Origin of oxygen vacancies in resistive switching memory devices

B. P. Andreasson¹, M. Janousch¹, U. Staub¹, G. I. Meijer², A. Ramar³, J. Krbanjevic³, and R. Schaeublin¹

¹ Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
² IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
³ École Polytechnique Fédérale de Lausanne (EPFL), Centre de Recherche en Physique des Plasmas, Association Euratom-Confédération Suisse, 5332 Villigen PSI, Switzerland

E-mail: pererik.andreasson@psi.ch

Abstract. The resistive switching state in Cr-doped SrTiO₃ was induced by applying an electric field. This was done in ambient air and in an atmosphere of H₂/Ar. The distribution of the thereby introduced oxygen vacancies was studied by spatially resolved X-ray fluorescence images. It was concluded that the oxygen vacancies were introduced in the interface between the SrTiO₃ and the positively biased electrode.

1. Introduction

The current pursue for a new generation of nonvolatile memories has led to different types of proposed memory techniques [1]. Some of these are, e.g., transition metal oxide based resistive switching memories [2], memories based on magnetic tunnel junctions [3], and chalcogenide glass based phase change memories [4]. For these memory techniques, a very simple capacitor like structure has been proposed. The material is sandwiched between two electrodes which measure the resistivity of the material, i.e., the memory state of the device. The conductivity of the sandwiched material is then switched by voltage pulses [2], magnetic fields [3], or heat [4]. The common advantage with those techniques is that this structure could achieve memories with higher density and faster reading-writing speeds than the current market dominating flash technique.

For the transition metal oxide based memory devices, several explanations for the resistive switching have been proposed in the literature. It is not yet clear if these effects take place in the bulk of the material [5] or in confined regions close to the electrodes [6]. Some of these materials are intrinsically insulating and they have to be exerted to a soft dielectric breakdown before resistive switching occurs. In this dielectric breakdown (hereafter called forming), an electric field is applied to the insulating samples and an insulator-to-metal transition is enforced.

In recent publications, concerning resistive switching, it was stated that oxygen vacancies and their movements were responsible for the change in resistivity in single crystalline SrTiO₃ [7]. In our previous work, the distribution of oxygen vacancies during the forming in ambient air was studied in Cr-doped SrTiO₃ [8]. It was stated, based on the observed distribution of vacancies

4 Present address: Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
and on a model for dielectric breakdown [9], that the oxygen vacancies were introduced at the positively biased electrode (hereafter anode) and percolated in a bifurcated structure towards the grounded electrode (hereafter cathode). In this paper, the difference between forming in air and in a highly reducing atmosphere is presented. The presented spatially resolved X-ray absorption near edge spectroscopy (µXANES) measurements together with the spatially resolved X-ray fluorescence (µXRF) maps elucidate the origin of the oxygen vacancies. Additionally, a focussed ion beam was used to gradually mill away material from a memory device which proved the spatial confinement of the conducting region.

2. Experimental
Single crystals of 0.2 mol% Cr-doped SrTiO$_3$, grown by floating-zone melting in a synthetic air atmosphere were used [10]. Platinum electrodes were patterned along the [010] axis on the polished [001] surface of the crystals. The electrodes measured 400 $\times$ 50 $\mu$m$^2$, were 100 nm thick and separated by a 50 $\mu$m gap. The electrical forming process was carried out in seven steps.

(1) A field of 80 kV/cm was applied until a current of 100 $\mu$A was reached, (2) 60 kV/cm until the current increased to 1 mA and (3)-(7) 40 kV/cm until currents of 2, 4, 6, 8, 10 mA were flowing. The forming in 1 bar H$_2$/Ar (2%/98%) was done at an electrical field of 40 kV/cm throughout the forming. In a final step the polarity was switched and the voltage was increased until a current of -10 mA was measured. After this forming, the device showed hysteresis in the I-V characteristics, indicating bistable resistance. The current was limited to a magnitude of 10 mA, and the voltage needed to switch the resistivity was approximately ±10 V. The time it took for the device to reach 100 $\mu$A was in general between three and five times shorter when the device was formed in H$_2$/Ar as compared to air. To examine the depth dependence of the conductivity in the device, a Focussed Ion Beam (FIB)/Scanning Electron Microscope (SEM) Zeiss NVision 40 located at the Paul Scherrer Institut, was used.

The µXANES and µXRF experiments were performed at the LUCIA beamline [11] of the Swiss Light Source at the Paul Scherrer Institut. The size of the X-ray beam on the sample was 4$\times$3 $\mu$m$^2$, and the probing depth 4 $\mu$m at an energy of $\sim$6000 eV. The sample made a 45$^\circ$ angle with the incoming beam, and the fluorescent X-rays were measured almost perpendicular to the beam. The fluorescence yield of the Cr Kα line and Ti Kα line was collected with a silicon drift detector. To enhance the Cr-to-Ti-fluorescence intensity ratio, approximately 0.5 mm of Teflon was placed in front of the detector. The X-ray energy was held constant and the sample was scanned in steps of 4 $\mu$m in the beam giving spatially resolved µXRF Cr and Ti maps. The scanning was centered between the electrodes over an area of 60$\times$96 $\mu$m$^2$ for the samples formed in air. The forming in H$_2$/Ar affected a bigger area than the forming in air, therefore these devices were scanned over an area of 120$\times$120 $\mu$m$^2$ in the plane of the sample. To prevent charging during the X-ray measurements one electrode was connected to ground and the other was positively biased. To normalize out the absorption from the Pt electrodes, the Cr raw µXRF maps were divided by the Ti maps, which were unaltered throughout the forming.

3. Results
The Cr K-edge µXANES measured on the device prior to the forming (R) and close to the anode-crystal interface (AI) on a device fully formed in H$_2$/Ar are seen in Fig. 1(a). Prior to the forming, the Cr K-edge µXANES showed no deviations when measured on different positions on the device. After forming, spectra taken close to the electrodes deviated from the reference spectrum. In general, more intensity was found in the pre-edge region, and the features on the edge were a bit less pronounced. The biggest difference, compared to before forming, was found close to the electrode-crystal interfaces. This was the case for devices formed in air, as well as for devices formed in H$_2$/Ar, exemplified in Fig. 1(a). The reference spectrum shows Cr$^{3+}$ in an octahedral configuration [10]. The enhancement of absorption in the pre-edge region for
Figure 1. (a) The Cr K-edge \( \mu \)XANES taken on the intrinsic device at a reference position (R) roughly 200 \( \mu m \) away from the electrodes. The \( \mu \)XANES measured in the anode interface (AI) on the device fully formed in H\(_2\)/Ar, inset shows the locations where the two spectra were obtained. (b) The difference between the two spectra seen in (a). The energy of the X-ray beam used in the \( \mu \)XRF maps (6004 eV) is marked with an arrow.

Figure 2. \( \mu \)XRF maps showing the distribution of oxygen vacancies in the memory device during the electrical forming. Both maps taken after forming in air and in H\(_2\)/Ar are shown: (a)-(d) were taken after forming in air, while (e)-(h) were taken after forming in H\(_2\)/Ar. Maps (a) and (e) were taken after a current of 100 \( \mu A \) was reached, (b) and (f) after currents of 1 mA were flowing, (c) and (g) after 4 mA, finally (d) and (h) were taken after the polarity had been switched, so that \( \pm 10 \) mA were flowing in the device. The color scale is relative, the max value is different for devices formed in air and in H\(_2\)/Ar. The contours seen in (a) and (h) are at half the intensity of respective map. The electrodes which were used as positively biased anode (A) and grounded cathode (C) during the forming are marked in (h).

The spectrum taken at the anode-crystal interface is due to oxygen vacancies in the first shell surrounding Cr [12]. In Fig. 1(b) the difference between the two spectra in (a) is seen. At the energy, where this difference showed the largest magnitude, \( \approx 6004 \) eV, detailed \( \mu \)XRF maps were taken. Since the difference is attributed to the introduction of an oxygen vacancy, maps taken at this energy show the distribution of oxygen vacancies in the devices.

A comparison between the distribution of oxygen vacancies during the forming in air and during the forming in H\(_2\)/Ar is seen in Figs. 2(a)-(h). The color scale in the figure is relative, the highest intensity seen in (d) is approximately half of the maximum intensity in (h). When compared to an extremely reduced reference, it is assumed that the maximum seen in (h) means
that approximately 60% of the octahedrons surrounding Cr have a missing oxygen ion. In Fig. 2(a), taken after a current of 100 µA was reached when forming in air, the map is dominated by the vacancies seen at the cathode. It can be observed that the distribution is triangular, with a narrow part on the anode and a broader part on the cathode interface, which is highlighted by a contour at half the intensity. Throughout the remaining forming in air, Figs. 2(b) and (c), this triangular distribution is preserved, with a smaller vacancy spot at the anode and a broader, more intense, at the cathode. At the end of the forming in air, Fig. 2(d), two equally intense and equally shaped vacancy concentrations are seen at the cathode and the anode. This difference arising with the polarity switch indicates that the oxygen vacancies move away from the less conducting path and equal out possible conductivity gradients in the dc-formed device. An important difference between the maps in Figs. 2(a) and (b) is that the intensity in the middle of the device is actually decreasing. Indicating that the vacancies leave this region when the forming current is increased by one order of magnitude, possibly descending deeper into the material and out of reach of the X-rays. This could suggest that the vacancies, together with the conductivity, would be laterally confined in a path beneath the surface, only in contact with the surface in the vicinity of the electrodes.

The map taken after forming to a current of 100 µA in H₂/Ar is seen in Fig. 2(e). In this map only a faint distribution of vacancies can be seen, centered at the cathode interface. In the map formed to 1 mA, Fig. 2(f), there is a significant difference seen between the in air and in H₂/Ar formed maps. In contrast to both Fig. 2(b) and Fig. 2(e), a large circular shaped vacancy distribution can be seen covering almost the entire gap between the electrodes, although clearly centered in the anode interface region. When forming in H₂/Ar to 4 mA, Fig. 2(g), the large vacancy spot is still seen at the anode, together with a smaller, less intense vacancy spot at the cathode. Here, in contrast to the case of devices formed in air, the vacancy intensity in the region between the electrodes is constantly increasing with increasing forming currents.

**Figure 3.** The measured resistivity of a device fully formed in air while milling away material between the electrodes (circles). The calculated resistivity (solid line) for a simulated milling experiment, when assuming a circular path of a diameter as long as the distance between the path and the surface. The arrows indicate respective scale.

To test if the oxygen vacancies are confined beneath the surface when the device was formed in air, the FIB was used to mill away material in the area between the electrodes on a fully formed device (±10 mA, corresponding to Fig.2(d)). Fig. 3 shows the resistivity in the device (circles) as a function of milling time, together with a simulation of the data (solid line). An approximately 75 µm wide and 10 µm broad trench was milled between the electrodes on a fully formed device, as sketched in the inset of Fig. 3. A bias current of 100 µA was held constant while the material in this region was slowly milled away. Initially the resistance was 600 Ω in the device, the milling then continued until the resistance was out of the tolerance range of...
the equipment, roughly in the order of 1 GΩ. The depth of the trench between the electrodes
of the nonconducting device was measured to be 10 µm after milling. To model the data, it
was assumed that the conducting region was confined in a circular path, 5 µm in diameter 5
µm beneath the surface of the crystal. In the model the milling speed is constant, which is
reflected in the sudden rise in resistivity (inverse area of path) at the end of the data set. In
the actual experiment the milling speed is decreasing since milled material tend to redeposit
on the surface. This together with the fact that the path probably not has a perfect circular shape
might explain the discrepancy between the data and the simulation.

4. Discussion
A model for the forming process was proposed based on the creation of a network of conducting
filaments by the applied electric field [9; 13; 14]. The model predicts a bifurcated structure
starting on the initial filament and broadens towards the other side. This model describes our
data in the initial forming step, seen in Fig. 2(a) and (e). Microscopically such a percolation
could arise by the creation of oxygen vacancies at the anode and a drift of these vacancies
towards the cathode in the applied field, creating a triangular network as highlighted by the
contour line in Fig. 2(a). This model is consistent with earlier publications on electrocoloration
and dc electrical degradation of SrTiO₃ single crystals [15; 16]. For the same step, when forming
in H₂/Ar, not such a clear structure is seen. This is explained by two main reasons, the lower
electric field and the reducing atmosphere. When the electric field in the crystal is lowered,
vacancies will be exerted to a smaller force, making them move more slowly through the crystal.
When the current in the device increases (still lower than 100 µA) more heat will be dissipated in
the device. The heating and the presence of air will oxidize parts of the material, thereby working
against the forming. In H₂/Ar on the other hand, the elevated temperature with the reducing
atmosphere will enhance the forming, leading to a shorter time for the device to accumulate
oxygen vacancies. There are approximately 10% more oxygen vacancies per area depicted in
Fig. 2(a) compared to (e).

As soon as a higher current flows (≥1 mA), Figs. 2(b)-(c) and (f)-(g), this percolation model
no longer applies, since the field in the conducting part at this level is very small. At this
stage the power dissipated will substantially heat the device. In air, this heating will lead to
re-oxidation of the surface. Then the lowest resistance will be beneath the surface, and the
conducting network will in this way descend deeper into the crystal, as seen when comparing
Figs. 2(a) and (b). In the electrode-to-crystal interfaces the vacancies will contact the electrodes,
making them mainly visible here. This was also probed directly with the FIB milling, as can be
seen in Fig. 3. For the device formed in the reducing H₂/Ar atmosphere no re-oxidation
can occur leaving the vacancies at the surface. The lower field and the supposedly increased
vacancy production rate, will leave a great deal of the vacancies close to the area where they
were originally introduced. This can be seen in Fig. 2(f), where the majority of the vacancies are
close to the anode. This strongly suggests that the vacancies are introduced at the anode-crystal
interface. When the current is increased, more and more vacancies will be created, and in the
H₂/Ar atmosphere not being re-oxidated, forming a path closer to the surface.

If the vacancies are produced at the anode interface, this region should dominate the power
dissipated in the device. If this is the case, the highest resistance should be over the anode
interface. That indeed the highest resistance is found over the anode interface has been
reported [12; 17].

5. Conclusion
In summary the presented X-ray fluorescence maps show oxygen vacancies in the Cr-doped
SrTiO₃ memory cells and how they form the conducting path when formed in air and H₂/Ar. A
model based on dielectric breakdown explains that oxygen vacancies are likely to be introduced
at the anode and how they percolate in a bifurcated structure towards the cathode. For the air-formed sample, after achieving a bifurcated structure at low currents, the path descents into the material, while the strong electrochemical processes keep the conducting path at the surface for the H$_2$/Ar-formed devices. The distribution of vacancies in the H$_2$/Ar-formed devices presents strong evidence that the vacancies are introduced in the crystal in the anode-crystal interface throughout the forming.

We thank S. F. Karg, J. G. Bednorz, and R. Allenspach for discussions; C. Zink and M. Ochsner for the profilometer measurements; R. Wetter for technical support. This work was performed at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland.

References
[1] Meijer G I 2008 Science 319 1625
[2] Waser R and Aono M 2007 Nature Mater. 6 833
[3] Parkin S S P, Kaiser C, Panchula A, Rice P M, Hughes B, Samant M and Yang S H 2004 Nature Mater. 3 862
[4] Wuttig M and Yamada N 2007 Nature Mater. 6 824
[5] Rozenberg M J, Inoue I H and Sanchez M J 2004 Phys. Rev. Lett. 92 178302
[6] Oka T and Nagosa N 2005 Phys. Rev. Lett. 95 266403
[7] Szot K, Speier W, Bihlmayer G and Waser R 2006 Nature Mater. 5 312–320
[8] Andreasson B P, Janousch M, Staub U and Meijer G I 2009 Appl. Phys. Lett. 94 013513
[9] Takayasu H 1985 Phys. Rev. Lett. 54 1099
[10] Meijer G I, Staub U, Janousch M, Johnson S L, Delley B and Neisius T 2005 Phys. Rev. B 72 155102
[11] Flank A M, Cauchon G, Lagarde P, Bac S, Janousch M, Wetter R, Dubuisson J M, Idir M, Langlois F, Moreno T and Vantelon D 2006 Nucl. Instrum. Meth. B 246 269–274
[12] Janousch M, Meijer G I, Staub U, Delley B, Karg S F and Andreasson B P 2007 Adv. Mater. 19 2232
[13] Dearnaley G, Morgan D V and Stoneham A M 1970 J. Non-Cryst. Solids 4 593
[14] Boksiner J and Leath P L 2003 Phys. Rev. E 67 066610
[15] Blanc J and Staebler D L 1971 Phys. Rev. B 4 3548–3557
[16] Waser R, Baiatu T and Härldt K H 1990 J. Am. Ceram. Soc. 73 1654–1662
[17] Odagawa A, Katoh Y, Kanzawa Y, Wei Z, Mikawa T, Muraoka S and Takagi T 2007 Appl. Phys. Lett. 91 133503