have shown that when the $LaAlO_3$ film is thinner than four unit cells, it is possible to locally dope the interface with conduction electrons. This was done with a conductive tip of an atomic force microscope, creating nanometer sized conducting regions [29].

All these systems display a variety of physical phenomena for which the influence of oxygen vacancies has not yet been fully clarified. Experimentally, detecting the presence of small amounts of oxygen vacancies has traditionally been difficult. In chapter 3 of this dissertation, work is presented that proves that a small amount (well below 1‰) of oxygen vacancies can be detected using X-ray absorption spectroscopy. SrTiO₃ has been used as a model system in this study, where 0.2% of the Ti ions were replaced with each of the ions in the 3*d* transition metal series. X-ray absorption spectroscopy at the relevant energies was used to prove that the oxygen vacancies were preferentially created in the nearest neighbor shell of the extrinsic 3*d* transition metal ions. These ions were then used as "tracer-ions" for oxygen vacancies, thereby creating a tool to quantitatively detect low, but to the electronic structure crucial, concentrations of oxygen vacancies.

In chapter 4 of this dissertation, the findings from chapter 3 are used to study the behavior of oxygen vacancies in a possible commercial application. The electronics industry is focused on improving the density, durability, and reading-writing speeds of non-volatile memories. These are currently dominated by the Flash memories which are important for almost all electronics, especially in hand-held mobile devices. The current main focus in this research field now lies on materials for which one can change the resistivity by controllable means. The main trends of this field are explained in reference [30]. Suggested techniques to change the resistivity are: Resistivity change of a metal-oxide-metal structure with applied electric field [20]. The resistivity can also be switched in a magnetic tunnel junction using magnetic fields [31]. In chalcogenide glasses, based on different GeSbTe alloys, the resistivity is changed when the material is switched between a crystalline and an amorphous phase with heat pulses [32].

Several materials used for the fabrication of metal-oxide memories controlled by the applied electric field are intrinsically conducting, in particular different manganese oxide compounds [33– 35], while other compounds, for example nickel oxide and different titanium oxides, have to be subjected to an electric field to induce conductivity and the resistive switching [36–38]. In most cases the resistive switching occurs when there is an asymmetry in the device, such as different types of electrodes (for example Rh/NiO/Pt and TiN/ZnO/Pt in references [39, 40]) or a DC voltage used to induce the switching state (for example Pt/NiO/Pt and $Pt/TiO_2/Pt$ in references [38, 41]). For Al/CuO/Cu based devices, the resistive switching was shown to be induced by either a DC electric field or by controlling the oxygen content in the device fabrication [42]. There are several explanations of the conductivity and resistive switching in the literature. Some of these are: the formation and rupture of filamentary paths by Joule heating [36]; bulk like conductivity in the high resistance state and localized conductivity in the low resistance state controlled by opening and closing of a "faucet" at the metal-oxide interface [43]; oxygen vacancies migrating to the electrode interface, locally doping the material with conduction electrons [37, 39, 44]. Recent reviews treat the resistive switching in more detail, see for example references [45–47]. The advantage with these memories over conventional Flash memories is that it would be possible to stack several cells on top of each other, thereby increasing the memory density per chip area [48, 49]. Other issues that need to be addressed in the development of a technique to replace Flash are the relatively slow write speed and the low number of read cycles.

In chapter 4 of this dissertation, work is presented that utilizes the above mentioned "tracer-ion" technique to study the introduction of oxygen vacancies in resistive switching memory cells. $SrTiO_3$ resistive switching memory devices with Cr as tracer-ions were studied with micro-focused X-ray absorption spectroscopy and spatially resolved X-ray fluorescence imaging. The results of these

experiments showed that the resistive switching state was induced together with oxygen vacancies. Also, the vacancies were shown to be highly mobile even in already conducting devices. Furthermore these results show where the oxygen vacancies are created and how they percolate through the device in the conditioning process leading to resistive switching.

CHAPTER 2

Materials and methods

2.0.1 Properties of SrTiO₃

 $SrTiO_3$ crystallizes in a cubic perovskite lattice, titanium is in the center of the unit cell octahedrally surrounded by six oxygen ions and a strontium ion in each corner. $SrTiO_3$ has the perfect cubic perovskite structure at temperatures above ~ 110 K, which means that all the oxygen octahedrons are sharing a corner with another oxygen octahedron. One unit cell of SrTiO₃ is displayed in figure 2.1. This structure is generally known as the "ABO₃" perovskite structure. A and B denote cations and are in SrTiO₃ represented by Sr and Ti. The crystallographic space group of SrTiO₃ is the cubic PM3M (221) structure, the length of the unit cell (lattice parameter a in figure 2.1) is 3.8996 Å at room temperature [50]. SrTiO₃ is known to have a structural phase transition below ~ 110 K, where the cubic structure turns into a tetragonal structure. It has been suggested that this phase transition corresponds to a rotation of one rigid TiO_6 octahedron and a mirrored rotation of the next neighboring TiO_6 octahedron, thereby doubling the unit cell in all three crystallographic directions [51]. $SrTiO_3$ with its $3d^0$ electronic configuration is intrinsically a band insulator and paraelectric at room temperature. Paraelectric materials can be polarized by an electric field. SrTiO₃ remains paraelectric when lowering the temperature, with a sharp increase of the dielectric constant. Below 4 K the dielectric constant is very large and does not vary. This was interpreted as a quantum mechanical phase, which stabilizes large ferroelectric fluctuations [52]. Furthermore, reduced, semiconducting $SrTiO_3$ was found to have a low-temperature superconducting phase, with transition temperatures ranging from 0.1 to 0.3 K, depending on the carrier concentrations [53, 54].



Figure 2.1: (a) The unit cell of the cubic perovskite SrTiO₃. The positions of the ions in the unit cell are: Sr (000), Ti $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and one O at $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$, and $(\frac{1}{2}\frac{1}{2}0)$ respectively. The lattice parameter is marked "a."

2.0.2 Fabrication of SrTiO₃ samples

A stoichiometric mixture of 99.8 mol% TiO₂ (99.999% purity, rutile, Sigma-Aldrich), SrCO₃ (99.995% purity, Sigma-Aldrich) and 0.2 mol% of the tracer-ion¹ oxide were machine-mixed for approximately 10 min. After the initial mixing, the mixture was annealed in air three times with 10 min machinemixing in between. The three annealing temperatures and times were: (1) 900 °C for 15 hours; (2) 1200 °C for 15 hours; (3) 1300 °C for 60 hours. After the final annealing, the SrTiO₃ powder was machine-mixed and used for three different purposes: (i) powder X-ray diffraction (XRD) to verify that the samples were single phase (for all tracer-ions); (ii) pressed into pellets for further annealing and measurements (Sc, Ni, Cu, Zn); (iii) pressed into rods and annealed in air at 1200 °C for 12 hours intended for crystal growing (V to Ni).

(i) Figure 2.2 shows the XRD pattern of $SrTiO_3$ powder with Ni as tracer-ion. The solid line represents the measured pattern and the open circles represent a pattern calculated for $SrTiO_3$ with the software CRYSTALMAKER. The pattern in figure 2.2 confirms that the samples are single phase $SrTiO_3$. Patterns taken with other 3*d* transition metals in $SrTiO_3$ are identical to the pattern in figure 2.2. (ii) The pellets were once again annealed in air at 1200 °C for two hours, thereby considered stoichiometric and hereafter referred to as "oxidized powder samples." (iii) The annealed rods were mounted vertically in focus of the lamps of a mirror furnace and rotated in opposite directions. Where the lamps are in focus, the ends of the rods melt and this area is referred to as the "floating zone." The furnace was evacuated and filled with synthetic air (O_2/Ar , 20%/80%; 10^5 Pa). In the floating zone, the temperature is about ~2100 °C which is higher than the melting temperature of $SrTiO_3$. To grow the crystal, the floating zone is set to move along the upper rod.

¹Tracer-ions are: Sc, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.



Figure 2.2: The X-ray diffraction pattern obtained from $SrTiO_3$ powder with Ni as tracer-ions. The solid line shows the measurement and the circles marks the diffraction spots as calculated fore pure $SrTiO_3$ with the software CRYSTALMAKER. The intensity is normalized on the second peak from the left.

In this procedure, the upper rod "drops down" on the lower rod when the floating zone is moved upwards. At the lower end, the material crystallizes out into a single crystal. Since the single crystals were grown in an atmosphere with sufficient oxygen partial pressure, the "as grown" crystals were considered to be stoichiometric and hereafter referred to as "oxidized single crystals." One advantage of this growth technique is that impurities, not incorporated in the crystal structure, stay in the floating zone. When the floating zone comes to the end of the rod, the not incorporated impurities are located in the last melted part of the rod. Therefore, tracer-ions in the single crystal are properly incorporated in the crystal structure.

One set of samples from (ii) and (iii), oxidized powder samples and single crystals, was subjected to a two-step reduction process in the mirror furnace. The furnace was evacuated and filled with H_2/Ar (2%/98%; 10⁵ Pa). In the first step the temperature was rapidly (4000 K/h) increased to approx. ~1800 °C and held for 5-7 min. In this time, the samples turned dark, after which the temperature was decreased to approx. ~1600 °C and held there for additionally 30 min. In this annealing procedure, it is assumed that oxygen ions are removed from the samples, thereby creating electron donating oxygen vacancies [27, 28, 55]. These samples are hereafter referred to as "reduced powder samples" for the treated samples from (ii) and "reduced single crystals" from (iii). Both reduced sample types were considerably darker than the oxidized, and were good conductors. Note that in the mirror furnace, the temperature is not known. The only controllable parameter is the current through the lamps. Additionally, an oxidized single crystal with Ni tracer-ions was subjected to a reduction process in a furnace with controlled temperature. The same H_2/Ar atmosphere was used and the temperature was increased (400 K/h) to 1600 °C, kept for 2 hrs, and then quenched to room temperature. This sample is called "slightly reduced single crystal." All the samples used in this work can be found in table 2.1.

Table 2.1: Summary of the $SrTiO_3$ samples with different tracer-ions. "P." denotes a polycrystalline powder sample and "S.c." denotes a single crystal sample. "Sl.Red" refers to the slightly reduced crystal.

Tracer-ion	Sc	V	Cr	Mn	Fe	Co	Ni	Ni	Cu	Zn
Type	Р.	S.c.	S.c.	S.c.	S.c.	S.c.	Р.	S.c.	Р.	Р.
Annealing	Ox	Ox	Ox	Ox	Ox	Ox	Ox	Ox	Ox	Ox
	Red	Red	Red	Red	Red	Red	Red	Red	Red	Red
								Sl.Red		
Figure	3.1(a)	3.3(a)	3.4(a)	3.5(a)	3.6(a)	3.7(a)	No^{a}	3.8(a)	$3.9(a)^{b}$	$3.10(a)^{b}$

^aData taken on these powder samples are identical to the data shown in figure 3.8(a)

^bData taken on oxidized powder is shown in figures 3.9(a) and 3.10(a).

Materials and methods



Figure 2.3: (a) Schematic view of one bit of the memory cell, with the two Pt electrodes and dimensions shown. (b) The device used in the experiments, which consists of a crystal bonded to an integrated circuit carrier with In wires. The white square is the part of the device depicted in (a). (c) A micrograph of the area between the electrodes when the device was conducting and the resistivity could be switched [56].

2.0.3 Fabrication of Cr:SrTiO₃ memory devices

To study the dielectric breakdown and the introduction of the resistive switching state, memory devices were prepared from single crystal SrTiO₃ with Cr as tracer-ions. To facilitate an X-ray absorption study of these devices, they were made ~500 times larger than devices intended for industrial applications. Oxidized single crystals were annealed in H₂/Ar (2%/98%; 10⁵ Pa) at 1200 °C for two hours. After this annealing, the absorption in the visible range changed, rendering the insulating crystals slightly more transparent. Disk shaped crystals, approximately 5 mm diameter and 1 mm thick, were polished on the [001] surface and 100 nm thick Pt electrodes were patterned in a planar structure with standard photolithography techniques. The electrodes measured $50 \times 400 \ \mu m^2$, were separated by a 50 μ m gap, and oriented along the [010] axis of the crystals. As shown in figure 2.3(a), the electrodes were provided with $200 \times 200 \ \mu m^2$ big contact pads. The crystals with electrodes were glued onto an integrated circuit holder, and the contact pads were manually bonded to the gold plated contacts on the circuit holder with 100 μ m thick indium wires. In figure 2.3(b) the entire circuit holder with five memory devices is shown. The insulating devices will be called "pristine" hereafter.





Figure 2.4: The electrical forming for the first step (a), the third step (b), and resistance hysteresis (c) of the device when treated in air. The low resistance state is 600 Ω and the high resistance state 4 k Ω , measured at 1 V.

2.0.4 Characteristics of memory devices

The pristine devices had a resistivity greater than 100 G Ω ·cm. The annealing of the pristine devices probably creates a small number of oxygen vacancies, possibly related to intrinsic defects or at grain boundaries. To render the SrTiO₃ conducting, in the order of 10^{18} electrons cm⁻³ are needed [57], which could be supplied by $5 \cdot 10^{17}$ oxygen vacancies cm⁻³. 0.2 mol% tracer-ions corresponds to $3.1 \cdot 10^{19}$ tracer-ions cm⁻³. The insulating pristine devices were assumed to have substantially (orders of magnitude) lower oxygen vacancy concentrations than this critical value. Before the device showed the characteristic resistive switching, a soft dielectric breakdown had to be enforced with an applied electric field, called "forming" hereafter. The forming was normally done in air, at room temperature, and ambient pressure. The memory cell was connected in series with a resistor and a Keithley source meter (model 2410), marked in figure 2.3(a) with R_{load} and V respectively. Details about the forming in air can be found in table 2.2. The first part of the forming was done with a constant applied field, until a current of 1 mA was reached. From 2 mA and above the voltage was increased in steps of 5 V, initially going from 0 V to 200 V, decreasing to -200 V and finally back to 0 V. In this sweeping phase, the current compliance was set to a constant value for three consecutive sweeps then increased by 2 mA until ± 10 mA was flowing through the device. After the forming, when the device was conducting, a narrow dark path was observed between the electrodes, figure 2.3(c). The reproducibility of this forming procedure was very good. In most cases, only two steps with constant applied voltage were necessary (figures 2.4(a) and (b)). To switch the resistivity, R_{load} was set to zero and when sweeping ± 15 V, the resistance changes in the device (different slopes in the I-V shown in figure 2.4(c)).

Table 2.2: Typical forming conditions, with time and current reached for the different steps, for the samples formed in air. Between step #4 and #5, the DC forming was replaced with the current sweeps as explained in the text, for which the time was always the same. Voltage was the initially applied voltage over the sample and R_{load} ; I_{form} the current reached in the device at the end of each step (marked in figure 2.3(a)).

Step No.	Voltage (V)	$\mathrm{I}_{\mathrm{form}}$	$\mathrm{R}_{\mathrm{load}}$	Step time	Figure
#1	400	300 nA	$1 \ \mathrm{G}\Omega$	${\sim}30~{\rm min}$	2.4(a)
#2	400	$1~\mu {\rm A}$	$1~\mathrm{M}\Omega$	$\lesssim \! 30 \ \mathrm{s}$	
#3	400	100 μA	$1~{\rm M}\Omega$	${\sim}6~{\rm min}$	2.4(b)
#4	300	$1 \mathrm{mA}$	100 k Ω	$\lesssim \! 30 \ \mathrm{s}$	
#5	± 200	$\pm 2~\mathrm{mA}$	$10~\mathrm{k}\Omega$		
#6	± 200	$\pm 4~\mathrm{mA}$	$10~\mathrm{k}\Omega$		
#7	± 200	$\pm 6 \text{ mA}$	$10~\mathrm{k}\Omega$		
#8	± 200	$\pm 8 \text{ mA}$	$10~\mathrm{k}\Omega$		
#9	± 200	$\pm 10~{\rm mA}$	$10~\mathrm{k}\Omega$		

As will be shown, the conductivity introduced by the forming is caused by oxygen vacancies. Memory devices form more easily in a H_2/Ar atmosphere than in air. To learn more and to trace back the origin of the oxygen vacancies, memory devices were also formed in the H_2/Ar mixture used for the reduction of the powder and single crystal samples. The details of the forming process in the H_2/Ar atmosphere are tabulated in table 2.3 and I-V are shown in figures 2.5(a)-(e). The forming in H_2/Ar showed more fluctuations in current with an applied constant voltage when compared to forming in air, which is most clearly visible in figures 2.5(c) and (e). The initial forming in H_2/Ar was faster and done with a lower electrical field strength compared to the same forming step in air. This is most notable in step #1 when comparing data presented in tables 2.2 and 2.3. After the forming, the resistance switched when sweeping the voltage between ± 30 V, figure 2.5(f).

Table 2.3: Forming conditions, with time and current reached for the different steps, for devices formed in H_2/Ar . Between step #4 and #5, the DC forming was replaced with the current sweeps as explained in the text, for which the time was always the same. Voltage was the initially applied voltage over the sample and R_{load} ; I_{form} the current reached in the device for each step.

Step No.	Voltage (V)	$\mathrm{I}_{\mathrm{form}}$	$\mathbf{R}_{\mathbf{load}}$	Step time (min)	Figure
#1	150	100 nA	$1 \ \mathrm{G}\Omega$	10	2.5(a)
#2	100	$1~\mu {\rm A}$	$1~{\rm M}\Omega$	5	2.5(b)
#3	100	$2.6~\mu\mathrm{A}$	$100~\mathrm{k}\Omega$	3	2.5(c)
#4	150	100 $\mu {\rm A}$	$100~\mathrm{k}\Omega$	17	2.5(d)
#5	150	$1 \mathrm{mA}$	$100~\mathrm{k}\Omega$	8	2.5(e)
#6	± 200	$\pm 2 \text{ mA}$	$10~\mathrm{k}\Omega$		
#7	± 200	$\pm 4 \text{ mA}$	$10~\mathrm{k}\Omega$		
#8	± 200	$\pm 6 \text{ mA}$	$10~\mathrm{k}\Omega$		
#9	± 200	$\pm 8 \text{ mA}$	$10~\mathrm{k}\Omega$		
#10	± 200	$\pm 10~{\rm mA}$	$10~\mathrm{k}\Omega$		



Figure 2.5: The current in the device during the forming with constant applied voltage (a)-(e) and resistance hysteresis (f) of the device when treated in the H₂/Ar mixture. The high resistance state was about 15 k Ω and the low resistance state about 700 Ω , as measured at 1 V.



Figure 2.6: The pulse induced resistance switching as measured on a memory device formed in air. The solid line is the applied voltage over the device (left hand scale) and the plus signs indicate the measured current (right hand scale).

For a practical device, the resistance is switched by short voltage pulses of different polarity. An example of pulse induced switching is shown in figure 2.6, where a small voltage bias (200 mV) was disrupted by ± 10 V pulses, leading to a resistance change observed in the changing current.



Figure 2.7: (a) The absorption of electromagnetic radiation. Incident light comes from the left (I₀), exponentially decays in the sample and is transmitted through the sample (I₁). The dashed arrows indicate fluorescent light that is emitted in all directions (I_f). (b) When the energy is increased, the absorption coefficient will make sharp jumps when the energy becomes large enough to excite the electrons of a core shell (L and K edges).

2.1 X-ray absorption spectroscopy

Since the discovery of X-rays in the beginning of the last century, the crystal structure for a vast amount of materials has been determined by X-ray diffraction. This method has made a major contribution to the understanding of the atomic arrangement in condensed matter. For a traditional diffraction experiment, the material needs to be at least polycrystalline with crystallites of the order of 10 nm or more in size. If this is the case, X-rays can be diffracted from the sample and the angles and intensities of these diffracted beams are used to produce a picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined. If, on the other hand, the material of interest contains no long range ordering or if one wish to study a specific element and the local structure around this element, traditional Xray diffraction does not necessarily give a straightforward answer. One of the techniques yielding information about the local chemical and structural environment without long range ordering is Xray absorption spectroscopy (XAS). XAS is element specific, i.e., each element has its characteristic energy ranges where the element strongly absorbs X-rays. By closely examining these energy ranges, information about the chemical state and the local environment of this element is obtained.

In a standard absorption experiment in transmission geometry, the intensity of the X-rays are measured before and after the sample, as illustrated in figure 2.7(a). Because of absorption, the

transmitted intensity of the light (I₁) is smaller than the incident intensity (I₀) and is exponentially decaying as a function of the thickness (x) and absorption coefficient (μ) of the sample [58]:

$$\mathbf{I}_1 = \mathbf{I}_0 \cdot \exp(-\mu x). \tag{2.1}$$

When the energy of the incident X-rays is increased, the absorption coefficient is predominantly decreasing ($\sim \frac{1}{E^3}$), and the light penetrates deeper into the material. At certain energies, the absorption makes almost discrete jumps, termed "edges," as schematically illustrated in figure 2.7(b). The edge represents the energy required to excite an electron of a tightly bound shell to an empty state above the Fermi energy, which corresponds to the "binding energy" of that particular electron. Individual absorption edges of Ni are sketched in figure 2.7(b). The excitation of the most tightly bound electrons (principal quantum numbers n = 1 and l = 0, 1s states) is called a K edge ((a) in figure 2.8), n = 2 are called L edges. In the case of the 3d transition metals also M edges (n = 3) exist. However, they are not discussed here. There are, for n = 2, eight possible electrons, which split this edge in three different energies: the L_1 edge (excitation of the 2s electrons), L_2 edge ($2p_{1/2}$ electrons, (b) in figure 2.8), and L_3 edge ($2p_{3/2}$ electrons, (c) in figure 2.8). Spectra taken on the K edge together with the L_2 and the L_3 edges will be presented in this dissertation.

When an electron is excited from a core state, it leaves a hole in this tightly bound shell of the atom, called "core hole." This core hole is rapidly filled (within $\sim 10^{-15}$ s) by an electron from a shell higher in energy. To facilitate this transfer, the electron that fills the core hole must expel its excess energy. The energy is released by emitting an X-ray photon, sketched on the right hand side in figure 2.8, or by non-radiative processes, for example, by an Auger event. In an Auger event, a lightly bound electron fills the core hole and the thereby gained energy can be coupled to a second outer shell electron which is emitted. The Auger event is dominating for lighter elements, up to element number 30. The filling of a core hole is proportional to the probability for absorption. Therefore, the fluorescent X-ray and the Auger electron yields can be used to measure the absorption coefficient. When measuring the transmission of the sample, the absorption can be extracted by taking the logarithm of the quota between the incident intensity and the transmitted intensity, $\mu x = \ln(I_0/I_1)$. When measuring the fluorescent X-rays or the Auger electrons, which both are directly proportional to the absorption, the absorption spectrum is obtained by dividing the yield by the incident intensity, $\mu = I_f/I_0$. One important difference between measuring the fluorescence and the Auger electrons is that the interaction with the sample is much higher for electrons than for photons. This means that fluorescence probes much deeper beneath the surface (in the order of μm for a few keV), while the Auger electrons originate from a few nm beneath the surface. A common way to measure the absorption is to measure the total drain current in the sample. This total electron yield will not only collect the Auger electrons, but mainly secondary electrons, which makes the technique even



Figure 2.8: The electronic energy levels with their configurations for the 3d transition metals. The letters on the left side give the edge names and the Greek letters on the right side give the names of the fluorescent K lines. Only the transitions responsible for filling a 1s core hole are shown.



Figure 2.9: The Ni K edge as measured on an oxidized SrTiO₃ sample with Ni as tracer-ions. (a) Shows the extended X-ray absorption fine structure and (b) shows the X-ray absorption near edge structure, as described in the text.

more surface sensitive. This technique is especially adequate for conducting samples.

The transitions resulting in the fluorescent X-rays obey the dipole selection rule, which states that the angular momentum quantum number can only be changed by ± 1 . Therefore, the dominating fluorescent X-rays filling a 1s core hole are from 2p to 1s transitions. This dominating fluorescence line is called $K\alpha$. Since the 2p electrons are split in two levels, the $K\alpha$ line is split in two lines, but for the here presented results, the fine structure of the fluorescence lines is of no importance. The weaker transitions from electrons with $n \geq 3$ are also visible in the $K\beta$ line. The transitions resulting in the fluorescence lines by filling a 1s core hole for the 3d transition metals are drawn on the right hand side in figure 2.8.

To collect an X-ray absorption spectrum, the energy is scanned over the K edge of the element of interest. In the important cases presented in this dissertation, the respective $K\alpha$ lines were measured. For the following discussion about XAS, Ni as tracer-ion in SrTiO₃ is chosen as an example for illustration. In figure 2.9(a) the XAS measured around the K edge of Ni is presented. The characteristic edge energy provides the information that it indeed is Ni that is being measured. The edge is not a discrete jump from a small absorption to a high absorption, which necessitates a consistent way of defining the edge energy. In this dissertation, I have chosen to define the edge energy (E_0) to equal the energy value where the absorption reaches half the value of the full absorption. In figure 2.9(a), where the absorption has been normalized, this corresponds to the energy at the value 0.5. Figure 2.9(b) presents a magnification of the edge jump. E_0 for Ni is in this case ~ 8345 eV (marked with an arrow in the figure). The figures 2.9(a) and (b) contain two more definitions used in this dissertation. In figure 2.9(a), starting from ~ 8450 eV, the X-ray absorption extended fine structure (EXAFS) is shown. Figure 2.9(b), only the edge step, shows the X-ray absorption near edge structure (XANES).

The EXAFS oscillations observed after the edge in figure 2.9(a) are characteristic to the solid state. These features are not observable in the purely atomic spectra, meaning that it is possible to detect if the absorbing atom is bound or not. This does not mean that there necessarily is long range order in the system; it indicates that the distance to at least one neighboring shell is defined. The physical processes responsible for these oscillatory features after the edge remained unrevealed between their discovery and the early seventies. In 1971, it was proposed that the oscillations were due to scattering of the photoelectron off neighboring atoms [59]. In this suggested model, the electrons ejected from the ion propagate through the material as a wave. Hence, the surrounding electron distribution is found by Fourier transforming the oscillations observed after the edge (explained in detail below). The difference between the two regions above, EXAFS and XANES, is often distinguished by the dominating processes. Right after the edge, where the photoelectron wavelength is long (low energy), it will be strongly scattered from several neighboring atoms (XANES). When the photoelectron wavelength gets shorter (higher energy), in the order of the nearest neighbor distance, the scattering will be dominated by scattering from the nearest neighbors (EXAFS). The scattering is resonant in nature, meaning that when the energy of the photoelectron wave equals the energy of the scattering orbitals, the scattering is especially strong.

In figure 2.10(a) the raw-data measured on a SrTiO₃ sample with incorporated Ni tracer-ions is shown. The solid line represents the untreated integrated intensity as measured on the Ni $K\alpha$ fluorescence line including some background. The dashed line represents the incoming intensity. The strong dip in the intensity around 8600 eV is an artifact of the beamline delivering monochromatic light. Figure 2.10(b) shows the resulting absorption spectrum where the integrated intensity of the $K\alpha$ line has been divided by the incoming intensity, eliminating the strong dip around 8600 eV. The absorption data are now normalized so that the intensity is zero before (background subtracted) and has an average value of one after the edge. For this, the background is approximated with a straight line (pre-edge line in figure 2.10(b)), and one line fitted to the absorption after the edge (post-edge line in figure 2.10(b)). The pre-edge line is subtracted from the total absorption, and the absorption is then divided by the post-edge line. To isolate and extract the fine structure observed in the wiggles behind the edge, a spline (dashed line in figure 2.10(c)) is fitted to the edge step and the absorption is normalized by this polynomial. In figure 2.10(c) the derivative of the absorption spectra is also displayed. At the energy where the derivative peaks, the edge energy is normally



Figure 2.10: The procedure of extracting X-ray absorption data from raw-data measured at the beamline. (a) Shows the raw fluorescence data (solid line) and the incoming intensity of the beam measured before the sample (dashed line). The incoming intensity is plotted on a different scale. (b) Shows an average of several scans. The individual raw-data spectra have been divided by the incoming intensity (solid line). The dashed and dash-dot lines show the pre-edge line and the post-edge line respectively. (c) Shows absorption data corrected for the incoming intensity (solid line) together with the atomic background used to normalize the edge step in the extraction of the extended fine structure data (dashed line). The dash-dotted line is the derivative of the absorption data. Where the derivative is maximal, E_0 is normally chosen (indicated by arrow). (d) Shows the isolated fine structure oscillations, the final EXAFS data.

taken (E_0 , as previously discussed). Physically, this corresponds to the upper most populated states of the absorber (Fermi energy). The exact position of the "Fermi energy" is strongly influenced by the presence of the core hole, but for K edges on the 3d transition metals the core hole is strongly screened and E_0 is close to the Fermi energy. For EXAFS data, the exact position of E_0 is normally fitted to experimental values. For XANES data, the most important consideration is to consistently chose E_0 when comparing different spectral features. In the last step, figure 2.10(d), the edge normalized absorption has been normalized to the atomic absorption. The resulting EXAFS data then becomes dimensionless and is normally called $\chi(E)$,

$$\chi(E) = \frac{\mu_{\chi}(E) - \mu_0(E)}{\mu_0(E)}.$$
(2.2)

 μ_{χ} is the edge normalized absorption and μ_0 is the atomic absorption shown in figure 2.10(c) as the dashed line. With the above discussed photoelectron wave interpretation, the EXAFS data is sensitive to the position and element number of the neighboring ions. Therefore, the EXAFS data is normally transformed so that the oscillations are displayed as a function of photoelectron wave number (k) instead of energy. The energy of the photoelectron wave $(E_{\rm ew})$ is given by $E_{\rm ew} = E - E_0$. With the definition from de Broglie, the photoelectron wave number becomes

$$k = \frac{1}{\hbar} (2m_e E_{\rm ew})^{1/2}, \tag{2.3}$$

where m_e is the mass of the electron. The EXAFS data extracted in figure 2.10(d) as a function of photoelectron wave number is depicted in figure 2.11(a), where the EXAFS data has been multiplied by k^2 to better visualize the oscillations far behind the edge. This weighting by k^2 emphasizes the high Z contributions to the spectrum since high Z elements have more scattering power at high values of k than low Z elements. Therefore, the use of a k^2 weighted EXAFS data makes the analysis equally sensitive to low and high Z elements. When the photoelectrons have roughly the same energy as the kinetic energy of the bound (outer shell) electrons of the scatterer, the scattering becomes more intense. This is why, for example, oxygen scatters stronger at low k values, in contrast to 3d transition metals which scatter at higher k.

The normalized and k^2 weighted EXAFS function was Fourier transformed to visualize the scattering between the individual atomic nearest neighbor coordination shells. The magnitude of the Fourier transform is interpreted as the electron density around the absorbing element. Before taking the Fourier transform, the χ data was multiplied by a window function. This window function is defined between two values (k_{min} and k_{max}) and zero elsewhere. k_{min} is in general between 3 and 4 Å⁻¹ where the single scattering starts to dominate the spectrum (as explained below). k_{max} is chosen where EXAFS oscillations no longer can be observed. With these definitions, the Fourier Materials and methods



Figure 2.11: (a) The EXAFS data $(\chi(k))$ weighted with k^2 , as extracted from pure absorption data $(\mu(E))$. (b) The magnitude of the Fourier transform of the EXAFS data shown in (a). Here the electron distribution of the nearest neighbor shells are clearly visible.

transform, with R being the distance from the absorber, is defined as

$$FT(R) = \frac{1}{\sqrt{\pi}} \int_{k_{min}}^{k_{max}} \chi(k) \exp(2ikR) dk.$$
(2.4)

The Fourier transformed (FT) data of the Ni k^2 weighted data are shown in figure 2.11(b). In this data set, two distinctive peaks are identified, the first around 1.5 Å and the second around 3.3 Å. The first peak corresponds to the oxygen nearest neighbors, and the second peak represents scattering from the two metallic nearest neighbors (Sr and Ti). The distance found in the FT data is about 0.2-0.5 Å shorter than the actual distances. This can be explained by the acceleration of the photoelectron when being in the vicinity of the different ions. This leads to phase shifts in the EXAFS data, which comes out as a different distance when taking the Fourier transform, as explained in section 2.1.1. To distinguish between the distance in real space and in the Fourier transformed EXAFS data, I will use r for distances in real space and R in Fourier space.

2.1.1 Heuristic derivation of the EXAFS equation

The theoretical description of the EXAFS equation was originally formulated by the authors of reference [59]. The here presented description is mainly taken from reference [60]. The source of the EXAFS oscillations can be derived from the photoelectron wave interpretation, which is illustrated in figure 2.12.

Absorption can only take place if there are unoccupied states around the absorbing element.



Figure 2.12: When the photon energy is clearly above the edge energy, the photoelectron propagates as a wave and scatters from the neighboring atoms. For certain wavelengths of the photoelectron wave (energies above the edge) the scattered wave is in phase (a) or out of phase (b) with the outgoing photoelectron wave, leading to increased or decreased EXAFS amplitude. (c) Shows a photoelectron wave scattering of two nearest neighbors before returning to the absorber. (This figure was inspired by reference [60].)

The EXAFS modulation is therefore proportional to the interference between the photoelectron waves, modulating the number of unoccupied states in the vicinity of the absorber. The outgoing photoelectron wave has the form e^{ikr}/r , where the k is the photoelectron wave number and r is the distance to the absorber. The scattered wave has the same form except that the origin of the wave is shifted to the scattering atom at r_j

$$\frac{|j|k|r-r_j|}{|r-r_j|}.$$
(2.5)

The backscattering wave is proportional to the scattering strength $(F_j(k)/k)$ of the ion in r_j and to the amplitude of the original wave at r_j . The EXAFS amplitude at the position of the absorbing ion (r = 0) then becomes

$$\chi_j(k) \propto \frac{F_j(k)}{k} \frac{e^{2ikr_j}}{(r_j)^2}.$$
 (2.6)

The phase shift, $2kr_j$, arises when the photoelectron with wave number k travels the distance $2r_j$ to and from the scattering atom. For a photoelectron wave moving in a constant potential, this is the only phase shift. The actual potential is modified by the absorbing and scattering ions, therefore an additional, k dependent, phase shift ($\delta_j(k)$) has to be added:

$$\chi_j(k) \propto \frac{F_j(k)}{k} \frac{e^{2ikr_j + \delta_j(k)}}{(r_j)^2}.$$
(2.7)

The absorption is modified by the backscattered wave, which constitutes the modulations. Since

absorption is the imaginary scatter at zero momentum transfer, the imaginary part of equation 2.7 is the EXAFS, which leads to:

$$\chi_j(k) = \frac{F_j(k)}{kr_j^2} \sin(2kr_j + \delta_j(k)).$$
(2.8)

Electrons are scattered and absorbed, therefore, damping needs to be added. This leads to a finite photoelectron mean free path $\lambda(k)$. This can be done by multiplying equation 2.8 with the exponentially decaying factor $e^{\frac{-2r_j}{\lambda(k)}}$. The EXAFS signal therefore transforms to:

$$\chi_j(k) = \frac{F_j(k)}{kr_j^2} \sin(2kr_j + \delta_j(k)) e^{\frac{-2r_j}{\lambda(k)}}.$$
(2.9)

This function is correct for one pair of atoms only. If many absorber-scatterer pairs of atoms are taken into account, their thermal disorder has to be incorporated. If their individual distances are assumed to be Gaussian distributed around the average distance (r_j) a Debye-Waller factor is multiplied with the EXAFS function:

$$\chi_j(k) = \frac{F_j(k)}{kr_j^2} \sin(2kr_j + \delta_j(k)) e^{\frac{-2r_j}{\lambda(k)}} e^{-2k^2 \sigma_j^2}, \qquad (2.10)$$

where the σ_j is the relative mean square displacement between the absorbing ion and the scattering ion around the distance $r = r_j$. To account for all scattering ions in the vicinity of the absorber in a real material, the EXAFS signals from the individual paths, χ_j , are summed together:

$$\chi(k) = \sum_{j} \chi_j(k).$$
(2.11)

In a crystal, the scatterers at the same distance from the absorber are often the same element and they are normally called a shell and are taken together in N_i number of neighbors of the *i*th shell. For example in figure 2.12(c), the four nearest neighbors in the first scattering shell get an additional $N_i = 4$ term, indicating the degeneracy of the *i*th scattering shell.

$$\chi(k) = \sum_{i} N_i \frac{F_i(k)}{kr_i^2} \sin(2kr_i + \delta_i(k)) e^{\frac{-2r_i}{\lambda(k)}} e^{-2k^2 \sigma_i^2}.$$
(2.12)

Here the index j has been replaced by the index i to indicate that the sum is no longer over individual ions but over shells of scatterers of the same type and at the same distance. This description of the EXAFS signal was found to give slightly larger values than the actual measured signals. This was attributed to the screening of the passive electrons of the absorbing ion. To account for this, a term S_0^2 (0.7 < S_0^2 < 1.0), called the passive electron reduction factor, is multiplied to equation 2.12. Lets discuss the most important features of the EXAFS signal here. The decaying scattering strength ($\frac{F_i k}{k}$) leads to smaller EXAFS signals for increasing photoelectron wave number, damping the EXAFS signal for high k. Furthermore, the damping factor due to thermal vibrations (Debye-Waller) $e^{-2k^2\sigma_i^2}$ also reduces the EXAFS signal for higher k. Note that this Debye-Waller definition is not the same as for diffraction, as only deviations of $|\vec{r} - \vec{r_j}|$ are relevant. A more detailed discussion about the description of EXAFS can be found in reference [60].

Up until now, only direct backscattering from neighboring ions has been discussed. In a more realistic situation, however, the strongest scattering is directly from close neighboring shells but there are contributions from photoelectron waves scattered off several neighbors. To account for this multiple scattering, the definition "shell" has to be slightly altered. Lets explain this with a discussion of the nearest neighbor shell shown in figure 2.12. Instead of viewing the first neighbors as a shell consisting of individual scatterers, they are viewed as one path with a certain degeneracy. For the first shell, this does not make a big difference, but when several scattering events occur for the photoelectron this view becomes more appropriate. Lets use again the photoelectron wave in figure 2.12. Let this wave scatter off the top right nearest neighbor (figure 2.12(c)), then scatter off the top left nearest neighbor, and finally returning to the absorbing ion. Obviously, this scattering event is weaker, since the photoelectron has a longer effective scattering path. When it returns, it will behave in the EXAFS like a single scattering event, but with different parameters. For example longer distance (path length), and instead of the Debye-Waller factor σ_i , $2 \cdot \sigma_i = \sigma_{\Gamma}$ is used, since the thermal vibrations of the nearest neighboring ion are taken into account twice. With this basic concept change, the EXAFS equation is as in equation 2.12 but with the summation over paths, including multiple scattering paths, instead of neighboring shells.

This concept is outlined in figure 2.13, where the TiO_2 plane of $SrTiO_3$ is shown with two single (a)-(b) and two different multiple scattering paths (c)-(d). In (a) and (b), the scattering of the oxygen nearest neighbor shell and titanium third neighboring shell are shown. The longer the way for the individual path, the weaker is the effect on the final absorption. Multiple scattering paths, as the one shown in (c), are in general relatively weak when the backscattering angle is less than 180° . The path in (d) is a focusing path, meaning that the scattering of such events add up at the absorber, making them relatively strong.

For photoelectron waves with high wave number (short wavelength), the scattering is dominated by single scattering events and the heuristically derived EXAFS equation (equation 2.12) holds. But when the wavelength of the photoelectron is in the order of the nearest neighbor distance or longer, the multiple scattering events dominate the picture, and equation 2.12 is not able to describe all the events. This transition region, as defined by the authors of reference [60], divides the spectrum between the XANES region and the EXAFS region. When moving closer to the edge, the interpretation of the spectrum is not as easily understood as the part of the spectrum further away from the edge. As discussed later, if a sufficient number of multiple scattering paths are



Figure 2.13: Some of the different paths a photoelectron wave can take before it returns to the absorber. The figure shows the TiO_2 plane in $SrTiO_3$. Each path is summed in the EXAFS equation. (a) Single, nearest neighbor scattering, (b) single third nearest neighbor scattering (second nearest is Sr located above/below the TiO_2 plane), (c) multiple scattering of two oxygen ions (paths with an angle other then 180° are generally weak), and (d) a focusing multiple scattering path (common in cubic systems and generally strong).


Figure 2.14: (a) The photo electric absorption schematically explained as a photon-in-electronout process creating a core hole. (b) The normalized absorption taken on the Cr K edge in Cr-doped SrTiO₃ schematically showing where in the spectrum the 1s to 4p transitions can be observed.

included, the edge can on a qualitative level be very well described. In addition, the near edge region is very sensitive to the chemical state of the absorber. The most obvious feature is that the edge moves in energy when the valence of the absorber changes. This can be easily explained by the screening by the outer electrons. If the number of screening electrons increase or decrease, the energy needed to expel a core electron correspondingly increases and decreases. These effects in the spectrum were discussed and explanations were suggested in the early literature on X-ray spectroscopy [61]. One of the biggest advantages of XANES over EXAFS is that the signal is much stronger. This is obvious from figure 2.10(d), where the features close to the edge are strong and the oscillations are diminishing further away from the edge.

The XANES is schematically explained in figure 2.14 with atomic Cr as an example atom. In (a), the absorption of a photon and the ejection of a core electron is schematically shown. The arrows indicate that XANES transitions are partly to empty bound states, whereas the EXAFS transitions leave the bound region and the photoelectron propagates through the material (continuum). Figure 2.14(b) shows the Cr K XANES spectrum adjusted to highlight the onset of the dipole

allowed transitions in the spectrum. As indicated, the highest intensity is where the possible 1s to 4p transitions are expected. It is proposed that it is possible to observe the dipole-forbidden 1s to 3d transition for energies just below the absorption edge, which reflects a quadrupole transition. The presence of the quadrupole transitions in the XANES has been debated the last decades [62, 63], and is thoroughly reviewed in reference [64]. In this context it is important to point out that the 1s core hole can be accurately described by the one-electron approximation. This approximation is however not valid for the p states, where the angular momentum can take several values. The conclusions presented later are based on K edge absorption of 3d transition metals ($21 \le Z \le 30$), where the photoelectron is highly screened from the core hole. For these metal edges the one electron model holds reasonably well.

2.2 Calculating X-ray absorption spectra

X-ray absorption can be described as the transition between an initial $|\psi_i\rangle$ and a final state $|\psi_f\rangle$. The initial state is the system in equilibrium together with an X-ray photon and the final state is the excited state with a photoelectron and a core hole. The transition between these two can be expressed by the Golden rule

$$\mu \propto |\langle \psi_i | \mathcal{H}_I | \psi_f \rangle|^2, \qquad (2.13)$$

where \mathcal{H}_I is the interaction Hamiltonian. Here, the final state $|\psi_f\rangle$ becomes a many body problem. There are several approximations and limitations applied to this expression, the most important being the one-electron and the dipole approximation. The one-electron approximation simplifies the many body problem of the final state to a single body problem. In the dipole approximation the spatial dependence of the electromagnetic field is neglected, which is valid for deep core excitations (for example, K edges). With these approximations, the basis for theoretical work on X-ray absorption is:

$$\mu(E) \propto \sum_{f} |\langle \psi_i | \left(\hat{\mathbf{e}} \cdot \mathbf{r} \right) | \psi_f \rangle |^2 \delta(E_f - E_i - \hbar \omega), \qquad (2.14)$$

where the sum runs over all possible final states. The vector $\hat{\mathbf{e}}$ describes the polarization direction of the incoming photon, and \mathbf{r} is the position operator acting on the electrons. E_f is the energy of the final state, E_i the energy of the initial state, $\hbar\omega$ the energy of the X-ray photon, and the delta function represents energy conservation in the process.

Calculations based on three different computer codes are presented in chapters 3 and 4. The phase shifts ($\delta_i(k)$ in equation 2.12) and the effective scattering amplitudes ($F_i(k)$ in equation 2.12) needed to fit the EXAFS spectra were calculated by FEFF6 [65]. To calculate the XANES spectra, the code FEFF8.4 was used [66]. Density functional theory (DFT) calculations were performed, where a tracer-ion replaced Ti in SrTiO₃ using the DMOL³ approach [67]. A detailed description of the algorithms used in FEFF6 and FEFF8.4, can be found in their respective documentations [68, 69]. A thorough review of the multiple scattering approach used in these codes can be found in reference [70].

In the FEFF6 code, a cluster approach to calculating the potentials of each atom type is used. The atom positions are defined with the origin of the system on the absorbing atom. The calculations are then performed by including paths of a certain length, defining the cluster. The potentials are approximated by a spherical potential centered on each atom together with a constant potential in interstitial space. This approximation is normally called the "muffin-tin" approximation. The radii of the atoms are calculated by integrating the charge distributions until they equal the atom number, the "Norman" radius. These radii are then decreased until the spheres just touch, which defines the radius of the muffin-tins. The interstitial potential and charge density is determined by averaging the charge left between the Norman radius and the muffin-tin radius for all atoms. After the potentials have been calculated, the different possible scattering paths are identified. The degenerate paths are identified and only calculated once. Thereafter, the scattering amplitudes and phase shifts for each path are calculated. These calculations are based on the scattering-matrix formalism described in reference [71]. FEFF8.4 is an improvement of the FEFF6 code. This introduces the self-consistent calculation of atomic potentials, allowing for charge transfer and a more accurate estimate of the X-ray absorption edge energy and thereby the XANES spectrum. In this dissertation, all EXAFS calculations were made using FEFF6 and all XANES were calculated using FEFF8.4.

In the DFT calculations the ground state of $SrTiO_3$ with and without tracer-ions was calculated. In these calculations, the positions of the ions were varied to find the positions minimizing the energy in the system. To describe the properties of the tracer-ions with DFT, a super cell of $3 \times 3 \times 3$ unit cells of $SrTiO_3$ was used, reflecting a 4% concentration of tracer-ions. The perovskite unit cell parameter used to create the super cell was 3.8979 Å. The outline of this super cell is marked in figure 2.15 as the dashed rectangle. With this super cell twenty DFT calculations were performed. Ten with the central Ti replaced by a tracer-ion (including Ti) and ten with a tracer-ion and an oxygen vacancy in the first shell of the tracer-ion, which reflects ~ 1% of vacancies in $SrTiO_3$. For all DFT calculations, the super cell is then repeated to obtain a cubic crystal.

The dashed circles in figure 2.15 show the size of the cluster used in the FEFF8.4 calculations. Here, r_{SCF} defines the cluster used to calculate the potentials and r_{FMS} defines the cluster for which multiple scattering paths were included. These distances strongly influence the computation time. They were varied from the nearest oxygen shell ($r_{SCF} = r_{FMS} = 2$ Å) until further included shells did not change the outcome of the calculations ($r_{SCF} = 4$ and $r_{FMS} = 6.8$ Å). In the input files for the FEFF8.4 calculations, the coordinates were taken from the relaxed atom positions generated by the DFT calculations. For each tracer-ion, two calculations were performed. One on a stoichiometric SrTiO₃ structure with a tracer-ion on the Ti position as absorber (unit cell in figure 2.16(a)) and one with an oxygen vacancy in the first shell surrounding the tracer-ion (unit cell in figure 2.16(b)).



Figure 2.15: The TiO₂ plane (Ti as closed circles and O as open circles) of the SrTiO₃ crystal with the positions of the out of plane Sr ions indicated by \times . The cluster size used in the self consistent field calculations (the potential calculation) is shown as the small dashed circle ($r_{SCF} = 4$ Å). The cluster size used in the full multiple scattering calculations is marked with the big dashed circle ($r_{FMS} = 6.8$ Å). The dashed square outlines one plane of the $3 \times 3 \times 3$ super cell used in the DFT calculations.



Figure 2.16: The two structures used to calculate the two different XANES spectra. Panel (a) shows the stoichiometric $SrTiO_3$ structure and (b) the structure with one oxygen missing and exaggerated atom displacements indicated by the arrows. These were surrounded in all directions by regular perovskite cells, repeated to obtain a sufficiently big crystal of cubic symmetry.



Figure 2.17: An overview of the LUCIA beamline connected to the Swiss Light Source. Please notice that the SLS is not correctly scaled.

2.3 Experimental details

The experimental results shown in chapters 3 and 4 (with three exceptions, marked as appropriate) were measured at the LUCIA beamline of the Swiss Light Source, Paul Scherrer Institut, Switzerland. An overview of the LUCIA (line for ultimate characterization by imaging and absorption [72]) beamline is presented in figure 2.17. The source is an undulator of the APPLE-II type with a magnetic structure made of 32 magnets and which have a period of 54 mm. Through a horizontal shift of the magnetic jaws, linearly polarized light from horizontal to vertical can be obtained as well as a circularly polarized beam. The size of the source is $200 \times 20 \ \mu\text{m}^2$ (H×V, FWHM).

The first optical element after the front end is a spherical mirror (incident angle = 0.4°) which provides a virtual focused horizontal source onto a set of adjustable slits. At this point, and according to calculations, the image of the source is $86 \times 760 \ \mu\text{m}^2$ at a full aperture of the front-end slits. Following is a set of two flat mirrors with a variable incidence angle $(0.4 - 1.3^{\circ})$ which acts as a low-pass filter. This filter minimizes the contamination by high-order harmonics delivered by the undulator, and reduces the thermal load received on the monochromator crystals. All mirrors are pure silicon coated with 70 nm of nickel which has its L and K edges at respectively 860 and 8333 eV, lying outside the useful energy range of the beamline. Both mirrors before the monochromator are water cooled. After each optical element, retractable beam monitors are installed. They allow to characterize the position and the intensity of the beam by means of a silicon diode and a YAG (Y₃Al₅O₁₂) crystal. All the mirror chambers of the beamline are under a vacuum in the 10^{-9} mbar range, while the monochromator chamber vacuum, due to the mechanics inside, is in the 10^{-7} mbar region.

The double crystal monochromator (DCM) was chosen to fit the energy range of the beamline. The DCM has a fixed exit and is of the "Lemonnier cam type" [73]: the two crystals are mounted on a common shaft which provides the rotation, and the second crystal translates to keep the exit beam at a constant height. Five pairs of crystals are available. They are positioned into the beam by a translation of the monochromator vessel which makes the change of the energy domain quite rapid. The angular scanning range is from 5° to 75° , which puts the lower limit reachable with the Si(111) around 2040 eV. Below this energy, four sets of crystals are used, InSb(111), YB₆₆(400), $KTiOPO_4(011)$ and beryl (1010). The final focusing of the beam is achieved by a Kirkpatrick-Baez (KB) [74] system. It provides a high X-ray flux over a wide energy range, a stable beam position on the sample during an energy scan while giving a fairly large working distance. The performance of the focusing system is determined by the quality of the mirrors, i.e., by the intrinsic RMS slope errors and the RMS surface roughness. With the aim to reduce the slope errors, two flat mirrors are elliptically bent. Based on a system developed at the ESRF [75], the benders have been designed to be UHV compatible, in order to avoid the absorption by air in the low energy range. The mirrors are also made of Si and coated by nickel, and the incident angle is 0.4°. A motorized four-jaw entrance slit defines the horizontal and vertical acceptance of the KB. The working distance between the end of the last mirror and the focus is about 90 mm. In order to correct the small but nevertheless noticeable loss of parallelism of the two-crystals over the large angular working range of the monochromator, the following scheme was developed. For each angular range of interest (typically 1 keV for EXAFS scans) the position of the beam on the sample is checked. The pitch, roll and height of the second crystal stage are optimized for a few values within this energy domain, in such a way that the beam stays at a fixed position on the sample with the highest flux. The resulting values are then fitted by a five terms polynomial as a function of the energy. Finally, during an energy scan, the position of the second crystal is adjusted according to these functions at each point. The focused beam can be stabilized within 1 μ m, and has the FWHM size of ~ 3 × 3 μ m² as determined by knife edge scans. The incident focused beam is monitored by measuring the total drain current of a polymer film coated with 50 nm of nickel, located at the exit of the KB system. To obtain an optical image of the sample, two microscopes (wide and narrow fields) are looking through a viewport to a mirror located in front of the sample.

XAS spectra are obtained by collecting the fluorescence using a mono-element energy dispersive silicon drift diode (SDD). Its resolution is 120 eV at the Si K edge, 150 eV at the Ti K edge at count rates up to about 50 kHz. It can be translated on a linear slide to adjust the collected solid angle. Data collected in the transmission mode was done by the use of a photo-diode positioned



Figure 2.18: An MCA spectrum taken at the energy 6004.3 eV on $SrTiO_3$ with Cr tracer-ions. Both lines depict the same spectrum, solid line linear y-scale and dashed line logarithmic. The regions of interest for the Ti and Cr $K\alpha$ lines are marked with vertical dash-dotted lines.

downstream behind the sample in the direct beam. For the samples described in the beginning of this chapter, the fluorescence yield was measured with the SDD detector. The photo-diode was used to measure the energy references, pure metal foils and binary oxides with respective tracer-ion. The signal from the SDD was fed into a multi-channel analyzer (MCA). Figure 2.18 shows an MCA spectrum measured on a SrTiO₃ sample with Cr as tracer-ion. The spectrum is plotted twice, once on a linear scale (Cr $K\alpha$ weakly visible) and once on a logarithmic scale. The incoming beam energy, observed as the elastic peak in the figure, was set to 6004.3 eV. For each energy point in a XAS spectrum, an MCA spectrum was measured. Regions of interest (ROI) were chosen around the $K\alpha$ lines from the element of interest. The integrated intensity in each ROI, marked in figure 2.18 with dash-dotted lines, constituted one energy point in the XAS spectrum.

Figure 2.18 illustrates one of the main experimental challenges while measuring the tracer-ion spectra. The Ti $K\alpha$ line is due to the concentrations 500 times stronger than the Cr $K\alpha$ line. To enhance the tracer-ion to Ti fluorescence ratio, a 0.5 mm thick Teflon filter was put in front of the SDD for Cr to Co. When increasing the element number, the tracer-ion $K\alpha$ line comes further away from the Ti $K\alpha$ line, and a stronger filter, 0.25 mm thick Al foil, was put in front of the SDD. The optimal thickness of the filter and the collected solid angle were tuned for 50000 total counts per second in the SDD. Both the Ti fluorescence and the elastic scattering signals were substantially bigger than the collected tracer-ion fluorescence. Therefore, the total count rate was dominated by Ti fluorescence and elastic scattering. The filters in front of the SDD were used to cut away Ti

Region	$E_{\rm start}~(eV)$	$E_{end} (eV)$	Step (eV)	Time (s)
1	5900	5990	2	2
2	5990.2	6010	0.2	4
3	6011	6100	1	2
4	6102	6300	2	4
5	6304	6650	4	12

Table 2.4: The energy steps and counting times used for the EXAFS measurement at the Cr K edge.

Table 2.5: The energy steps and counting times used for the XANES measurement at the CrK edge.

Region	$E_{\rm start}~(eV)$	$E_{end}~(eV)$	Step (eV)	Time (s)
1	5900	5990	2	4
2	5990.2	6020	0.2	8
3	6021	6100	1	4

fluorescence, but by cutting Ti fluorescence the relative intensity of the elastically scattered beam also increased. The filter settings had to be optimized for each case, where the parameters were: sample-detector distance, X-ray flux, and the thickness and type of filter.

As can be deduced from equation 2.12, the EXAFS signal decreases with increasing photoelectron wave number. For the measurements this means that at higher energies, the counting time was chosen longer than closer to the edge in order to compensate for the weaker EXAFS amplitude in relation to the total absorption. The energy ranges for a typical EXAFS and a typical XANES measurement for the Cr K edge are listed in tables 2.4 and 2.5, respectively.

The incoming light from the synchrotron source is polarized in the plane of the electron orbit $(\vec{E} \text{ in figure 2.19})$. In all measurements with the SDD, it measured the fluorescent X-rays almost perpendicular to the incoming beam, sketched in figure 2.19. This was chosen because the intensity of the elastic scattering is reduced by a squared cosine function of the angle between the direction of the beam and the direction of observation. The setup in figure 2.19 therefore minimizes the elastic scattering contribution $(\cos^2(90^\circ) = 0)$. Figure 2.19 also indicates the scan directions for



Figure 2.19: Top view of the sample setup. The scan direction y points out of the page (indicated by dot in circle). The sample was scanned in x and up-/down-stream (scan depth, z) simultaneously to keep the focus on the sample (focal plane dashed line). The arrow denoted \vec{E} indicates the direction of polarization.

the sample, these are: up-/down-stream (z) in the beam, vertical y, and horizontal x. The sample stage was mounted on stepping motors for movements in the μ m range and piezoelectrical motors for movements in the sub- μ m range.

Chapter 3

Detecting oxygen vacancies

3.1 X-ray absorption near edge spectroscopy

In this chapter, the main results of this dissertation are presented and discussed. These include XANES and EXAFS measurements on the 3d transition metal K edges. The measurements were performed on SrTiO₃ single crystal and powder samples, with a small amount of Ti substituted by the other 3d transition metals. It is shown that the 3d transition metal ions can be used as "tracer-ions" for oxygen vacancies. Before presenting the measurements, a few general remarks are made to facilitate the discussion. All shown spectra were normalized to a unit step, as shown in figure 2.10(b). The absorption data in figures 3.1-3.10 contain four common types of spectra for each tracer-ion. The first two are K edge XANES measured on an oxidized sample and on a reduced sample; hereafter called "Ox-spectrum" and "Red-spectrum," respectively. The third type is a K edge XANES calculated for a stoichiometric structure with the tracer-ion as absorber in an octahedral symmetry, which is referred to as "O_h-spectrum." The fourth is a calculated spectrum for a structure with an oxygen vacancy in the nearest neighbor shell of the absorber, that is, the tracerion is in a pyramidal configuration, hereafter referred to as the " P_y -spectrum." The experimental edge shift (ΔE) is defined as E_0 (E_0 is defined on page 20) of the Red-spectrum subtracted from E_0 of the Ox-spectrum. Similarly, ΔE for the calculated spectra is defined as E_0 of the P_y-spectrum subtracted from the E_0 of the O_h -spectrum. The position of the edge is sensitive to the chemical state of the absorber and, to a smaller extent, its coordination. Thus, ΔE physically represents a valence shift and possibly a change in coordination for the absorber. A valence shift changes the ionic size and thereby the bond distance to the surrounding oxygen ligands [76]. In the FEFF8.4 calculations, changing the bond distance therefore represents a valence change of the absorber. The resolution of the detector was insufficient to distinguish the $K\alpha_1$ from the $K\alpha_2$ line, therefore in the

Table 3.1: The binding energies of the 1*s* electrons (*K* edges) for the 3*d* transition metals together with the energies for the corresponding $K\alpha$ lines. The $K\alpha$ line energy is taken as the average of the $K\alpha_1$ and $K\alpha_2$ lines. For Ti also the energy of the $K\beta_1$ is given. Taken from reference [77].

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$1s \; (eV)$	4492	4966	5465	5989	6539	7112	7709	8333	8979	9659
$K\alpha$ (eV)	4088	4508	4948	5410	5893	6397	6923	7470	8038	8627
$K\beta$ (eV)		4932								

following discussion these two are treated as one line $(K\alpha)$. In table 3.1, the energies of the K edges of the 3d transition metals together with the energies of the $K\alpha$ lines are shown. The following K edge spectra, taken on the SrTiO₃ samples, were measured by integrating the intensity of respective $K\alpha$ fluorescence line as a function of X-ray energy.

In figures 3.1(a) and (b), the measured and calculated Sc K edge XANES for SrTiO₃ with Sc tracer-ions are presented. The two samples measured here consisted of polycrystalline powder pressed into pellets. Sc incorporated in the SrTiO₃ matrix is expected to have the electronic configuration $3d^0$ (Sc³⁺). This being a noble-gas configuration (argon), the probability for a valence change should be low and a negligible edge shift due to a valence change is expected. Comparing Ox- and Red-spectrum in figure 3.1(a), the edges of the two spectra are indeed on the same position. ΔE extracted from the measured Sc spectra was 0.11 eV with a standard deviation of 0.13 eV. Such a small ΔE probably originates from small differences in the normalization of the data (figure 2.10), and is therefore considered zero. The statistically significant difference between the two spectra is the small depression right after the edge in the Red-spectrum (centered at ~4509 eV). The calculated spectra in figure 3.1(b), show fairly good agreement with the measured spectra. For the O_h-spectrum, the features on the edge are slightly less pronounced, while for the P_y-spectrum these features are almost washed out. The P_y-spectrum shows a depression at the same energy as the Red-spectrum, but clearly overshoots the first peak after the edge (at ~4518 eV). In contrast to the measured spectra, a ΔE is observed between the two calculated spectra.

In figure 3.2(a), the Ti K edge XANES measured on an oxidized and on a reduced single crystal of SrTiO₃ with Co as tracer-ion are shown. Figure 3.2(b) shows calculations of the Ti K edge spectra for pure SrTiO₃ and with an oxygen vacancy in the first shell of the absorbing Ti. The two measured spectra are identical within the measurement precision. This was also observed for the

Detecting oxygen vacancies



Figure 3.1: (a) Experimental and (b) calculated Sc K edge XANES for SrTiO₃ samples with Sc as tracer-ion.

Figure 3.2: (a) Experimental Ti K edge XANES measured on a SrTiO₃ sample with Co as tracer-ion and (b) calculated for pure SrTiO₃.

samples with the other tracer-ions, the Ti spectrum was always unaffected by the reduction. The calculated spectra for Ti, figure 3.2(b), show an edge shift because in the calculation it is possible to use a particular Ti ion as absorber, thereby exaggerating the oxygen vacancy concentration. In the experiment, this signal is washed out at these low concentrations of oxygen vacancies. The agreement between the calculation of the O_h -spectrum and the measurement for Ti is poorer than for Sc, mainly the sharp peak at the edge step is poorly reproduced in the calculations.

In figures 3.3(a) and (b) spectra measured and calculated for the V K edge are presented. The measured spectra are not very detailed because the statistics in the experiment were poor. The reason for this was that the Ti $K\beta$ line overlapped with the V $K\alpha$ line and therefore increasing the apparent intensity, numerical values are listed in table 3.1. Data were collected with the regions of interests set to the V $K\alpha$ line lying on the Ti $K\beta$ line, generating a considerable background. It can be said with certainty that the measured spectra show an edge shift when comparing the Oxand Red-spectrum in figure 3.3(a). For the calculated spectra, figure 3.3(b), a small edge shift is observed when introducing an oxygen vacancy in the first shell surrounding V.

Figure 3.4(a) shows Cr K edge XANES spectra measured on oxidized and reduced $SrTiO_3$

Detecting oxygen vacancies



Figure 3.3: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with V as tracer-ion.



Ox

Red

(a) Cr Exp

(b) Cr Calc

1

0.5

0

1

culated tracer-ion K edge XANES of SrTiO₃ samples with Cr as tracer-ion. In (b), a spectrum calculated with the unmodified atom positions is shown (Orig).

samples with Cr as tracer-ions. The Cr Red-spectrum shows a clear edge shift and a broadening when compared to the Ox-spectrum. Figure 3.4(b) shows calculated spectra for a stoichiometric structure and with a first shell oxygen vacancy. The calculated O_h -spectrum agrees well with the Ox-spectrum. When calculating the spectra based on the coordinates with a vacancy in the first shell, a significant discrepancy between the calculated and the measured spectra was found. This spectrum is shown as "Orig" in figure 3.4(b) and corresponds to $Cr^{2.6+}$ [76]. This discrepancy was corrected by decreasing the average nearest neighbor distance (Cr-O distance) by 5%. This is shown as the and P_y -spectrum in figure 3.4, which shows good agreement with the Red-spectrum. The physical interpretation is that in the oxidized sample Cr^{4+} is surrounded by a full oxygen octahedron and in the reduced sample the Cr-ion is reduced to Cr^{3+} with an oxygen vacancy in the first shell.

Figures 3.5(a) and (b) show the measured and calculated K edges for Mn incorporated in SrTiO₃. Additionally, one spectrum measured at the Mn K edge on LaMnO₃ as Mn³⁺ reference in octahedral configuration is presented. The Ox-spectrum agrees with the edge measured on SrMnO₃, where Mn is tetravalent, (data not shown), indicating that the Ox-spectrum represents Mn in the 4+ valence



Figure 3.5: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with Mn as tracer-ion. In (a), a Mn³⁺ reference is shown. In (b), a spectrum calculated with unmodified atom positions is shown (Orig).

Figure 3.6: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with Fe as tracer-ions. In (a), a Fe³⁺ reference is shown.

state. The Red-spectrum shows a large edge shift. Comparing this edge to the edge measured on the 3+ reference suggests that Mn is in the 2+ valence state after reduction. The Red-spectrum does not show a broadening of the edge, in contrast to the edges measured on the SrTiO₃ samples with other tracer-ions. The O_h-spectrum agrees well with the Ox-spectrum. When calculating the spectrum with a vacancy in the first shell surrounding Mn a big discrepancy was found. This spectrum is shown as "Orig" in figure 3.5(b) and corresponds to Mn³⁺ [76]. The agreement was greatly improved by increasing the average nearest neighbor distance for Mn by 10% in the calculation with a vacancy. This is shown as the P_y-spectrum in figure 3.5(b), which shows good agreement with the Red-spectrum. The modified nearest-neighbor distance increase of 10% corresponds to Mn²⁺-O distances [76]. This is in agreement with results of EPR experiments in Mn-doped SrTiO₃ when annealed in H₂/N₂ [78]. In the samples with Mn tracer-ions, Mn is 4+ with a full nearest-neighbor oxygen shell in the oxidized sample, and 2+ in the reduced sample with an oxygen vacancy in the first shell.

Fe K XANES measured and calculated for Fe incorporated in SrTiO₃ are shown in figures 3.6(a) and (b) respectively. The Ox-spectrum is similar to the edge measured for the Fe³⁺ reference, LaFeO₃, suggesting that Fe is close to the 3+ valence state in the oxidized crystal. The Redspectrum shows a clear shift and a broadening of the edge, washing out the sharp features observed in the Ox-spectrum. With the same reasoning as above, the shift of Fe upon reduction indicates that Fe is in the 2+ state in the reduced crystal. The O_h-spectrum agrees well with the Ox-spectrum and the P_y-spectrum shows similar structure as the Red-spectrum, but the edge shift is underestimated in the calculated spectra. Calculations of the Fe P_y-spectrum were made with increased nearest neighbor distances (bigger valence change). These additional calculations reproduced the edge shift but the overall structure of the edge was poorly described.



Figure 3.7: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with Co as tracer-ions. In (a), a Co³⁺ reference spectrum is shown. The experimental data were collected at the MicroXAS and at the SuperXAS beamlines of the Swiss Light Source.



Figure 3.8: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with Ni as tracer-ions. In (a), the Ni K edge XANES measured on the slowly reduced crystal is shown. The experimental data were collected at the SuperXAS beamline of the Swiss Light Source.

Figures 3.7(a) and (b) display the measured and calculated Co K XANES when Co is incorpo-

rated in SrTiO₃. The main features of the XANES are broadened and the edge is clearly shifted when reducing the crystal, but two strong features dominate the pre-edge region, which were not observed in any of the previous spectra. The Co³⁺ reference measured on LaCoO₃ indicates that Co is 3+ when incorporated in the oxidized crystal. The Ox-spectrum was very well reproduced by the O_h-spectrum. The Red-spectrum, however, is not very well reproduced by the calculations. The edge shift is considerably larger for the experimental, and the two features observed on the edge are absent in the calculated spectra.

In figures 3.8(a) and (b) measured and calculated spectra for Ni in SrTiO₃ are shown. The Ni Ox-spectrum has similar features to the other spectra collected on oxidized single crystals, indicating Ni in an octahedral oxygen cage. The Ni Red-spectrum shows similar features in the edge as the Co Red-spectrum. The spectrum measured on the slightly reduced single crystal is also presented, with smaller ΔE and without the two features in the edge. The O_h-spectrum shows good agreement with the Ox-spectrum. When calculating spectra with an oxygen vacancy in the first shell, the edge shifts and broadens but the two features in the Red-spectrum could not be reproduced. The P_y-spectrum agrees very well with the spectrum measured on the slightly reduced single crystal, indicating that the stronger reduction may have caused major changes to the system.

Figure 3.9(a) displays a spectrum measured on oxidized $SrTiO_3$ with Cu tracer-ions. The spectrum was taken on a polycrystalline powder sample pressed into a pellet. When scanning the reduced pellet with the X-ray beam, the Cu $K\alpha$ signal was not homogeneously distributed throughout the sample. This indicates that reduction of the powder causes Cu to precipitate. For this reason, the XANES obtained on this sample is excluded from figure 3.9(a). In figure 3.9(b), the Cu O_h- and P_y-spectra are shown. The O_h-spectrum indicates a clear "white line" structure, not observed in the Ox-spectrum. One reason for the differences between the Ox- and O_h-spectrum can be that Cu was not properly incorporated in the SrTiO₃ structure. The different intensities of the Cu $K\alpha$ line at different locations on the reduced powder sample indicate regions of other Cu compounds. Cu and CuO were measured as references and no linear combinations of these two properly fit the Oxor any Red-spectrum. In the calculated spectra, the expected shift and broadening of the edge is observed when introducing an oxygen vacancy, cf., O_h- and the P_y-spectrum in figure 3.9(b).

In figure 3.10 the Zn Ox-spectrum together with O_h - and P_y -spectra are shown. The measured spectrum shows a clear white line structure, in agreement with the O_h -spectrum. In the case of Zn, the same discovery was made as for the Cu tracer-ions, the Zn seems to cluster unevenly when reducing the samples. Therefore, the Zn Red-spectrum is excluded from figure 3.10(a).

In figure 3.11(a) an overview of all the measured tracer-ion Ox- and Red-spectra is presented. The data is the same as already presented in figures 3.1-3.10 shown in one single figure to illustrate



Figure 3.9: (a) Experimental and (b) calculated tracer-ion K edge XANES of $SrTiO_3$ samples with Cu as tracer-ions. The experimental data were collected at the SuperXAS beamline of the Swiss Light Source.

Figure 3.10: (a) Experimental and (b) calculated tracer-ion K edge XANES of SrTiO₃ samples with Zn as tracer-ions. The experimental data were collected at the SuperXAS beamline of the Swiss Light Source.

the general trend. When reducing a sample the edge shifts towards lower energy and the structure of the edge changes. In the case of Sc, the change is very subtle; whereas the biggest change was found for Mn tracer-ions, with the largest edge shift and clearly a new edge structure. The most important observation is that the Ti spectra are identical when comparing spectra measured on oxidized and reduced samples. This is always observed for the Ti K edge XANES collected on the SrTiO₃ samples with all the 3*d* transition metal tracer-ions. This is the most important result so far, indicating that the change induced by the reduction affects the tracer-ions or their surroundings to a higher degree than Ti. This suggests that the induced conductivity is related to or induced by changes in the regions close to the tracer-ions.

Figure 3.11(b) shows an overview of all the calculated tracer-ion O_h - and P_y -spectra. The P_y spectra for Cr and Mn based on the calculations with the altered nearest neighbor distances are shown. The calculated spectra are based on stoichiometric coordinates that agree very well with the spectra measured on oxidized samples, except in the case of Cu. When incorporating an oxygen vacancy in the first shell of the tracer-ion, the edge shifts and the sharper features in the spectra



Figure 3.11: (a) Experimental K-edge XANES spectra measured on the SrTiO₃ samples with different tracer-ions (Sc to Zn). Data were taken on oxidized samples (solid lines) and on reduced samples (dashed lines). (b) Multiple-scattering XANES calculations with a full oxygen octahedron surrounding the tracer-ion (octahedral coordination, O_h) and with an oxygen vacancy in the first shell surrounding the tracer-ion (pyramidal coordination, P_y). The energy scale has been shifted such that the half edge step of the spectra (E₀) measured on oxidized samples (calculated with full octahedron) coincide for all tracer-ions [79].





Figure 3.12: (a) Experimental (filled squares) and calculated (filled circles) edge shift of the X-ray absorption spectra induced by the reduction. The experimental edge shifts are with the reduced Ni:SrTiO₃ sample and the theoretical edge shifts with the spectra calculated with unmodified coordinates for Cr and Mn. (b) Experimental and calculated edge shifts. For experimental Ni, this is with the slightly reduced crystal and Cr and Mn are calculated with modified coordinates. The lines are guides to the eyes.

are broadened which agrees well with the general trend in the measurements. This suggests that the changes observed in the experimental spectra, upon reduction of the samples, indeed originate from a first-shell oxygen vacancy.

Figures 3.12(a) and (b) show ΔE extracted from the measured and calculated spectra. The ΔE plotted as filled squares in figure 3.12(a) represent the edge shifts between spectra measured on oxidized and on reduced single crystals. The ΔE plotted as filled circles in figure 3.12(a) represent the edge shifts between the two calculated spectra (with and without oxygen vacancy). These calculations were based on the coordinates yielded by the relaxation of the atom positions in the DFT ground state calculations.

In figure 3.12(b), one experimental ΔE and two calculated ΔE have been replaced in order to increase the agreement between experimental and calculated edge shifts. The experimental Ni ΔE in figure 3.12(b) is the difference in E_0 between the spectra measured on the oxidized and on the slightly reduced crystal. The theoretical Cr ΔE in figure 3.12(b) is the difference in E_0 between the spectra calculated without oxygen vacancy and with an oxygen vacancy in a slightly smaller nearest neighbor shell. For the theoretical Mn ΔE , the nearest neighbor shell with oxygen vacancy has been made slightly larger. The change of the experimental Ni ΔE was motivated by the fact that the edge on the slightly reduced crystal followed the general trend to a greater extent than the edge measured on the reduced crystal. The change of the two theoretical ΔE greatly improved the agreement between experiment and calculation.



Figure 3.13: The calculated energy to incorporate tracer-ions (squares) and to incorporate tracer-ions together with a first shell oxygen vacancy (circles) in the $SrTiO_3$ matrix. The lines are guides to the eyes.

The observed trend that the edge shifts, when reducing the samples (quantified in figure 3.12(b)), is dependent on both valence changes and structural changes around the absorber. As observed in figure 3.1(a), the edge shift for Sc is practically zero. When comparing to the other 3d transition tracer-ions, the shift is greatest on Mn then decreases until Ni. It is therefore reasonable to propose that this trend reflects the number of possible valence states for each ion. That is to say, it is assumed that Sc is in a 3+ state, giving the noble gas electronic configuration $3d^0$, making a valence change improbable. When filling the 3d states, the tendency for different elements to change valence is enhanced. This is valid until the 3d states are close to full, again making a valence change improbable. This is clearly the case for Zn, which is expected to be $3d^{10}$ when incorporated in SrTiO₃. The start of this trend is shown by Fe and Co, where the edge shift has decreased when compared to Mn. Since Cu and Zn generally prefers to be in the 2+ valence state with a large ionic size, it is likely that the reduced Cu and Zn ions do not fit in the structure and precipitate when reduced. Another aspect of some of the 3d transition metals is the ability to occupy different spin states in the octahedral configuration. Different spin states generate, for example, different ionic sizes and magnetic effects, which would affect the XANES. None of the effects of different spin states were taken into account here, the calculations generating the spectra were spherically averaged with respect to the polarization of the incoming light.

As described in the previous chapter, all the coordinates used in the multiple scattering calculations were obtained from the relaxed atom positions generated by the DFT calculations. The energy needed to incorporate a tracer-ion and to incorporate a tracer-ion with an oxygen vacancy in the first shell were also generated in the DFT calculations. The resulting energies are shown in figure 3.13, with zero defined as the energy needed to create pure stoichiometric SrTiO₃. The filled

Detecting oxygen vacancies



Figure 3.14: The O-binding energy as obtained form the DFT calculations for each different tracer-ion element. The line is a guide to the eyes.

squares represent energies required to incorporate the tracer-ions with full nearest neighbor shell and the filled circles the energies for additionally incorporating an oxygen vacancy. When replacing Ti with the other 3d transition metals, the incorporation energy is low for Sc and V, intermediate (and practically constant) for Cr, Mn, Fe, Co, and Ni. When replacing Ti with Cu or Zn, clearly more energy is needed for their incorporation. This step for Cu and Zn suggests that these two ions might not get correctly incorporated in the SrTiO₃ matrix. The experimental XANES for Cu, figure 3.9(a), does not agree well with the calculated spectrum. This indicates a different local structure than expected with Cu on the Ti position in SrTiO₃. The fact that the incorporation energies in figure 3.13 are higher for Cu could therefore explain the disagreement between the calculated and the measured spectrum, as well as the inhomogeneities detected in the reduced samples. However, if this effect is enhanced in polycrystalline material or if single crystals would lead to an incorporation, can not be described with the data at hand.

When subtracting the two energies for each tracer-ion, presented in figure 3.13, the specific binding energy for an oxygen in the first shell surrounding the tracer-ion is obtained. The quantification of the specific oxygen binding energies for different tracer-ions is shown in figure 3.14. The highest binding energy is found for Ti (stoichiometric unit cell) and lower for all the other tracer-ions. This indicates that it is energetically favored to incorporate a vacancy in the first shell of a tracer-ion when the sample is reduced. The calculated energies in figure 3.13 together with the experimental and calculated Cu and Zn edges in figures 3.9 and 3.10 exclude Cu and Zn as good tracer-ions. With Cu and Zn excluded, figure 3.14 can be used to rate the quality of the different 3d transition metals as oxygen vacancy tracer-ions in SrTiO₃.

The fact that the Ti K edge is unaffected by the reduction together with the fact that the tracer-ion spectra are so strongly affected, proves that the associated oxygen vacancies are prefer-

ably introduced in the nearest neighbor shell of the tracer-ions. This has also been studied with electron paramagnetic resonant measurements (EPR) on Mn and Fe incorporated in SrTiO₃, which concluded that oxygen vacancies were indeed associated with the Mn and Fe centers [80]. The most important prerequisite for this conclusion is that the reduction of the SrTiO₃ crystals introduces oxygen vacancies. Due to the low concentrations of oxygen vacancies needed to make the SrTiO₃ metallic, no conclusions can be drawn from gravimetric measurements. The influence of oxygen vacancies on the conductivity in SrTiO₃ has been extensively studied, with several publications on pure SrTiO₃ and on transition metal doped SrTiO₃. The Hall mobility was studied in reduced SrTiO₃ and Nb-doped SrTiO₃, with the conclusion that the reduction induces conductivity in reduced single crystals was introduced [28]. For SrTiO₃ doped with Fe and Ni it was found that the conductivity increased and decreased with reduction and oxidation [81]. Therefore, there is evidence that oxygen vacancies are responsible for the conductivity in reduced SrTiO₃.

3.2 Extended X-ray absorption fine structure

In order to strengthen the conclusions form the previous section, EXAFS data were collected on the oxidized and reduced crystals with the different tracer-ions. EXAFS data both determine if the tracer-ions have the right coordination and are highly sensitive to first shell changes (e.g., oxygen vacancies). The background in the absorption data taken on all samples, except for Sc, was mainly composed of Ti fluorescence. Most notably, in the V spectra the characteristic structure of a tracerion in an octahedral configuration was washed out due to the high background. For the other 3dtransition metal tracer-ions, increasing the element number beyond 23 (V), the contribution from the Ti fluorescence in the background gradually decreases, improving the statistics of the spectra. The Ti fluorescence was also partly suppressed by the different filters as discussed in chapter 2. For the powder sample with Sc, there were difficulties to get a clear EXAFS signal due to interference of Bragg peaks in the spectrum. These Bragg peaks probably originated from micrometer sized crystallites in the powder. Since no change was observed in the XANES data for the Ti edge, little could be learned from obtaining Ti EXAFS data. With the problems previously discussed for Cu and Zn, these were not considered for EXAFS measurements. With the three first and the two last elements of the 3d transition metal tracer-ions ruled out for EXAFS data, EXAFS spectra were measured for Cr, Mn, Fe, Co, and Ni samples. For Cr, oscillations were observed but when EXAFS was extracted, the resulting data was too noisy to analyze properly. Cr EXAFS data will be presented in chapter 4 that were taken under slightly different conditions on memory devices. In





Figure 3.15: (a) The k^2 weighted EXAFS data extracted from absorption spectra taken on a single crystalline SrTiO₃ with Mn as tracer-ions. The solid line depicts a spectrum taken on the oxidized single crystal and the dashed line shows a spectrum taken on the reduced single crystal. (b) The magnitude of the Fourier transformed EXAFS data presented in (a).

the stainless steel beamline environment, Fe and Co EXAFS oscillations with this low concentration of Fe and Co in the samples were not considered reliable. Elastic scattering from the sample excited Fe and Co in the beamline environment and substantially enhanced the background, rendering the EXAFS signal-to-noise ratio too small to extract reliable data. EXAFS spectra with distinctive features were collected on the oxidized and reduced SrTiO₃ single crystals with Mn and Ni as tracerions. The extraction of the EXAFS data from the X-ray absorption measurements is explained in figure 2.10(a)-(d). The treatment and the linear combination fits of EXAFS data were performed using the graphical user interface ATHENA [82] based on the computer code IFEFFIT [83]. The fitting of theoretical spectra to measured ones was done using the graphical user interface ARTEMIS [82], which is also based on the computer code IFEFFIT [83]. Theoretical spectra for the EXAFS analysis were obtained by the FEFF6 code [65].

The k^2 weighted Mn K edge EXAFS data taken at room temperature on oxidized and reduced single crystals are presented in figure 3.15(a) with the magnitude of the Fourier transform of this EXAFS data in figure 3.15(b). The EXAFS in figure 3.15(a) shows clear oscillations for the oxidized crystal and slightly damped oscillations for the reduced crystal. The damping of the EXAFS oscillations upon reduction is consistent with a reduction of the number of nearest neighbors, N_i . For the first shell path, N_i would decrease from six in the oxidized to five in the reduced sample, indicative of an oxygen vacancy in the first shell. These data were Fourier transformed with the



Figure 3.16: (a) The k^2 weighted EXAFS data extracted from absorption spectra taken on a single crystalline SrTiO₃ with Ni as tracer-ions. The solid line depicts a spectrum taken on the oxidized single crystal and the dashed line shows a spectrum taken on the slightly reduced sample. (b) The magnitude of the Fourier transformed k^2 weighted EXAFS data taken on the oxidized single crystal (solid line) and on the slowly reduced single crystal (dashed line).

window function defined for $4.2 \leq k \leq 12$ Å⁻¹. The magnitude of this Fourier transform, as presented in figure 3.15(b), show the characteristic SrTiO₃ peaks around 1.5 Å and 3.3 Å. The second peak consists of Sr and Ti as well as multiple scattering. The splitting between the Sr and the Ti peaks were only partly resolved with this data, manifesting itself as the shoulder on the second peak. Traditional fitting of the Mn EXAFS data was not possible, because the background contribution was too large.

The most accurate EXAFS measurements were performed on crystals with Ni as tracer-ions. EXAFS spectra were successfully extracted from the absorption data taken on the oxidized crystal as well as on the slightly reduced crystal. The k^2 weighted EXAFS data are shown in figure 3.16(a) and the magnitude of the Fourier transform in figure 3.16(b). The measurements were done at a temperature of 125 K, clearly above the temperature of the phase transition of SrTiO₃. This temperature was chosen to avoid a measurement of the rotated octahedrons while still suppressing the thermal vibrations in the crystal (which decrease the EXAFS signal with increasing k, see equation 2.12). The EXAFS data was Fourier transformed with the window function defined for $3 \le k \le 11$ Å⁻¹. For the oxidized crystal there is a distinctive peak in the Fourier transform at 1.5 Å, indicative of an octahedrally coordinated absorber and another more intense peak around 3.3 Detecting oxygen vacancies



Figure 3.17: (a) The k^2 weighted EXAFS data taken on the oxidized single crystal (solid line), on the slowly reduced single crystal (dashed), and the Ni metal foil (dash-dotted). (b) The spectrum measured on the reduced single crystal together with a linear combination of 50% spectrum measured on the oxidized crystal and 50% Ni foil spectrum.

same position as the first Ni peak in a spectrum measured on metallic Ni.

The Ni EXAFS data measured on the slightly reduced crystal was fitted in k-space for $3 \le k \le$ 11.7 Å⁻¹ with a linear combination of the EXAFS data taken on the oxidized crystal and EXAFS data taken on a reference Ni foil. In figure 3.17(a), the two EXAFS spectra from the oxidized crystal and the Ni foil are shown together with the spectrum measured on the slowly reduced crystal. The spectrum from the slowly reduced crystal follows the spectrum from the Ni foil with additional damping. The fit result was that the EXAFS spectrum taken on the slightly reduced crystal can be reproduced by 50% of the spectrum measured on the oxidized crystal and 50% of the Ni foil reference spectrum. In figure 3.17(b) the resulting linear combination spectrum together with the spectrum from the slightly reduced sample are shown. The fit matches the spectrum well, indicating that there were strong contributions from metallic Ni in the slowly reduced single crystal.

A stoichiometric SrTiO₃ with the central Ti replaced by Ni was used to calculate the scattering factors and the phase shifts to reproduce the spectra measured on the oxidized crystal. With these coordinates, FEFF6 generated the scattering paths shorter than 4 Å. Seven paths were chosen, the single scattering paths (O, Sr, Ti), two focusing multiple scattering paths (Ti \rightarrow O, O \rightarrow Ni \rightarrow O), and two multiple scattering paths (O \rightarrow O, Sr \rightarrow O). All seven fitted paths are marked (1)-(7) in figure 3.18. In these seven paths, six parameters were left free and fitted in *R*-space. The free parameters were: the electron reduction factor, S_0^2 ; the correction to E_0 , ΔE_0 ; two different Debye-Waller factors, σ_1^2



Figure 3.18: The photoelectron wave paths used in the fitting of the EXAFS data taken on the oxidized single crystal with Ni as tracer-ions. The solid circles represent Ni for outgoing photoelectron waves and Ti for scattered photo electron waves. This is the TiO₂ plane, where \times are out of plane Sr ions. The numbering starts on the shortest effective path and ends on the scattering path with the longest effective length, for (1) it is 1.95 Å and for (7) 4.04 Å.

and σ_2^2 ; two different corrections to the path lengths, ΔR_1 and ΔR_2 . σ_1^2 and ΔR_1 were used for pure oxygen scattering paths and σ_2^2 and ΔR_2 for the other paths. The fit was done with the path length as given from crystallographic input plus the correction, $R_{\text{fit}} = R_{\text{cryst}} + \Delta R$, as shown in figure 3.18 for the shortest single scattering path (1). The result of the fit together with the data are displayed in figure 3.19(a) and the fitted numerical values of the free parameters are listed in table 3.2. To determine the precision of this fit (and the following EXAFS fits) the **R**-factor is used. The **R**-factor is defined as

$$\mathbf{R} = \frac{\sum (\xi - \hat{\xi})^2}{\sum \xi^2},\tag{3.1}$$

where ξ is the array with the EXAFS data and the $\hat{\xi}$ is the array with the fitted data.

Led by the linear combination in figure 3.17(b), two models were used to fit the EXAFS spectrum measured on the slightly reduced crystal (figure 3.16(b)). The two models are: stoichiometric



Figure 3.19: (a) Magnitude of the Fourier transform of the k^2 weighted EXAFS data (solid line) taken on the oxidized single crystal SrTiO₃ with Ni as tracer-ions. The dashed line shows the fitted spectra based on a model with Ni on the octahedral place in SrTiO₃. (b) The magnitude of the Fourier transform of the EXAFS data (solid line) taken on the slightly reduced Ni:SrTiO₃, together with the fit based on a model of 37% octahedrally coordinated Ni in SrTiO₃ and 63% metallic Ni.

Table 3.2: Fitting parameters obtained for the fit of the EXAFS data obtained from the oxidized crystal with Ni tracer-ions. The **R**-factor reflects the goodness of the fit, as defined in equation 3.1.

Fit parameter	Fitted value
k -range (k^2 -weighted)	$4.56 \le k \le 10 \text{ Å}^{-1}$
R-range fitted	$1 \leq R \leq 4.14$ Å
S_0^2	0.98 ± 0.21
ΔE_0	$-9.54\pm1.47~\mathrm{eV}$
ΔR_1	0.01 ± 0.01 Å
ΔR_2	$-0.03\pm0.01~\mathrm{\AA}$
σ_1^2	$0.009 \pm 0.003 ~\rm{\AA^2}$
σ_2^2	$0.008 \pm 0.002 ~\rm{\AA^2}$
\mathbf{R} -factor	1%

SrTiO₃, with Ni as central absorber, and pure Ni metal. The parameters obtained from the fit of the oxidized sample (table 3.2) were set fixed, except for a modified S_0^2 (hereafter called $S_0^2|_{\text{STO}} \cdot \alpha$). An EXAFS spectrum collected on a Ni foil was fitted in the first shell, the resulting fit of the free parameters are listed in table 3.3. The second model used in the fitting the spectrum from the slightly reduced crystal was based on the parameters in table 3.3 except for a modified S_0^2 , hereafter called $S_0^2|_{\rm Ni} \cdot \beta$. The scattering paths included to fit the spectrum obtained on the slightly reduced crystal were the single scattering paths for $SrTiO_3$, one focusing multiple scattering path (Ti \rightarrow O) and the first shell path for metallic Ni. The parameters left free in the fit were $S_0^2|_{\text{STO}} \cdot \alpha$, $S_0^2|_{\text{Ni}} \cdot \beta$, and a common ΔE_0 . The resulting fit together with the data are shown in figure 3.19(b), and the numerical values of the fitting variables are listed in table 3.4. The $S_0^2|_{\text{STO}} \cdot \alpha$ and $S_0^2|_{\text{Ni}} \cdot \beta$ fitted to the EXAFS from the slightly reduced crystal confirm that there indeed are clusters of metallic like Ni in the crystal after reduction. The α and β parameters were introduced in order to extract the percentage of $SrTiO_3$ and metallic Ni in the spectra measured on the slightly reduced crystal. A comparison of the S_0^2 measured on the oxidized crystal and on the Ni foil suggests that the metallic like Ni contribution is $\beta = 63\%^1$ and the SrTiO₃ contribution is $\alpha = 37\%$ after reduction. From this analysis, it is clear that Ni cluster in the sample upon reduction, but no conclusions can be drawn about the character of these metal clusters. The single crystals were disc shaped, 5 mm in diameter and approximately 1 mm thick. Possible grain boundaries or surface effects could not be excluded with these samples. To minimize grain boundary effects, epitaxially grown films can be used. Using thicker crystals, thorough polishing of the reduced surfaces, and grinding to powder can minimize the surface effect. These two techniques can determine whether the Ni clusters are related to grain boundaries or the surface.

EXAFS spectra obtained with the absorber in an octahedral symmetry in a cubic crystal normally show similar features, with small changes with a change of absorber. Therefore, the EXAFS spectra extracted from the Mn and Ni absorption data, figure 3.15(a) and figure 3.16(a), were expected to show similar main features. Small deviations, when comparing Mn and Ni spectra, were nevertheless expected. The EXAFS spectrum is very sensitive to the local surrounding geometry, influenced by the ionic size of the absorber. Deviations, when comparing Mn and Ni spectra, can also be introduced due to slightly different manufacturing processes. The precursors were determined to be single phase with XRD, but different furnaces were used to grow the Mn and the Ni crystals. It is possible that the temperatures, rotation speed of the melt and other factors result in, for example, different grain boundaries which might attract oxygen vacancies and tracer-ions, distorting the EXAFS.

For k < 6 Å⁻¹, the spectra show similar oscillations, for k > 6 Å⁻¹ the Mn spectra show a

¹These numbers were extracted after normalizing
$$\alpha$$
 and β , $\beta + \alpha = 1$, by $\beta = \frac{\frac{0.60}{0.81}}{\frac{0.60}{0.81} + \frac{0.43}{0.98}} = 0.628$.

Table 3.3: Fitting parameters obtained for the fit of the EXAFS data obtained from the Ni reference foil. The **R**-factor reflects the goodness of the fit, as defined in equation 3.1.

Fit parameter	Fitted value
k -range (k^2 -weighted)	$3.8 \le k \le 11.1 \text{ Å}^{-1}$
R-range fitted	$1.6 \leq R \leq 2.7$ Å
S_0^2	0.81 ± 0.14
ΔR	$-0.007 \pm 0.011 ~\rm{\AA}$
σ^2	$0.006 \pm 0.001 ~\rm{\AA^2}$
ΔE_0	$6.7\pm1.9~{\rm eV}$
\mathbf{R} -factor	0.03%

Table 3.4: Fitting parameters obtained for the fit of the EXAFS data obtained from the slowly reduced crystal with Ni tracer-ions. The **R**-factor reflects the goodness of the fit, as defined in equation 3.1.

Fit parameter	Fitted value		
k -range (k^2 -weighted)	$4 \leq k \leq 11 ~\rm{\AA}^{-1}$		
R-range fitted	$1 \leq R \leq 4.5$ Å		
$S_0^2 _{ ext{STO}}\cdot lpha$	0.43 ± 0.08		
$S_0^2 _{ m Ni}\cdoteta$	0.60 ± 0.07		
ΔE_0	$5.0{\pm}1.0~{\rm eV}$		
R-factor	7.6%		

phase shift compared to the Ni spectra. Both the Fourier transformed spectra measured on oxidized crystals show the main peaks at the same value of R, the characteristic SrTiO₃ positions. This proves that both Mn and Ni get incorporated on the expected Ti place when fabricating the samples. The magnitude of the oxygen scattering peak in the Fourier transformed Ni EXAFS seems to be only one third compared to the Mn EXAFS. When comparing the data obtained on oxidized crystals (in figures 3.15(b) and 3.16(b)) with published Ti K EXAFS on SrTiO₃ [84, 85], the conclusion is drawn that the magnitude of the oxygen peak in figure 3.15(b) is too large. It was concluded from the analysis of the Mn EXAFS data that the background in the spectra could not be correctly determined, attributing the large oxygen peak to contributions from the background. It is impossible to compare the EXAFS spectra on the reduced crystals due to the strong Ni metal contamination in the Ni spectrum. Nevertheless, it is clear from the data in figure 3.15(b) that Mn does not drastically change its nearest neighbor distance upon reduction.

Fitting the Ni EXAFS spectrum of the oxidized crystal to a stoichiometric SrTiO₃ model, further supported that Ni is incorporated at the Ti site with six nearest neighboring oxygen ions. The strong Ni contribution in the spectrum for the slightly reduced crystal (figure 3.16(b)) could also be a Ti contribution; these two can not be distinguished. A possible scenario with strong Ti contribution is that there are no oxygen ions in the first shell, only nearest neighboring Ti ions. With the precipitation of Cu and Zn, small clusters of Ni seem equally possible as a general collapse of the structure generating Ti as nearest neighbors. Interestingly, the Co EXAFS spectrum taken on the reduced single crystal (data not shown) had few similarities to the Co foil spectrum in contrast to the Ni EXAFS spectrum resembling the Ni foil spectrum. The Ni EXAFS was expected to show strong similarities with the Co EXAFS, since the XANES spectra for Co and Ni (figure 3.11(a)) show similar features not explained by the multiple scattering calculations. This might be explained by the fact that the XANES is sensitive further away form the absorber (low k), compared to EXAFS (high k). In the case of Co, no convincing conclusions can be drawn from the data at hand.

Detecting oxygen vacancies



Figure 3.20: (a) Mn K edge XANES measured on the oxidized single crystal (solid line) together with two calculated Mn K edge XANES, where Mn has replaced Ti (dashed line) and where Mn has replaced Sr (dash-dotted line). (b) The magnitude of the Fourier transform of the Mn K edge EXAFS data measured on the reduced single crystal (solid line) together with the calculated contributions of the first oxygen shell when Mn is replacing Ti (dashed line, sixfold coordination) and when Mn is replacing Sr (dash-dotted line, twelve-fold coordination).

The above presented findings are both supported and questioned by EPR measurements in similar systems in several publications [86–88]. The EPR technique is, as X-ray absorption, element specific which makes it a very versatile tool to study low concentrations of ions in different materials. The EPR technique requires an unpaired electron in the ion of interest. When the valence changes, an absence of this signal is interpreted as the presence of another valence state. Dielectric and EPR spectroscopy suggest that Mn is incorporated on the Ti site when Mn is in the 4+ state and that it is incorporated on the Sr site when Mn is in the 2+ state [86]. Our X-ray absorption results showed that Mn was incorporated as 4+ on the Ti site and that annealing in H₂/Ar reduced Mn to 2+. To resolve this issue, the Mn K edge XANES measured on the oxidized single crystal is shown together with two calculations where Mn is replacing Ti and Sr, figure 3.20(a). Figure 3.20(b) shows the magnitude of the Fourier transform of the Mn K edge EXAFS taken on the reduced crystal together with calculated contributions from the first shell in the two cases with sixfold and twelvefold coordination of Mn in $SrTiO_3$, on the Ti and Sr positions respectively. It is clear that the twelve-fold coordination does not fit to the measured XANES or the EXAFS data. The work shown in reference [86] claims that Mn substitutes both Ti and Sr, depending on the annealing conditions while synthesizing the samples. In air or oxygen atmosphere, Ti substitution is possible, which supports the results presented above. These assumptions were used to deduce the lattice site for Mn in $Sr_{0.98}Mn_{0.02}TiO_3$ ceramics [89]. Other published results claim that it is *not* possible to control at which site Mn is incorporated in SrTiO₃ single crystals [87]. This shows that the coordination of Mn is difficult to determine. The data and calculations shown in figure 3.20 clearly prove that the Mn ions are incorporated in oxidized and reduced samples on the Ti position.

3.2.1 Oxygen vacancy sensitivity

One of the most important practical issues, during an experiment, would be to quantify the oxygen vacancy concentration. One simple strategy to do this is to choose a suitable tracer-ion and deduce the vacancy concentrations from a linear combination of the Ox-spectrum and the Red-spectrum to reproduce the spectrum measured in the sample. This is used to measure the oxygen vacancy concentrations in the memory devices, as will be shown in chapter 4. When changing ions throughout the 3d series, it is observed that the edge shift changes. After reduction of two SrTiO₃ crystals (with different tracer-ions) in the same atmosphere, for the same time and at the same temperature, it is reasonable to believe that the amount of vacancies introduced is roughly the same for both crystals. When comparing the reduced Fe samples with the reduced Co and Ni samples in figure 3.11(a), Fe shows a higher agreement with the calculated spectra than Co and Ni. With the same amount of vacancies in the samples, this might indicate that Co or Ni tracer-ions are more sensitive to oxygen vacancies. For example, in samples where low concentrations are expected, Co or Ni are better suited as tracer-ions. It is further possible that this reflects the number of different stable valence states known for each element. Mn is known to range from 2+ to 6+ easily changing valence, leading to the greatest ΔE and the biggest oxygen vacancy tolerance. Therefore, when oxygen vacancy concentrations are expected to be high. Mn is the better chosen tracer-ion. Note that by changing the tracer-ion concentration, the sensitivity for detecting vacancies can be varied, leading to a very powerful tool to detect oxygen vacancies in $SrTiO_3$.

CHAPTER 4

Tracing oxygen vacancies

4.1 Tracer-ions in resistance memory devices

In this chapter, the main result of experiments performed on resistive switching memory devices are presented. These devices, designed to facilitate the X-ray absorption measurements, were fabricated from $SrTiO_3$ single crystals with 0.2% of the Ti replaced by Cr as tracer-ions. The resistive switching devices used here were prepared as described in chapter 2, fully formed in ambient conditions and with confirmed resistive switching. When measuring the Cr K edge XANES with the micro-focused X-ray beam on different locations on the sample, three different spectra were found, while no changes were observed on the Ti K edge. The three different Cr K edge spectra are shown in figure 4.1(a). The reference spectrum which was taken far away from the electrodes prior to the forming, one spectrum at the anode below the Pt layer, and one at the end of the anode, close to the anodecrystal interface. Previously published results on these devices showed that the reference spectrum corresponds to Cr^{3+} in an octahedral symmetry [90]. After forming, the spectrum taken beneath the anode shifted slightly towards higher energy. The shift is interpreted as a chemical shift representing a valence change from Cr^{3+} to Cr^{4+} . Furthermore, it is identical to the spectra taken on the oxidized single crystal (figure 3.4(a)). The spectrum at the anode-crystal interface (AI) in figure 4.1(a) shows more intensity in the pre-edge region and some broadening of the edge. Figure 4.1(b) shows the difference between the spectra measured at the anode interface and the reference. The curve in figure 4.1(c) represents the difference between the spectrum measured beneath the anode and the reference. The dip around 6007.3 eV is thought to arise from the Cr^{4+} signal from the anode. The sketch of the device in figure 4.1(d) shows the locations where the spectra were measured.

The spectrum measured at the anode-crystal interface of the device showed the same trend as the Cr Red-spectrum with increased intensity in the pre-edge and a broadening of the main edge. This



Figure 4.1: (a) The Cr K edge XANES obtained on the memory device prior to forming (solid line), on the fully formed device at the anode-crystal interface (dashed line), and on the fully formed device beneath the anode (dash-dotted line). (b) The difference between the anode interface spectrum and the reference spectrum, and (c) the difference between the anode spectrum and the reference spectrum. (d) Depicts the locations where the spectra in (a) were measured. The reference was taken 100 μ m away from the electrodes.



Figure 4.2: The three Cr K edge XANES in (a) were taken on two different samples. The reference was taken on a memory device prior to forming, "Red" (dashed line) was taken on the reduced single crystal sample (same as in figure 3.4(a)), and the anode-interface spectra was taken on the fully formed memory device. (b) The linear combination of the "Ref" spectrum and the "Red" spectrum fitted to the anode interface (AI) spectrum.


Figure 4.3: Shows the raw intensity of the Cr $K\alpha$ line (a) and the Ti $K\alpha$ line (b) while scanning the sample spatially in the beam. The maps were collected simultaneously and the X-ray energy was set to 6004.3 eV. The averaged intensity in the black boxes was used to normalize the absorption from the Pt electrodes.

change is interpreted as the introduction of an oxygen vacancy in the first shell surrounding Cr. To quantify the amount of oxygen vacancies introduced when forming the memory cell, the spectrum found at the anode-crystal interface was fitted to a linear combination of the reference spectrum and the reduced single crystal spectrum. The individual components are shown in figure 4.2(a) and the resulting fit consisting of $34\pm1\%$ reduced single crystal spectrum and $66\pm1\%$ reference spectrum is shown in figure 4.2(b). The **R**-factor, as defined in equation 3.1, for this fit was calculated to be 0.03%. This implies that when the device was fully formed 34% of the Cr atoms were missing an oxygen in the first shell. In $SrTiO_3$, there are three oxygen ions per unit cell, and with 0.2% of Ti replaced by Cr, the total oxygen vacancy concentration equals 0.02% $(\frac{1}{3} \cdot 0.002 \cdot 0.34 = 2.13 \cdot 10^{-4})$. The maximum intensity of the difference observed in figure 4.1(b) is therefore directly related to oxygen vacancies in the sample and can be used to quantitatively determine oxygen vacancy concentrations as small as $2.3 \cdot 10^{-4}$ with a precision of $6.7 \cdot 10^{-6}$. The distribution of oxygen vacancies is likely not perfectly homogeneous, therefore, the oxygen vacancy concentration number reflects an average in the probed volume. This volume was defined by the size of the focused X-ray beam (~ 3×3 μ m²) and the penetration depth of four micrometers. The X-ray energy was set to the value where the difference of the spectrum taken at the anode interface and the reference spectrum is maximal (6004.3 eV, figure 4.1(b)). The sample was then spatially scanned in the beam and the Cr $K\alpha$ fluorescence together with the Ti $K\alpha$ were collected generating micro-resolved X-ray fluorescence $(\mu$ -XRF) oxygen vacancy maps.

When scanning the sample in the beam, the fluorescent X-rays were partly absorbed by the Pt electrodes. In figure 4.3(a) and (b) the intensity of the Cr $K\alpha$ and Ti $K\alpha$ lines are shown while

Tracing oxygen vacancies



Figure 4.4: μ -XRF maps at an X-ray energy of 6004.3 eV showing the distribution of the oxygen vacancies in the octahedrons surrounding Cr atoms over the anode and cathode regions. They are taken in seven steps during the forming in air: (a) prior to forming; (b)-(h) after the device was formed to 100 μ A, 1 mA, 2 mA, 4 mA, 6 mA, 8 mA, and 10 mA, respectively. A, P, and C depict integration regions used to quantify the movements of the oxygen vacancies. The concentration is given for the X-ray probed volume [91].

scanning the fully formed sample in the beam. The beam energy was 6004.3 eV, which was the value for which the Cr spectrum was most sensitive to oxygen vacancies. The electrodes are clearly visible in both maps, decreasing the intensity by approximately one third in these regions. The Ti fluorescence shows no changes during the forming, therefore, the Ti maps were used to normalize the Cr raw maps and eliminate the intensity dip due to absorption from the Pt electrodes. The Pt normalized Cr maps (Cr_i^{Norm} , where *i* is the corresponding step with the X-ray beam, "pixel") is defined by the following formula:

$$\operatorname{Cr}_{i}^{\operatorname{Norm}} = \operatorname{Cr}_{i}^{\operatorname{Raw}} + \left[\frac{\operatorname{Ti}_{i} - \operatorname{Ti}_{\operatorname{Bkg}}}{\operatorname{Ti}_{\operatorname{Min}} - \operatorname{Ti}_{\operatorname{Bkg}}}\right] \cdot (\operatorname{Cr}_{\operatorname{Bkg}} - \operatorname{Cr}_{\operatorname{Min}}).$$
(4.1)

Where Cr_i^{Raw} corresponds to pixel *i* in figure 4.3(a), Ti_i is the *i*th pixel in figure 4.3(b), Cr_{Min} the average of the unmarked black squares in figure 4.3(a), Cr_{Bkg} the average of the "Bkg" marked black squares in figure 4.3(a). Ti_{Min} and Ti_{Bkg} are taken as the average of the corresponding black squares in figure 4.3(b). The white contours outlining the Pt electrodes in figures 4.3(a) and (b), as well as the following maps, are plotted at the value $(Ti_{Bkg} + Ti_{Min})/2$.

Figure 4.4 displays the Pt-normalized μ -XRF oxygen vacancy maps taken during the forming



Figure 4.5: The distribution of oxygen vacancies in the two last forming steps. (a) Shows the device formed with positively biased anode to 10 mA and (b) the device after applying negative bias for the first time to the anode. The concentration is given for the X-ray probed volume [91].

of the device in air. The device probed in the measurement was formed slightly different than the device described in table 2.2. In the first DC forming steps, currents of 100 μ A and 1 mA were reached. After, forming was performed by voltage sweeps, always with positive voltage on the anode. Steps with forming currents of 2, 4, 6, 8, and 10 mA were made. The pristine device is shown in figure 4.4(a). After forming the memory cell to 100 μ A (figure 4.4(b)) the oxygen vacancies are distributed in a roughly triangular shape, highlighted by the contour between the electrodes. Higher intensity is found close to the cathode and a gradual decrease towards the anode. After continuing the electrical forming to 2 mA the distribution of vacancies centers more around the cathode interface, figures 4.4(c) and (d). For higher forming currents, the oxygen vacancies also become clearly visible at the anode interface, as shown in figures 4.4(e)-(h).

When the device has reached its maximal current, 10 mA, during the forming (figure 4.4(h)) there is one circular vacancy-concentration spot at the anode interface and one more ellipse-shaped at the cathode interface. At this stage, the resistance in the device has been reduced to a few k Ω . Note that during the experiment the anode was always positively biased and the cathode grounded. In order to finally obtain the bi-stable resistive memory state, the voltage was swept from 0 to 200 V in steps of 5 V and thereafter swept to -200 V, with a current compliance set to 10 mA, limiting the voltage output to keep the current below 10 mA. It is important to state that the fully formed devices were always in the low resistance state during the X-ray measurements. Map (h) from figure 4.4 is shown together with the map taken after this final forming step in figures 4.5(a) and (b), respectively.



Figure 4.6: A 4×5 resistor network for simulations of dielectric breakdown. (a) Shows the layout of the resistor network before the voltage over the network has been increased. (b) The first node has become conducting, and in (c) the triangular conducting network structure is illustrated, although not yet conducting fully (high resistance contact between anode and cathode). The bold lines indicate broken resistors. Adapted from reference [93].

Applying negative bias to the anode, as a last forming step, resulted in a decrease of oxygen vacancies at the cathode interface and an increase at the anode interface, equalizing the intensities at both electrode interfaces. The resistance in the device was further lowered in this last forming step. At this stage the energy dissipated in the device was substantially larger (~ 0.1 W) than in the early forming process. Therefore, it is assumed that the oxygen vacancies quite easily diffuse and re-arrange themselves due to the elevated temperature caused by the dissipated energy.

4.1.1 Forming model

A model describing dielectric breakdown was suggested based on creating a network of conducting filaments induced by the applied electric field [92]. Computer simulations of such networks were performed which showed that the conducting filaments were percolating in a bifurcated structure [93, 94]. The computer simulations were performed by applying voltage on a rectangular network of resistors, as shown in figure 4.6(a). In this resistor model the individual resistances were randomly varied around an average value. The individual resistor-nodes break down and become conducting when the field exceeds a predetermined maximum value over each node. Figure 4.6 shows schematically the results of the initial steps in the computer simulations. Figure 4.6(b), the first node has broken and conducts current; figure 4.6(c) shows the beginning of the triangular network generated by the computer simulations.

This describes qualitatively the data in the initial forming step, highlighted in figure 4.4(b) by



Figure 4.7: An illustration of the model assigned to the forming procedure in the memory devices. (a) The electric field distribution in the initial stage of the forming. (b) As soon as a small region close to the anode has become conducting, the electric field will be concentrated on this small region and induce further filament growth directly from this region. (c) The field generates this percolation of the filaments which widens the network when approaching the cathode. (d) The final bifurcated conducting network, as visible in figure 4.4(b).

the contour. Microscopically such a percolation could arise due to creation of oxygen vacancies at the anode and a drift of these vacancies towards the cathode in the applied field. This model is consistent with earlier publications on DC electrical degradation of $SrTiO_3$ single crystals [95, 96]. A sketch of the introduction of oxygen vacancies is shown in figure 4.7. In figure 4.7(a), the field is applied over the still insulating device. In figure 4.7(b) a small number of oxygen vacancies has been introduced at the anode, making the electric field diverge from this vacancy spot towards the cathode. In figure 4.7(c) and (d) the vacancies percolate towards the cathode in the diverged field, creating a triangular network of conducting vacancies. The triangular structure comes from the fact that the probability is equally big for an oxygen vacancy to percolate in any direction in the electric field. The diverged electric field therefore creates the bifurcated network of vacancies. Figure 4.7(d) then corresponds to an early stage of the device forming (figure 4.4(b)).

As soon as a significant current flows ($\geq 1 \text{ mA}$), figures 4.4(c)-(h), this percolation model no longer applies. At this stage the energy dissipated heats the device. In air, the heating leads to re-oxidation

Tracing oxygen vacancies



Figure 4.8: (a,b) SEM images displaying the bubbles observed beneath the anode. On the right hand of the images, the edge of the anode is shown. (a) Mainly secondary electrons were collected and (b) mainly backscattered electrons were collected. The square in (c) shows the location where the SEM images in (a) and (b) were collected.

of the surface forming it back to an insulating state. In particular after the forming current has been switched off. Then the lowest resistance is beneath the surface, and the conducting network descends in this way deeper into the crystal. At the electrode-to-crystal interfaces the vacancies contact the electrodes, which lie well within the probed X-ray depth. This makes them mainly visible at the electrode interfaces for higher currents (≥ 4 mA). Between figures 4.4(c) and (h) only the magnitude of the oxygen vacancy concentration changes. The increasing oxygen vacancy concentration leads to increased conductivity without a change of the shape of the network. As long as the anode is positively biased, shown in figures 4.4(b)-(h), the network keeps the triangular shape. The base of the triangle manifests itself as the broader spot at the cathode and the top of the triangle as the narrow spot at the anode, figure 4.4(h). Conductivity caused by oxygen vacancies introduced at the anode is suggested in reference [97]. However, contrary to the explanation presented here, the authors of reference [97] suggested that the path was created by piling up the oxygen vacancies starting at the cathode. The structure observed in figure 4.4(b), together with the resistor model [93] strongly suggests that such a pileup at the cathode can only occur after the network has percolated from the anode to the cathode.

In the part of the anode closest to the anode-crystal interface, bubbles were observed on fully formed devices. In figure 4.8(a) and (b), secondary and backscattered electron scanning electron microscopy (SEM) images of this part of the anode are shown. The rectangle in figure 4.8(c) shows schematically where on the memory device the SEM images were collected. Due to the nature of the secondary electrons (mainly low energetic electrons) figure 4.8(a) represents the surface of the Pt anode, with a big number of topological bumps visible on the electrode. The contrast in figure 4.8(b), with mostly backscattered electrons collected, originate from deeper structures in the sample. This contrast comes from different electron density. The darker spots in figure 4.8(b), at the same locations as the topological bumps in figure 4.8(a), are therefore interpreted as stemming from gas-filled bubbles. It is assumed that the gas-bubbles were produced in the electrochemical reaction during the forming. Bubbles beneath the anode have also been observed in reference [92]. The right hand of figures 4.8(a) and (b), at the edge of the anode show strong irregularities. In this region, parts of the anode have been destroyed. Both electrodes show these destroyed regions close to the electrode-crystal interface. This damage is inflicted when higher currents ($\gtrsim 6$ mA) are flowing in the device.

4.1.2 Forming in H_2/Ar

The introduction of oxygen vacancies, together with the bubbles beneath the anode (figure 4.8) indicate that an electrochemical reaction takes place in the device during the forming. To better understand this electrochemical reaction, devices were formed in several different atmospheres. Most ordinary laboratory gases (O₂, N₂, Ar) or vacuum do not lead to forming of the devices. When forming in the same gas as used in the reduction of the samples (H_2/Ar) , as described in section 2.0.2), the devices showed clear changes in the forming behavior. It is expected that the reducing atmosphere enhances the vacancy production by creating water when binding to the oxygen in the devices. As described in chapter 2, the forming in H_2/Ar was done with a lower initial voltage over the device during a shorter time. As for the devices formed in air, the Cr K edge XANES was measured with a micro-focused beam on different locations on the H_2/Ar formed devices. On these devices, two different Cr K edge XANES were found, while the Ti spectrum was unaffected. These two XANES are shown in figure 4.9(a). The reference spectrum was taken on the unformed device and one spectra was taken at the anode-crystal interface. The spectrum measured beneath the anode is shown for comparison, mimicking the reference spectrum closely. In figure 4.9(b) and (c) the reference spectrum subtracted from the anode-interface spectrum and the reference spectrum subtracted from the anode spectrum is shown respectively. The scale is the same as in figure 4.1 for direct comparison. The locations on the sample where these spectra were obtained are visualized in figure 4.9(d). The two difference-spectra, figures 4.9(b) and (c), strongly indicate the presence of oxygen vacancies at the anode-crystal interface and the absence of Cr^{4+} in the area beneath the anode.

In a similar manner as for the air formed devices, the spectrum taken at the anode interface was fitted with a linear combination of the device reference spectrum and the Cr Red-spectrum (figure 3.4(a)). The result of this fit was that $33\pm2\%$ of the reference spectrum and $67\pm2\%$ of the



Figure 4.9: (a) The Cr K edge XANES obtained on the memory device prior to forming (solid line), at the anode-crystal interface of the device fully formed in H₂/Ar (dashed line), and beneath the anode of the device fully formed in H₂/Ar (dash-dotted line). The curve in (b) shows the difference between the anode interface spectrum and the reference spectrum; (c) shows the difference between the anode spectrum and the reference spectrum. (d) Depicts the locations where the spectra in (a) were measured, the reference spectrum was taken 100 μ m to the left of the anode.

reduced single crystal spectrum reproduced the anode interface spectrum. The **R**-factor, as defined in equation 3.1, for this fit was 0.2%. The individual components with the anode interface spectrum are shown in figure 4.10(a) and the resulting fit together with the anode interface spectrum are shown in figure 4.10(b).

To study the distribution of the vacancies during the forming in H₂/Ar, the X-ray energy was set to the value where the difference in figure 4.9(b) is maximal (6004.3 eV) and the device was scanned in the beam to obtain μ -XRF vacancy maps. The absorption from the Pt electrodes was normalized out according to the formula in equation 4.1. The forming steps were the same as for the air-formed device: 100 μ A, 1, 2, 4, 6, 8, 10, and ±10 mA. The distribution of oxygen vacancies in these maps can therefore be directly compared to the maps taken on the air-formed device. The series of maps taken on the H₂/Ar formed device is shown in figures 4.11(a)-(h).

The map taken after forming to a current of 100 μ A in H₂/Ar is shown in figure 4.11(a). In this map only a faint distribution of vacancies can be observed, centered at the cathode interface, showing similarities with the maps taken on the device formed in air (figure 4.4(b)). In the map formed to 1 mA, figure 4.11(b), there is a significant difference compared to the map taken on the air-formed device. In contrast to figure 4.4(c) a large circular shaped vacancy distribution covers



Figure 4.10: The three spectra in (a) were taken on two different samples. The reference was taken on a memory device prior to forming, the reduced was taken on a reduced single crystal sample (same as in figure 3.4(a)), and the anode-interface spectra was taken on a memory device fully formed in H_2/Ar . In (b) the fitted linear combination of the reference spectrum and the reduced single crystal spectrum together with the anode interface spectrum.



Figure 4.11: The distribution of oxygen vacancies in the memory device during the electrical forming in H₂/Ar. Map (a) is taken after a current of 100 μ A was flowing, (b)-(h) after currents of 1, 2, 4, 6, 8, 10, and of ±10 mA were flowing through the device. The concentration is given for the X-ray probed volume.

a large region of the gap between the electrodes. This vacancy distribution was preserved when increasing the current to 2 mA (figure 4.11(c)) with a clear decrease in total intensity, mainly in the center part between the electrodes. In figure 4.11(d) when the current was allowed to reach 4 mA, a significant increase in intensity at the cathode interface is observed. This distribution, with a larger and circular spot at the anode interface and a smaller more triangularly shaped spot at the cathode interface, was preserved throughout the forming. This is observed in figures 4.11(d)-(h), where a contour highlights the main features in figure 4.11(h). The absolute value of the integrated intensity is larger in figure 4.11(b) than in figure 4.11(c), as well as larger in figure 4.11(f) than in figure 4.11(g). The integrated intensity in each map does not increase linearly with the increasing forming current, as for the air formed devices. These fluctuating intensities reflect the fact that the forming in H₂/Ar showed less stability compared to the forming in air.

To explain the maps shown in figure 4.11, the same model as for the air formed devices is initially used. However, in the reducing H₂-enriched atmosphere, as soon as a current is flowing in the device, the hydrogen (and the absence of oxygen) prevents the re-oxidation of the surface layers, leaving the vacancies closer to the surface. With hydrogen, vacancies are more easily created, leading to an abundance of oxygen vacancies in the device. In this scenario, an initial vacancy is introduced at an arbitrary position on the anode. This concentrates the electric field and enforce further vacancies emanating from this initial vacancy. The positive vacancies then diverge from this initial vacancy towards the cathode in the direction of the electric field, in a similar way as described for the air formed devices in section 4.1.1. In figure 4.11(a), a rather undefined distribution of vacancies is observed at the cathode-crystal interface. For higher currents, figures 4.11(b)-(h), a large amount of vacancies is observed between the electrodes, contrary to the devices formed in air. This suggests that the re-oxidation process in air, previously described, is in fact a correct interpretation of the data. The higher intensities on the anode-interface side suggests that the resistivity is higher in this region. For higher current, the majority of the energy is dissipated where the resistance is higher. It can be assumed that the vacancies are introduced in this high resistance region due to the elevated temperatures and higher field strength. Therefore, a speculative conclusion that the oxygen vacancies are introduced at the anode can be drawn.

4.1.3 Discussion of air and H_2/Ar as forming atmospheres

In the previous discussion about the forming model, the suggestion was made that the vacancies re-oxidize on the surface. For this reason it was suggested that figure 4.5(b) represents a conducting cylindrical region of oxygen vacancies. This region can be observed at the electrode interfaces, but it is too deep to probe with X-rays between the electrodes. To gain more insight into the possible



Figure 4.12: (a) Integrated intensities in three regions of interest on the air-formed sample [91]. The regions of interest are outlined in figure 4.4(a). (A) around the anode interface, (P) around the center of the path, and (C) around the cathode interface. The lines are guides to the eyes. (b) The resistivity of the air formed device as measured (circles) during milling between the electrodes with a focused ion beam. Calculated resistivity (solid line) based on the model that the conductivity is confined in a circular path 5 μ m beneath the surface.

scenario of a deeper lying conducting path, the intensities in the μ -XRF maps taken on the device while forming in air was integrated in three regions, outlined in figure 4.4(a). The regions are as follows: One region at the anode interface (A), one region in the center of the path (P), and one region at the cathode interface (C). The integrated intensities for each region are shown in figure 4.12(a). The horizontal scale shows conductance, which corresponds to the forming steps in figure 4.4. For the anode and cathode regions, the intensity is increasing with increasing conductance, while the intensity in the path region is highest for the second step, corresponding to 100 μ A, figure 4.4(b). Beyond this step the intensity is almost constant, slightly increasing for higher conductance. The drop in intensity of the path region after the second step, figure 4.12(a)P, indicates that either the oxygen vacancies migrate away (diffusion) or are removed (re-oxidation) from this area.

In order to prove that the oxygen vacancies were confined deeper in the crystal for higher conductance, a trench was milled between the electrodes on a device fully formed in air. For this purpose, a focused ion beam equipped with a scanning electron microscope (FIB/SEM Zeiss NVision 40) located at Paul Scherrer Institut was used. An approximately 100 μ m wide and 10 μ m broad trench was milled between the electrodes on a device fully formed in air. A current was applied (100 μ A) while the material in this region was slowly milled away. To model the resistivity measurement during the FIB milling, it was assumed that a homogeneously conducting region was confined to a circular path, 5 μ m in diameter 5 μ m beneath the surface of the crystal. The measured resistivity





Figure 4.13: Data showing the size and depth of the trench milled between the electrodes of the memory device formed in air. (a) Line profile, (b) surface profile, and (c) a SEM image of the entire memory cell.

together with the simulated as a function of the depth is shown in figure 4.12(b).

After the FIB milling, the trench was carefully characterized. Figure 4.13 shows the depth, size and position of the trench. Figure 4.13(a) shows a line profile, figure 4.13(b) a contour plot, and figure 4.13(c) a SEM image of the entire memory device after the FIB milling. The model used to calculate the resistivity during the FIB milling is shown schematically in figure 4.14(a)-(c). A cross section of the conducting path with 5 μ m insulating SrTiO₃ above is shown in figure 4.14(a), the ion beam hits the path in figure 4.14(b) and only a thin filament of the conducting path is still visible in figure 4.14(c). In the model the milling speed is constant, which is reflected by the sudden rise in resistivity (inverse area of path) at the end of the milling process (figure 4.12(b)). This is a source of discrepancy between the data and the simulation. In the experiment the milling speed decreases over time since milled material tends to redeposit on the surface. It is also possible that the path has another shape than circular, for example oval-shaped or triangular. Another shape would also explain the discrepancies between the modeled and measured resistance during the FIB milling. Despite the discrepancy between the data and the model, it can be concluded that the oxygen vacancies indeed are confined in a region ~5 μ m beneath the crystal surface.

The conducting region confined as a path is supported by studies on Pt/CuO/Pt devices [98, 99]. In these devices, a $2 \times 30 \ \mu m^2$ path of reduced CuO was detected by SEM and photo-electronemission-microscopy imaging [99]. The path in the Pt/CuO/Pt devices was cut with a focused ion



Figure 4.14: The model used for simulating the resistance data while milling with the focused ion beam between the electrodes on the memory device. (a) Milling the insulating $SrTiO_3$, (b) milling the conducting path, and (c) the majority of the conducting path milled away.

beam, in similar manner to the data presented in figure 4.12(b), which returned the device to the pristine state, confirming a confined spatial distribution of the conducting region.

4.2 Cr valence maps

The Cr K XANES spectrum taken beneath the anode on the device formed in air was the same as the Cr Ox-spectrum, figure 3.4(a), indicating that they represent Cr^{4+} in an octahedral symmetry. A discussion of the behavior of the Cr valence in the forming process is necessary. To monitor the change in chromium valence during the electrical forming, the X-ray energy was set to the value where the difference between the reference and the anode spectra, figure 4.1(c), showed its largest magnitude. At this energy, 6007.3 eV, the sample was spatially scanned in the beam over a 100×150 μ m² large area centered at the gap between the electrodes, generating a "Cr-valence" map. The absorption from the Pt electrodes was normalized according to equation 4.1. A decrease in intensity of the normalized maps indicates the presence of Cr^{4+} , whereas unchanged intensity reflects Cr^{3+} .

The results of these measurements are shown in figures 4.15(a) and (b): (a) was taken in the initial part with voltage applied but no current flowing and (b) was taken after the sample was fully formed (current ± 10 mA and showing resistive switching). The memory state of the device in figure 4.15(b) was in the low resistance. The brighter area represents Cr^{3+} , the darker area corresponds to Cr^{4+} . It is observed that initially the Cr^{4+} region is restricted to the anode¹ with

¹This is the case beneath the entire anode, including the contact pads, see figure 2.3(a).



Figure 4.15: (a) The μ -XRF map taken at 6007.3 eV after voltage has been applied but without current flowing and (b) the μ -XRF map taken at 6007.3 eV on the fully formed sample [56]. In these maps the darker regions represent Cr⁴⁺ and the brighter regions correspond to Cr³⁺. This device was formed in air.

some intensity in a small region around the anode. After the forming, the Cr^{4+} retracts from the area where the oxygen vacancy path connects to the electrode in the conducting state.

In the initial state the formal valence of chromium is homogeneously 3+ throughout the sample. When applying a voltage, at first no current is flowing but the chromium valence changes to 4+ beneath the anode. When a small current is flowing, the valence changes back to Cr^{3+} beneath the part of the anode that has contact with the conducting part of the crystal. Therefore, in the beginning the positively biased anode attracts the negatively charged electrons from the anode-region and may locally polarize the $SrTiO_3$. A higher (1 mA) flowing current leads to a close to zero effective electrical potential which decreases the Cr valence back to its ground state as Cr^{3+} . As the path (in both high and low resistance) was found to be metallic [90], the Cr^{4+} is therefore not likely playing a role in the switching process. The chromium valence change observed previously [90] is probably an initial phenomenon due to the strong electrical potential in the forming process. This strong evidence together with the absent Cr^{4+} signal in the memory devices formed in H_2/Ar proves that the valence change is unimportant for the conductivity and the resistive switching.

Recent EPR measurements performed on similar memory cells of Cr-doped SrTiO₃ proposed that after forming of the devices the oxygen vacancy resided in the third oxygen shell [100]. In that study, the Cr^{3+} EPR signal decreased when the device was formed. The conclusions drawn in reference [100] was that the large change in resistivity had to be caused by structural changes in the bulk and therefore an oxygen vacancy alone could not explain the conductivity. To test the suggested model with a vacancy in the third oxygen vacancy shell, multiple scattering calculations were performed. The atom positions used in these multiple scattering calculations were generated



Figure 4.16: The TiO₂ plane with the $3 \times 3 \times 4$ super-cell (dashed square) used in the DFT calculations for the ground state with an oxygen vacancy in the third O shell. The large dashed circle ($r_{\rm FMS} = 6.8$ Å)shows the cluster where multiple scattering paths were included.

by DFT calculations, as in the case for the spectra shown in chapter 3. The super-cell used in the DFT calculations was for this case chosen to be $3 \times 3 \times 4$ unit cells. In a symmetric super cell, a third shell oxygen vacancy has the same distance on both sides of the tracer-ion. The influence from the third shell oxygen vacancy on the absorber is then equally strong from both sides, yielding a possible net absorber-displacement zero. The displacement of the absorber changes the local surroundings, thereby changing the XANES. Therefore the super-cell was enlarged in the direction of the oxygen vacancy to break this symmetry, as shown in figure 4.16.

A first O shell vacancy in the atom positions used in the multiple scattering calculations agrees well with the measured Cr spectrum, as presented in figure 4.17 as "1st shell" and "Exp" respectively. The third O shell vacancy calculations badly reproduces the measured spectrum, shown in figure 4.17 as "3rd shell" and "Exp" respectively. It is from these results not possible to exclude an additional vacancy in the third shell, because the multiple scattering paths with this distance have little influence on the spectrum. However, it is clear that there indeed is an oxygen vacancy



Figure 4.17: Multiple scattering calculations with the vacancy in the first O shell, and in the third O shell (sixth neighboring shell), compared with the Cr Red-spectrum.

in the first shell. The authors of reference [100] also suggest that the conductivity has to be due to structural changes of the bulk. The increase in resistance with milling of the path, in figure 4.12(b), proves that the conductivity is confined to a defined region in the crystal. The EPR technique lacks the spatial sensitivity to further strengthen this suggestion and is only sensitive to weak deformations of the open 3d shell.

4.3 Interaction between the X-ray beam and the memory device

When forming the devices, a dependence on total forming time and total exposure to X-rays was found. This resulted in deviations in the μ -XRF maps when comparing maps taken on devices heavily exposed to X-rays with maps taken on devices partly or fully formed outside the X-ray measurement chamber. The total time for a typical device to form was ~1.5 hours. The devices used for the X-ray measurements had, in general, several hours between the different forming steps. In the case of air formed devices, this dependence was subtle. μ -XRF vacancy maps taken on devices formed in air outside the X-ray measurement chamber were similar to the map in figure 4.5(b).

For devices formed in H_2/Ar , a high sensitivity to the total forming time and exposure to X-rays was found. This can be deduced from the fluctuating intensities in figures 4.11(a)-(h). The elapsed time (one μ -XRF map takes about one hour) between the different forming steps seems to have



Figure 4.18: The distribution of oxygen vacancies in the device in three steps during the forming in the H_2/Ar atmosphere. (a) The formed device without interruption until a current of 1 mA was flowing, (b) formed to 4 mA, and (c) the final forming step with 10 mA current flowing and the polarity has been switched. Note that (a), (b), and (c) depict different devices. The concentration is given in percent of Cr that have an oxygen vacancy in the probed volume.

decreased the number of oxygen vacancies in the device. For example figure 4.11(c) contains less visible vacancies than figure 4.11(b) and figures 4.11(g) and (h) contain less visible vacancies than figure 4.11(f). Figure 4.18 depicts memory devices formed in H₂/Ar to 1 mA, 4 mA, and ±10 mA without X-ray measurements in the intermediate steps. In this device the vacancies tend to remain on the surface to a much greater extent than in figure 4.11. In the map in figure 4.18(c), the entire path is close to the surface. The reducing character of the H₂/Ar forming atmosphere prevents a possible re-oxidation of the surface. One reason for the partly re-oxidation of the surface, observed in figures 4.11(a)-(h), might be caused by the fact that the H₂/Ar gas was pumped out of the chamber before the μ -XRF map was taken. Since a small bias was held over the device during the measurement, this could have facilitated the re-oxidation observed in figures 4.11(a)-(h), by moving ions with the X-ray beam. Therefore, when keeping the H₂/Ar atmosphere in the chamber and minimizing the elapsed time between the forming steps, no re-oxidation occurs leaving the entire path visible, figure 4.18(c).

The interaction between the memory devices conducting properties and the beam was significant in all cases. When the X-ray beam illuminated the conducting path, the device immediately switched to the low resistance state. This may indicate that the device accumulates charges close to the conducting parts, sustaining a beam-induced electric field that switches the device, or that the drain current induced by the beam switches the device. This behavior was found to be X-ray flux dependent. When reducing the incoming flux, the time it took for the beam to induce a switch to the low resistance state increased. To prevent the device from charging during the synchrotron



Figure 4.19: X-ray induced voltage maps when the device was (a) positively (100 nA) and (b) negatively (-100 nA) biased compared to the forming direction. V_0 represents the voltage applied when the X-ray beam was clearly outside the electrode-crystal interfaces.

measurement, the device was biased at 100 nA. To keep the current constant at 100 nA, a voltage between 0 and 0.5 V was applied. During the measurements this voltage was read out by the software collecting the μ -XRF maps, giving spatially resolved beam induced voltage maps. With the ohmic behavior of the device at these low currents and voltages, these maps represent the spatially resolved resistance of the device. In figure 4.19, two such maps with different bias polarities are shown. In figure 4.19(a) the anode was positively biased, and in figure 4.19(b) negatively biased. These maps were taken on devices fully formed in air.

As shown in figure 4.19(a), higher resistance was found at the anode-crystal interface when the device was biased with the same polarity as during the forming. At the cathode-crystal interface, on the other hand, the resistance was lower. When reversing the polarity, as in figure 4.19(b), the situation reversed, with higher resistance beneath the cathode-crystal interface and lower resistance at the anode-crystal interface. No deviation from V_0 was observed from the undistorted system in the central part of the memory device. This indicates that this part is not accessible with X-rays, while the conducting path is deeper in the crystal, as shown in figure 4.12.

This technique can be used to measure the local resistivity of the devices and may be applied to other systems in which the resistivity varies laterally. The currently generally applied technique to measure local conductivity, by using a conductive tip of an atomic force microscope has much better resolution than is yet possible with X-rays. However, the conducting AFM only measures the top atomic layers, while the X-rays penetrate several microns into the sample. It is also possible to use an electron beam to perform this kind of spatially resolved conductivity studies. For example,



Figure 4.20: The resistive switching taken after the device has been exposed to the synchrotron beam.

the creation and rupture of conducting filaments were studied with an electron beam in resistive switching memory devices [101].

When a device was formed in air and switched between high and low resistance state, the difference resistance between these states was about one order of magnitude (compare 4 k Ω and 600 Ω from figure 2.4(f)). With the device in the beam, and subsequent resistive switching, the difference between the two states was reduced to about a factor of two. In figure 4.20, switching is shown where the high resistance state has decreased to 1000-1200 Ω , and the low resistance state around $600 \ \Omega$. The decrease in resistance difference between the memory states indicates that the exposure to X-rays permanently changes the switching mechanism of the device. The beam induced electric field might be locally stronger than the field used in the forming, which leads to further forming of the device, lowering the high resistance state. As suggested by observing the devices formed in H_2/Ar , figure 4.11(b), the highest resistance is likely at the anode interface. The beam induced field is therefore highest at this interface, locally forming this interface further. The data presented in this dissertation were always collected with the device in the low resistance state, making a discussion of the switching mechanism speculative. Photo-electron-emission-microscopy with a resolution smaller than 80 nm could not find any differences between the high and low resistance state in Pt/CuO/Ptdevices [99]. Assuming a similar mechanism for the resistivity switching in the Pt/CuO/Pt devices as in the here presented devices leads to the conclusion that with a resolution of $3 \times 3 \ \mu m^2$ a difference between the high and low resistance state can not be detected.





Figure 4.21: (a) The k^2 weighted EXAFS function $\chi(k)$ as extracted from the data. (b) The magnitude of the Fourier transform of the data shown in (a). Solid lines represent data taken on the unformed reference and dashed lines show data taken at the cathode-interface.

4.4 Extended X-ray absorption fine structure

In addition to the μ -XRF maps, Cr K edge EXAFS spectra were collected with the micro-focused beam on a device fully formed (±10 mA) in air. The EXAFS spectra were collected on different locations to confirm the suggested presence of oxygen vacancies in the device. Spectra were measured on a reference position far away from the electrodes and at the cathode-crystal interface. Figure 4.21(a) shows the k^2 weighted EXAFS function $\chi(k)$. The solid line shows data taken at the reference position, unaffected by the forming. The dashed line shows data taken at the cathodecrystal interface of a fully formed device. The location at the cathode interface was chosen where the XANES data showed the highest deviation from the unformed reference. This location was chosen where figure 4.5(b) showed highest intensity. The EXAFS spectra in figure 4.21(a) show clear oscillations for the entire displayed k range. Small damping is observed in the spectrum measured at the cathode interface, indicating fewer nearest neighbors. In figure 4.21(b), the magnitude of the Fourier transformed data is shown, with the window function defined for $4 \leq k \leq 9$ Å⁻¹. Both spectra show peaks at the characteristic SrTiO₃ positions, around 1.5 Å and 3.3 Å, confirming the perovskite structure. The damping is here observed as decreased intensity of both peaks, with the oxygen peak slightly shifted when comparing the reference and the cathode-interface spectrum.

FEFF6 calculations of the back-scattering amplitudes and phase factors were based on an undistorted crystal structure of $SrTiO_3$ with lattice parameter 3.95 Å and the absorbing Ti replaced by Cr. The theoretical spectra were fitted in *R*-space to the experimental ones between 1 and 4 Å. All

Tracing oxygen vacancies



Figure 4.22: The magnitude of the Fourier transformed k^2 weighted EXAFS function together with the fitted spectra. (a) The spectrum taken on the unformed device (solid line) together with the fitted spectrum (dashed line). (b) The spectrum taken in the cathode-crystal interface on the fully formed device (solid line) and the fitted spectrum (dashed line).

paths shorter than 4 Å were included in the fit. These include paths (1)-(6) illustrated in figure 3.18 and additionally three multiple scattering paths ($O \rightarrow O$; $O \rightarrow Ni \rightarrow O$; $O \rightarrow Ti \rightarrow O$). The free parameters were: two passive electron reduction factors, S_0^2 and $S_0^2|_{Ti,Sr}$; change in average nearest neighbor distance; ΔR ; shift in energy, ΔE ; two Debye-Waller factors, σ_{Ti}^2 and σ_{Sr}^2 . Initially in the analysis, the Debye-Waller factor σ_O^2 for oxygen was fitted to 0.0038 Å² and kept constant throughout the rest of the analysis. To minimize the number of free parameters, only one ΔR was chosen. Since all distances in the crystal are known, ΔR was expected to be zero within the errors. The resulting fit together with the data are shown in figure 4.22(a) as solid and dashed lines respectively. The fitting parameters are listed in table 4.1.

From the XANES spectra shown in figure 4.1(a), an oxygen in the first shell of Cr was expected in the cathode interface. Since N and S_0^2 are completely correlated in the EXAFS equation, one missing oxygen in the octahedron (N = 5) was used for the interface fit. With these assumptions, the passive electron reduction factors S_0^2 and $S_0^2|_{\text{Ti,Sr}}$ were expected to fit to the same value as for the unformed reference. The same paths and parameters were used as for the fit of the reference spectrum, with the constraint that ΔE was not supposed to change. The resulting fit and data of fully formed SrTiO₃ are shown in figure 4.22(b) as solid and dashed lines respectively. The fitted parameters are presented in table 4.2.

As shown in tables 4.1 and 4.2, both electron reduction factors take the same value in the fits.

Fit parameter	Fitted value
k -range (k^2 -weighted)	$4 \leq k \leq 9 \text{ Å}^{-1}$
R-range fitted	$1.1 \leq R \leq 3.8$ Å
S_0^2	0.92 ± 0.41
$S_0^2 _{ m Ti,Sr}$	4 ± 4
ΔE_0	$-4.6\pm12.0~{\rm eV}$
ΔR	$-0.03\pm0.08~\mathrm{\AA}$
$\sigma_{ m Ti}^2$	$0.005 \pm 0.016~{\rm \AA^2}$
$\sigma_{ m Sr}^2$	$0.02\pm0.02~\mathrm{\AA^2}$
\mathbf{R} -factor	6%

Table 4.1: Fitting parameters obtained for the fit of the Cr K edge EXAFS data obtained on the unformed memory device.

Table 4.2: Fitting parameters obtained for the fit of the Cr K edge EXAFS data obtained in the cathode-crystal interface on the fully formed memory device.

Fit parameter	Fitted value
k -range (k^2 -weighted)	$4 \le k \le 9 \text{ Å}^{-1}$
R-range fitted	$1 \leq R \leq 3.9 \ {\rm \AA}$
S_0^2	0.92 ± 0.15
$S_0^2 _{ m Ti,Sr}$	4.1 ± 1.7
ΔR	$-0.016 \pm 0.013 ~\rm{\AA}$
$\sigma_{ m Ti}^2$	$0.009 \pm 0.007 ~\rm{\AA^2}$
$\sigma^2_{ m Sr}$	$0.020 \pm 0.004 ~\rm{\AA^2}$
\mathbf{R} -factor	2%



Figure 4.23: The areas of interest chosen for the six anode and cathode positions. The device used in these measurements had been formed in H_2/Ar and coated with 1 nm of Pt to prevent the device from charging.

Furthermore, the average change in path length, ΔR , is very close to zero or zero within the errors, indicating that the assumed model is correct. With these results, it is concluded that the general structure around the Cr does not change when introducing an oxygen vacancy. Models including strong structural changes to explain the conductivity in the devices can therefore be ruled out [100].

4.5 Soft X-ray spectroscopy

In order to improve the spatial resolution and possibly map the region where the resistance switch, O K edge and Ti $L_{3,2}$ edges were extracted from series of images made with a photo-electron-emissionmicroscope (PEEM), located at the SIM beamline of the Swiss Light Source. Improved spatial resolution is needed to investigate more realistic devices, since these are in the 200 nm range. The area around the electrode-crystal interfaces, devices as described in chapter 2, was irradiated with monochromatic synchrotron light and the photo-electrons were directed into the microscope with an electric field. To obtain the series of images, the energy was increased in steps over the Ti $L_{3,2}$ and the O K edge. A fixed area of interest was chosen, and the integrated intensity in this region for one energy was then used as one point in the absorption spectra. As explained in chapter 2, the photo-electron yield is directly proportional to the absorption. The areas of interest chosen are shown in figure 4.23. Due to the poor conductivity in the samples, the devices were charged in the electric field from the microscope and had to be covered with a 1 nm Pt layer. Therefore, only fully formed crystals detached from the integrated circuit carrier could be used, preventing any *in situ* measurements.



Figure 4.24: (a) The O K edge spectra taken close to the anode on a device fully formed in H_2/Ar (solid and dashed lines) together with a reference taken further away from the electrodes (dash-dot). (b) The Ti L_3 and L_2 edges taken on the same locations.

In figure 4.24 the spectra extracted around the anode are shown. The differences between the regions are very small and hard to interpret quantitatively as well as qualitatively. The spectra obtained around the cathode, figure 4.25, also show very small differences. The arrow in figure 4.25(a) indicates a region where reports in the literature have claimed to observe transitions to the conduction band [102]. For higher concentrations of oxygen vacancies, it would probably be possible to observe changes both on the Ti L_3 and L_2 edges and the O K edge. For oxygen vacancy concentrations as high as 10% considerable damping of the O K spectrum was found [103]. For even higher concentrations, 25%, the splitting of the two Ti L edges was suppressed [103].

The X-ray energy was also scanned over the Cr L edge to obtain spectra. With the low concentrations of tracer-ions in the devices (0.2% Ti was replaced by Cr), it was impossible to isolate the Cr spectra from the background. The low concentrations of Cr, together with the preclusion of the *in situ* measurements, the PEEM experiments were performed on a test level and no conclusions could be drawn from these measurements.



Figure 4.25: (a) The O K edge spectra taken close to the cathode on a device fully formed in H_2/Ar (solid and dashed lines) together with a reference taken further away from the electrodes (dash-dot). (b) The Ti L_3 and L_2 edges taken on the same locations. The arrow is explained in the text.

Chapter 5

Conclusions

5.1 Oxygen vacancies in SrTiO₃

The results in chapter 3 show that reduction of single crystalline $SrTiO_3$, with 0.2% of Ti replaced with 3d transition metal tracer-ions, introduces oxygen vacancies preferably in the first shell of the tracer-ions. The position of the K edge in the X-ray absorption spectra of these tracer-ions shift towards lower energies and the overall structure of the spectra broadens upon reduction. The Ti K edge spectrum, on the other hand, shows no changes after reduction of the crystals. The changes of the tracer-ion K edge spectra are explained using theoretical spectra calculated by applying a multiple scattering code. The code calculated the tracer-ion K edges with a full nearest neighbor shell and with one oxygen missing in the nearest neighbor shell. The calculated spectra show that when removing an oxygen in the octahedron, the edge shifts and the spectrum broadens in agreement with experiment. This interpretation is further substantiated by DFT calculations, which show the energy required in order to remove an oxygen atom in the crystal is decreased if Ti is substituted by another 3d transition metal. The shift of the spectra occurs for most of the 3d transition metals incorporated as tracer-ions. Since the shift is observed for several different tracer-ions, it may well be applicable for use as an oxygen vacancy localizer in other 3d transition metal oxides.

The presence and influence of oxygen vacancies are important for a range of transition metal oxides (for example see chapter 1). It is possible that this method could be implemented for other systems than $SrTiO_3$. It is logical that when disturbing a system by incorporating tracer-ions, the crystal will be more susceptible to changes in these non-stoichiometric regions. If this is the case, the impact could be substantial in the field of strongly correlated electron physics in transition metal oxides. Moreover, this method has a high versatility when applied to other systems. As shown, it is possible to choose from a range of tracer-ions. Therefore, the tracer-ions can be tailored not to

Conclusions

disturb the studied phenomenon in the parent system. For example, if the parent system shows magnetic characteristics, possibly influenced by oxygen vacancies, a non-magnetic tracer-ion should be chosen.

5.2 Oxygen vacancies in memory devices

In chapter 4, results were presented where the above described tracer-ion technique was used. Given that oxygen vacancies bind to tracer-ions in $SrTiO_3$, resistive switching memory devices of $SrTiO_3$ with Cr as tracer-ions were fabricated. When inducing the switching state, a micro-focused X-ray beam was used and Cr K edge spectra were collected from different locations on the memory devices. It was found that the Cr K edge X-ray absorption spectrum changed with increasing conductivity in the device. Spectra collected between the electrodes showed changes indicative of oxygen vacancies in the first shell of Cr. It was concluded that in the conducting region, 35% of the Cr ions have a nearest neighbor vacancy when the switching state was induced in air. In a reducing atmosphere, as many as 68% of the Cr ions are associated with an oxygen vacancy. The energy of the X-ray was set to the point at which the Cr K X-ray absorption spectrum showed biggest sensitivity to oxygen vacancies. At this energy, the devices were scanned in the beam and spatially resolved oxygen vacancy maps were generated.

These oxygen vacancy maps show how the vacancies form a conducting path while inducing the switching state. A model based on dielectric breakdown explains qualitatively that oxygen vacancies are introduced at the anode and how they percolate in a bifurcated structure towards the cathode. In air, after achieving a bifurcated structure at low currents, the path descends into the material, while the strong electrochemical processes keep the conducting path at the surface whilst under a H_2/Ar atmosphere. Additionally, when comparing air and H_2/Ar it was shown that the valence of the chromium dopant is not crucial for the conductivity of the resistive switching state.

Finally, an interaction between the resistance switching behavior and the X-ray beam was found. This effect can be used to directly map the conductivity of the device laterally in microscopic regions. Unfortunately, the interaction between the beam and the sample was too large to draw any further conclusions on the resistivity in the different regions. This interaction also precluded a successful interpretation of the resistance switching mechanism.

CHAPTER 6

Outlook

To generalize the tracer-ion technique, studying another system and proving the presence of oxygen vacancies is of great interest. This can be combined with a resistive switching study, to test the model here presented. Ideally, a tracer-ion should be chosen such that its fluorescence lines can be excited without exciting the fluorescence lines of the matrix material. There are several materials which fit this description and at the same time show resistive switching, such as Cr in $SrZrO_3$ [20], V in SrZrO₃ [104], or Ti in NiO [105]. To develop a general quantification technique, studying another "guinea pig" system with tracer-ions is useful. Systematically varying the tracer-ion contents and oxygen vacancy content while measuring the tracer-ion X-ray absorption spectrum could yield more insight in how the spectrum changes with different parameters. Comparing to the quantified results here presented, it may be possible to predict under what kind of premises oxygen vacancies are favorable and when another explanation for the observed phenomena has to be sought. To investigate the high resistance state with X-ray absorption, either time resolved measurements or very low incoming intensity can be used. In time resolved measurements, short X-ray pulses accompanied with voltage pulses to restore the high resistance state could generate usable XANES. With lower intensities, the time to acquire one single spectrum would be very large. Experiments on Cr:SrTiO₃ memory devices fabricated for commercial applications $(100 \times 100 \text{ nm}^2)$, to compete with Flash memory) have shown that the resistive switching is not stable enough [106]. Future non-volatile memories will therefore likely not be based on Cr:SrTiO₃. As briefly discussed in the introduction, devices based on NiO have been shown promising [48, 49].

As a concluding remark, I will present an experiment that would confirm the presence of oxygen vacancies in the interface between LaAlO₃ and SrTiO₃ [24]. If there are vacancies close to the interface in the SrTiO₃, these could possibly be detected by the method described in chapter 3. An experiment to detect oxygen vacancies in a thin layer of SrTiO₃ is suggested in figure 6.1. A thin film of SrTiO₃ with Mn as tracer-ions has been grown on the bulk SrTiO₃ substrate, with a film of

Outlook



Figure 6.1: Suggested experiment to detect oxygen vacancies in the conducting interface between $SrTiO_3$ and $LaAlO_3$. The solid lines show incoming X-ray beam under grazing incidence and the dashed line indicates the Mn fluorescence.

 $LaAlO_3$ four unit cells thick grown on top. It is necessary to tune the thickness of the Mn:SrTiO₃ layer to the thickness of the interface, and irradiate the entire sample with X-rays under grazing incidence. The resulting Mn fluorescence is then collected perpendicular to the sample surface.

In this way, possible changes in the Mn spectrum would indicate oxygen vacancies in the thin Mn:SrTiO₃ layer. This could be used to prove the presence or absence of oxygen vacancies. The Mn:SrTiO₃ film would be grown in several thicknesses and on both TiO₂ and SrO terminated SrTiO₃ substrates. By varying the thickness (indicated by x in figure 6.1), a quantitative depth of oxygen vacancies could be determined. When comparing the spectra measured on films grown on differently terminated SrTiO₃ surfaces, the presence or absence of oxygen vacancies could be investigated in a quantitative way. Here Mn is chosen as tracer-ion since its spectrum showed the biggest change with present oxygen vacancies (shown in figure 3.5(a)). These experiments would be quite challenging due to the small concentration of tracer-ions and the very limited thickness of the films, however, with today's instrumentation at synchrotron radiation sources, such as the Swiss Light Source, such an experiment would indeed be feasible.

Bibliography

- [1] C. Kittel Introduction to Solid State Physics John Wiley & Sons, Inc. (1996).
- [2] F. Gebhard The Mott Metal-Insulator Transition Springer (1997).
- [3] J. H. de Boer and E. J. W. Verwey Proc. Phys. Soc. London 49 (1937) 59.
- [4] H. Kajueter, G. Kotliar and G. Moeller Phys. Rev. B 53 (1996) 16214.
- [5] W. S. Baer Phys. Rev. 144 (1966) 734.
- [6] D. B. McWhan, T. M. Rice and P. H. Schmidt Phys. Rev. 177 (1969) 1063.
- [7] M. Imada, A. Fujimori and Y. Tokura Rev. Mod. Phys. 70 (1998) 1039.
- [8] N. Mott Proc. R. Soc. London, Ser. A 382 (1982) 1.
- [9] W. Shockley, J. Bardeen and W. H. Brattain Science 108 (1948) 678.
- [10] G. E. Moore *Electronics* **38** (1965) 114.
- [11] "International Technology Roadmap for Semiconductors, 2008 Update" (Accessed Aug 2009) http://www.itrs.net/Links/2008ITRS/Update/2008_Update.pdf.
- [12] J. G. Bednorz and K. A. Müller Z. Phys. B: Condens. Matter 64 (1986) 189.
- [13] A. Schilling, M. Cantoni, J. Guo and H. Ott Nature 363 (1993) 56.
- [14] T. Murakami and A. Yamaji Am. Ceram. Soc. Bull. 55 (1976) 572.
- [15] M. Fujimoto and W. D. Kingery J. Am. Ceram. Soc. 68 (1985) 169.
- [16] E. N. Bunting, G. R. Shelton, A. S. Creamer and B. Jaffe J. Research NBS 47 (1951) 15.
- [17] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz and K. Samwer Phys. Rev. Lett. 71 (1993) 2331.

- [18] T. W. Hickmott J. Appl. Phys. 33 (1962) 2669.
- [19] J. G. Simmons and R. R. Verderber Proc. R. Soc. London, Ser. A 301 (1967) 77.
- [20] A. Beck, J. G. Bednorz, C. Gerber, C. Rossel and D. Widmer Appl. Phys. Lett. 77 (2000) 139.
- [21] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara and H. Koinuma *Science* **291** (2001) 854.
- [22] J. M. D. Coey, M. Venkatesan and C. B. Fitzgerald Nature Mater. 4 (2005) 173.
- [23] Y. Ohno, D. K. Young, B. Beschoten, F. Matsukura, H. Ohno and D. D. Awschalom Nature 402 (1999) 790.
- [24] A. Ohtomo and H. Y. Hwang Nature 427 (2004) 423.
- [25] G. Herranz, M. Basletić, M. Bibes, C. Carrétéro, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzić, J.-M. Broto, A. Barthélémy and A. Fert Phys. Rev. Lett. 98 (2007) 216803.
- [26] P. R. Willmott, S. A. Pauli, R. Herger, C. M. Schlepütz, D. Martoccia, B. D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca and Y. Yacoby *Phys. Rev. Lett.* **99** (2007) 155502.
- [27] O. N. Tufte and P. W. Chapman Phys. Rev. 155 (1967) 796.
- [28] L. C. Walters and R. E. Grace J. Phys. Chem. Solids 28 (1967) 239.
- [29] C. Cen, S. Thiel, G. Hammerl, C. W. Schneider, K. E. Andersen, C. S. Hellberg, J. Mannhart and J. Levy Nature Mater. 7 (2008) 298.
- [30] G. I. Meijer *Science* **319** (2008) 1625.
- [31] S. S. P. Parkin, C. Kaiser, A. Panchula, P. M. Rice, B. Hughes, M. Samant and S.-H. Yang Nature Mater. 3 (2004) 862.
- [32] M. Wuttig and N. Yamada Nature Mater. 6 (2007) 824.
- [33] M. Quintero, P. Levy, A. G. Leyva and M. J. Rozenberg Phys. Rev. Lett. 98 (2007) 116601.
- [34] Y. B. Nian, J. Strozier, N. J. Wu, X. Chen and A. Ignatiev Phys. Rev. Lett. 98 (2007) 146403.
- [35] X. Chen, N. Wu, J. Strozier and A. Ignatiev Appl. Phys. Lett. 89 (2006) 063507.
- [36] S. H. Chang, J. S. Lee, S. C. Chae, S. B. Lee, C. Liu, B. Kahng, D.-W. Kim and T. W. Noh Phys. Rev. Lett. 102 (2009) 026801.

- [37] K. Szot, W. Speier, G. Bihlmayer and R. Waser Nature Mater. 5 (2006) 312.
- [38] K. M. Kim, B. J. Choi, D. S. Jeong, C. S. Hwang and S. Han Appl. Phys. Lett. 89 (2006) 162912.
- [39] C. Yoshida, K. Kinoshita, T. Yamasaki and Y. Sugiyama Appl. Phys. Lett. 93 (2008) 042106.
- [40] N. Xu, L. Liu, X. Sun, X. Liu, D. Han, Y. Wang, R. Han, J. Kang and B. Yu Appl. Phys. Lett. 92 (2008) 232112.
- [41] I. K. Yoo, B. S. Kang, Y. D. Park, M. J. Lee and Y. Park Appl. Phys. Lett. 92 (2008) 202112.
- [42] P. Zhou, H. B. Lv, M. Yin, L. Tang, Y. L. Song, T. A. Tang, Y. Y. Lin, A. Bao, A. Wu, S. Cai,
 H. Wu, C. Liang and M. H. Chi J. Vac. Sci. Technol. B 26 (2008) 1030.
- [43] I. H. Inoue, S. Yasuda, H. Akinaga and H. Takagi Phys. Rev. B 77 (2008) 035105.
- [44] S. X. Wu, L. M. Xu, X. J. Xing, S. M. Chen, Y. B. Yuan, Y. J. Liu, Y. P. Yu, X. Y. Li and S. W. Li Appl. Phys. Lett. 93 (2008) 043502.
- [45] Y. Watanabe Ferroelectrics **349** (2007) 190.
- [46] R. Waser and M. Aono Nature Mater. 6 (2007) 833.
- [47] A. Sawa Mater. Today 11 (2008) 28.
- [48] I. Baek, M. Lee, S. Seo, M. Lee, D. Seo, D.-S. Suh, J. Park, S. Park, H. Kim, I. Yoo, U.-I. Chung and J. Moon *IEEE IEDM Tech. Dig.* **IEDM 04** (2004) 587.
- [49] I. Baek, D. Kim, M. Lee, H.-J. Kim, E. Yim, M. Lee, J. Lee, S. Ahn, S. Seo, J. Lee, J. Park, Y. Cha, S. Park, H. Kim, I. Yoo, U.-I. Chung, J. Moon and B. Ryu *IEEE IEDM Tech. Dig.* IEDM 05 (2005) 750.
- [50] Y. A. Abramov, V. G. Tsirelson, V. E. Zavodnik, S. A. Ivanov and I. D. Brown Acta Crystallogr., Sect. B: Struct. Sci 51 (1995) 942.
- [51] H. Unoki and T. Sakudo J. Phys. Soc. Jap. 23 (1967) 546.
- [52] K. A. Müller and H. Burkard Phys. Rev. B 19 (1979) 3593.
- [53] J. F. Schooley, W. R. Hosler and M. L. Cohen Phys. Rev. Lett. 12 (1964) 474.
- [54] J. F. Schooley, W. R. Hosler, E. Ambler, J. H. Becker, M. L. Cohen and C. S. Koonce Phys. Rev. Lett. 14 (1965) 305.

- [55] U. Balachandran and N. G. Eror J. Solid State Chem. 39 (1981) 351.
- [56] B. P. Andreasson, M. Janousch, U. Staub, G. I. Meijer and B. Delley Mater. Sci. Eng. B 144 (2007) 60.
- [57] P. Calvani, M. Capizzi, F. Donato, S. Lupi, P. Maselli and D. Peschiaroli Phys. Rev. B 47 (1993) 8917.
- [58] C. Nordling and J. Österman *Physics Handbook* Studentlitteratur (1999).
- [59] D. E. Sayers, E. A. Stern and F. W. Lytle Phys. Rev. Lett. 27 (1971) 1204.
- [60] A. Bianconi, B. A. Bunker, S. P. Cramer, E. D. Crozier, P. J. Durham, S. M. Heald, R. Ingalls, D. C. Koningsberger, R. Prins, J. J. Rehr, D. E. Sayers, E. A. Stern and J. Stöhr X-Ray Absorption – Principles, Applications, Techniques of EXAFS, SEXAFS and XANES John Wiley and Sons (1988).
- [61] J. D. Hanawalt Phys. Rev. 37 (1931) 715.
- [62] L. A. Grunes Phys. Rev. B 27 (1983) 2111.
- [63] H. Modrow, S. Bucher, J. J. Rehr and A. L. Ankudinov Phys. Rev. B 67 (2003) 035123.
- [64] T. Yamamoto X-Ray Spectrom. 37 (2008) 572.
- [65] J. J. Rehr, R. C. Albers and S. I. Zabinsky Phys. Rev. Lett. 69 (1992) 3397.
- [66] A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson Phys. Rev. B 58 (1998) 7565.
- [67] B. Delley J. Chem. Phys. 113 (2000) 7756.
- [68] "FEFF" (Accessed Aug 2009) http://leonardo.phys.washington.edu/feff/Docs/feff/ feff6.ps.
- [69] "Users Guide, FEFF V8.40" (Accessed Aug 2009) http://leonardo.phys.washington.edu/ feff/Docs/feff8/feff84/feff84.pdf.
- [70] J. J. Rehr and R. C. Albers Rev. Mod. Phys 72 (2000) 621.
- [71] J. J. Rehr and R. C. Albers Phys. Rev. B 41 (1990) 8139.
- [72] A. M. Flank, G. Cauchon, P. Lagarde, S. Bac, M. Janousch, R. Wetter, J. M. Dubuisson, M. Idir, F. Langlois, T. Moreno and D. Vantelon Nucl. Instrum. Meth. B 246 (2006) 269.

- [73] M. Lemonnier, O. Collet, C. Depautex, J. M. Esteva and D. Raoux Nucl. Instr. and Meth. 152 (1978) 109.
- [74] P. Kirkpatrick and A. V. Baez J. Opt. Soc. Am. 38 (1948) 766.
- [75] L. Zhang, R. Hustache, O. Hignette, E. Ziegler and A. Freund J. Synchrotron Rad. 5 (1998) 804.
- [76] N. E. Brese and M. O'Keeffe Acta Cryst. B 47 (1991) 192.
- [77] "X-ray Data Booklet" (Accessed Aug 2009) http://xdb.lbl.gov/xdb.pdf.
- [78] K. Blazey, J. Cabrera and K. Müller Solid State Commun. 45 (1983) 903.
- [79] B. P. Andreasson, M. Janousch, U. Staub, T. Todorova, B. Delley, G. I. Meijer and E. Pomjakushina Phys. Rev. B 80 (2009) 212103.
- [80] R. Merkle and J. Maier Phys. Chem. Chem. Phys. 5 (2003) 2297.
- [81] R. L. Wild, E. M. Rockar and J. C. Smith Phys. Rev. B 8 (1973) 3828.
- [82] B. Ravel and M. Newville J. Synchrotron Rad. 12 (2005) 537.
- [83] M. Newville J. Synchrotron Rad. 8 (2001) 322.
- [84] M. Fischer, A. Lahmar, M. Maglione, A. San Miguel, J. P. Itié, A. Polian and F. Baudelet Phys. Rev. B 49 (1994) 12451.
- [85] A. Kodre, I. Arčon, J. P. Gomilšek and B. Zalar AIP Conference Proceedings 882 (2007) 481.
- [86] A. Tkach, P. M. Vilarinho and A. L. Kholkin Acta Mater. 54 (2006) 5385.
- [87] V. V. Laguta, I. V. Kondakova, I. P. Bykov, M. D. Glinchuk, A. Tkach, P. M. Vilarinho and L. Jastrabik Phys. Rev. B 76 (2007) 054104.
- [88] M. E. Zvanut, S. Jeddy, E. Towett, G. M. Janowski, C. Brooks and D. Schlom J. Appl. Phys. 104 (2008) 064122.
- [89] V. V. Shvartsman, S. Bedanta, P. Borisov, W. Kleemann, A. Tkach and P. M. Vilarinho Phys. Rev. Lett. 101 (2008) 165704.
- [90] G. I. Meijer, U. Staub, M. Janousch, S. L. Johnson, B. Delley and T. Neisius Phys. Rev. B 72 (2005) 155102.
- [91] B. P. Andreasson, M. Janousch, U. Staub and G. I. Meijer Appl. Phys. Lett. 94 (2009) 013513.

- [92] G. Dearnaley, D. V. Morgan and A. M. Stoneham J. Non-Cryst. Solids 4 (1970) 593.
- [93] H. Takayasu Phys. Rev. Lett. 54 (1985) 1099.
- [94] J. Boksiner and P. L. Leath Phys. Rev. E 67 (2003) 066610.
- [95] J. Blanc and D. L. Staebler Phys. Rev. B 4 (1971) 3548.
- [96] R. Waser, T. Baiatu and K.-H. Härdtl J. Am. Ceram. Soc. 73 (1990) 1654.
- [97] J. R. Jameson, Y. Fukuzumi, Z. Wang, P. Griffin, K. Tsunoda, G. I. Meijer and Y. Nishi Appl. Phys. Lett. 91 (2007) 112101.
- [98] K. Fujiwara, T. Nemoto, M. J. Rozenberg, Y. Nakamura and H. Takagi Jpn. J. Appl. Phys. 47 (2008) 6266.
- [99] R. Yasuhara, K. Fujiwara, K. Horiba, H. Kumigashira, M. Kotsugi, M. Oshima and H. Takagi Appl. Phys. Lett. 95 (2009) 012110.
- [100] F. La Mattina, J. G. Bednorz, S. F. Alvarado, A. Shengelaya and H. Keller Appl. Phys. Lett. 93 (2008) 022102.
- [101] C. Rossel, G. I. Meijer, D. Bremaud and D. Widmer J. Appl. Phys. 90 (2001) 2892.
- [102] T. Higuchi, T. Tsukamoto, S. Yamaguchi, K. Kobayashi, N. Sata, M. Ishigame and S. Shin Nucl. Instrum. Methods Phys. Res., Sect. B 199 (2003) 255.
- [103] D. A. Muller, N. Nakagawa, A. Ohtomo, J. L. Grazul and H. Y. Hwang Nature 430 (2004) 657.
- [104] C.-C. Lin, B.-C. Tu, C.-C. Lin, C.-H. Lin and T.-Y. Tseng *IEEE Electron Device Lett.* 27 (2006) 725.
- [105] K. Tsunoda, Y. Fukuzumi, J. R. Jameson, Z. Wang, P. B. Griffin and Y. Nishi Appl. Phys. Lett. 90 (2007) 113501.
- [106] G. I. Meijer "Private communication" (Sept 2009) .
Acknowledgments

Att slåss med troll, befria prinsessor och döda varulvar, det är att leva.

A.Strindberg, 1849–1912

Being possibly the most read part of a general dissertation, I will organize the acknowledgments in three parts. In each part, the names will appear in alphabetical order, sorted on the surname or institution name, *not* sorted on importance. In part one, I thank the people who gave their best to make me the physicist I now am. A great deal of thanks go to: Markus Janousch, G. Ingmar Meijer, Urs Staub, and J. Friso van der Veen.

In the second part I thank the people contributing to the material presented in this dissertation. Thanks go to: Rolf Allenspach, J. Georg Bednorz, Camelia Borca, Bernhard Delley, Arantxa Fraile-Rodriguez, Miryam Garcia-Fernandez, Daniel Grolimund, Messaoud Harfouche, Thomas Huthwelker, Fabio la Mattina, Loïc Joly, Siegfried F. Karg, Julijana Krbanjevic, Pierre Lagarde, Philippe Lerch, Maarten Nachtegaal, Mirjam Ochsner, Stephan Pauli, Ekaterina Pomjakushina, Jörg Raabe, Amuthan Ramar, Nicholas Reynolds, Robin Schaeublin, Teodora Todorova, George Tzvetkov, Reto Wetter, Markus Willimann, Philip Willmott, and Christian Zink.

In the third part I thank, more generally, the involved institutions for their extensive support: ETH Zürich, IBM Research – Zurich, Paul Scherrer Institut, and the Swiss Light Source.

This work was performed at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland. Till Strindberg, tack för att du hade tuperat hår.

Research Interests

Non-volatile memory techniques, X-ray Absorption techniques (XANES, EXAFS, and μ -XRF), Insulator-to-metal transitions, Perovskites, Dilutely doped oxide systems

EDUCATION

ETH Zürich, Zürich, Switzerland

Dr. sc. (ETH Zürich), September 2009

- Dissertation Topic: "Oxygen vacancies in SrTiO₃: An X-ray absorption study"
- Advisor: Prof. Dr. J. F. van der Veen

Göteborg University, Gothenburg, Sweden

M.Sc. Physics, January 2006

- Thesis Topic: "Nanofabrication of TiO₂ to increase photoconversion in sensitized solar cells"
- Advisor: Prof. Dr. B. Kasemo

University of Zürich, Switzerland

Selected courses: Astrophysics; German

Naval officer service KA4 Göteborg and Karlskrona naval base, Sweden

Group leader education; rank: Leading rate (Corporal). August 1998 – July 1999

ACADEMIC EXPERIENCE

Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland

$Graduate \ Student$

May 2006 to October 2009

• Includes research for doctoral degree: X-ray Absorption, Resistive Switching

ETH Zürich, Zürich, Switzerland

Teaching Assistant

Winter Semester 2007 to Spring Semester 2009

- Physics II for mechanical engineering students, head teaching assistant.
- Advanced solid state physics, giving and assessment of exercises.
- Physics I for Informatics students, giving and assessment of exercises.
- Physics practical course, guiding and assessment of laboratory work.

Chalmers University of Technology, Gothenburg, Sweden

$Undergraduate \ Researcher$

January 2005 to August 2005

• Includes M.Sc. research: Thin film fabrication and characterization for use in dye-sensitized solar cells.

PUBLICATIONS

- B. P. Andreasson, M. Janousch, U. Staub, T. Todorova, G. I. Meijer, B. Delley, and E. Pomjakushina Detecting oxygen vacancies in SrTiO₃ by 3d transition-metal tracer ions Physical Review B 80, 212103 (2009)
- B. P. Andreasson, M. Janousch, U. Staub, G. I. Meijer, A. Ramar, J. Krbanjevic, and R. Schaeublin Origin of oxygen vacancies in resistive switching memory devices Journal of Physics: Conference Series 190, 012074 (2009)
- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer Spatial distribution of oxygen vacancies in Cr-doped SrTiO₃ during an electric-field-driven insulator-to-metal transition Applied Physics Letters 94, 013513 (2009)
- B. P. Andreasson, M. Janousch , U. Staub, G. I. Meijer, and B. Delley Resistive switching in Crdoped SrTiO₃: An X-ray absorption spectroscopy study Materials Science and Engineering B 144, 60 (2007)
- M. Janousch, G. I. Meijer, U. Staub, B. Delley, S. F. Karg, and B. P. Andreasson Role of Oxygen Vacancies in Cr-Doped SrTiO₃ for Resistance-Change Memory Advanced Materials 19, 2232 (2007)

Oral Presentations

- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer Localizing oxygen vacancies in SrTiO₃ by 3d-impurities 14th International Conference on X-ray Absorption Fine Structure, Camerino, Italy, 26–31.7.2009
- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer In situ defect microscopy during the electric-field-driven insulator-to-metal transition in Cr:SrTiO₃ 13th European Conference on X-Ray Spectrometry, Cavtat, Dubrovnik, Croatia, 16–20.6.2008
- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer Spatial evolution of oxygen vacancies in Cr-doped SrTiO₃ during the insulator-to-metal transition in electric fields Annual Meeting of the Swiss Physical Society, Geneva, Switzerland, 26–27.3.2008
- B.P. Andreasson, M. Janousch, U. Staub, G.I. Meijer, and B.Delley In Situ monitoring of oxygen defects to understand resistive switching in Cr:SrTiO₃ European Materials Research Society 2007 Spring Meeting, Strasbourg, France, 28.5–1.6.2007
- B. P. Andreasson, M. Janousch, U. Staub, G. I. Meijer, and B. Delley In Situ monitoring of oxygen defects to understand resistive switching in Cr:SrTiO₃ Workshop on X-ray absorption spectroscopy and theory of XAS, Villigen, Switzerland, 27.2–2.3.2007

POSTER PRESENTATIONS

- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer In situ defect microscopy during the electric-field-driven insulator-to-metal transition in Cr:SrTiO₃ 9th International Conference on X-ray Microscopy, Zürich, Switzerland, 21–25.07.2008
- B. P. Andreasson, M. Janousch, U. Staub, G. I. Meijer, B. Delley, and S. F. Karg Resolving nonvolatile memory effects in Cr:SrTiO₃ using synchrotron radiation Annual Meeting of the Swiss Physical Society, Zürich, Switzerland, 20–21.2.2007
- B. P. Andreasson, M. Janousch, U. Staub, and G. I. Meijer In situ monitoring of oxygen defects to understand resistive switching in Cr:SrTiO₃ 6th PSI Summer School, Zuoz, Switzerland,18– 25.8.2007

Curriculum vitae

PROFESSIONAL EXPERIENCE

Teliasonera Sweden AB, Gothenburg, Sweden

 $Administrative\ support\ personnel$

Guided the cell phone retailers of Teliasonera AB.

AstraZeneca AB, Södertälje, Sweden

Teacher at summer science school

Organized and held two weeks project based physics and scientific working courses, in collaboration with Södertälje municipality.

Consilium Fire & Gas AB, Gothenburg, Sweden

Fire and gas alarm technician

Manufactured and tested customized security solutions intended for commercial freighters and ferries.

Manpower AB, JEFF Electronics AB, Gothenburg, Sweden

Different minor positions in logistics and electronics production.

Positions of Responsibility

Chairman, treasurer and member of the committee of the west section of Swedish Federation of Young Scientists. *Responsibilities:* arranging weekend activities for up to 80 persons at different locations in Sweden; economic and administrative responsibilities etc.

LANGUAGES

Swedish (first language), English (fluently), German (fluently)

Computer Skills

Scientific software: Mathematica, MATLAB/Femlab, OriginLab Languages: IDL, Python, Perl, Fortran, Unix shell scripts. Applications: LATEX, MS Office, Adobe Creative Suite Operating Systems: OSX, Unix/Linux, Windows.

CONTACT INFORMATION

Email: bpa@starkodder.net Phone: +46768088808 Summer 2005 and 2004

Summer 2004 and 2003