Spatial distribution of oxygen vacancies in Cr-doped SrTiO₃ during an electric-field-driven insulator-to-metal transition

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Spatially resolved x-ray fluorescence maps are presented that show the introduction and the evolution of oxygen vacancies in chromium-doped strontium titanate during an electric-field-driven insulator-to-metal transition. The vacancies are introduced at the anode and diffuse through the crystal toward the cathode. The spatial distribution of vacancies is explained by a model describing the electrical breakdown as a percolation process. Strong differences in the vacancy distribution were found when the transition took place in air and in a hydrogen-enriched atmosphere. In air, the vacancies disappeared from the surface, whereas in the reducing hydrogen atmosphere, they remained at the surface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3069140]

Traditional nonvolatile memory devices consist of so-called flash memory cells, where the information is stored as charge on a floating gate. Currently, alternative memory devices are under intense investigation.¹ Some of these are resistance-change memory based on transition-metal oxides,² magnetic random-access memory,³ and phase-change memory.⁴

Transition-metal based resistance-change memory devices have two (or more) stable resistance states. The resistance state of the memory device is set by a voltage pulse. Resistance-change effects have been observed for various transition-metal oxides, e.g., perovskite such as SrTiO₃ (Refs. 5 and 6) and Pr_{0.7}Ca_{0.3}MnO₃,⁷ and binary oxides such as NiO (Ref. 8) and TiO₂.⁹ SrTiO₃, TiO₂, and NiO are intrinsically insulating and a transition to a conducting state, called electrical forming hereafter, is necessary to achieve resistance switching. Proposed microscopic origins for the resistance switching include (i) interface effects, e.g., Mott metal-insulator transition at the interface,¹⁰ and (ii) bulk effects, e.g., phase separation of nonpercolative metallic domains.¹¹ The role of oxygen vacancies in resistance switching of transition metal oxides has recently been proposed by several groups.^{12–14} Using micro-x-ray absorption near edge spectroscopy (μ XANES) and micro-x-ray fluorescence (μ XRF) mapping, the importance of oxygen vacancies in the resistive switching of Cr-doped SrTiO₃ was demonstrated.¹⁵

In this letter we present the results on x-ray absorption experiments to investigate the electrical forming process of Cr-doped SrTiO₃ memory devices in ambient air and in a H₂/Ar gas mixture. These experiments show that oxygen vacancies are introduced and how the distribution of oxygen vacancies evolves during the formation of the conducting state in these gases.

Single crystals of 0.2 mol % Cr-doped SrTiO₃ grown by floating-zone melting in a N₂/O₂ atmosphere were used.¹⁶ Platinum electrodes were patterned along the [010] axis on the polished [001] surface of the crystals. The electrodes measured 400×50 μ m² were 100 nm thick and separated by a 50 μ m gap. Initially the crystals were insulating with a

resistivity larger than 100 G Ω cm. The electrical forming process was carried out in the following seven steps. (1) A field of 80 kV/cm was applied until a current of 100 μ 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, and 10 mA were flowing. The forming in 1 bar H₂/Ar (2%/98%) was done at an electrical field of 40 kV/cm throughout the forming.

The x-ray absorption and fluorescence measurements at the Cr *K*-edge were performed at the LUCIA beamline of the Swiss Light Source at the Paul Scherrer Institut. The size of the x-ray beam on the sample was 4×3 μ m² and the probing depth was 4 μ m at an energy of ~6000 eV. The fluorescence yields of the Cr *K_α* line and Ti *K_{α,β}* lines were collected with a silicon drift detector. Approximately 1 mm of Teflon was placed in front of the detector to enhance the Cr-to-Ti-fluorescence intensity ratio. The sample was scanned in the beam over an area of 60×96 μ m², giving spatially resolved μ XRF Cr and Ti maps. To prevent charging during the x-ray measurements one electrode was connected to ground and the other was positively biased. The Cr fluorescence was normalized by the Ti fluorescence.

Cr *K*-edge μ XANES spectra of Cr-doped SrTiO₃ taken on three different locations on memory devices formed ($\pm$ 10 mA) in air and in H₂/Ar are shown in Fig. 1. The reference (R) shows the characteristic shape of Cr³⁺ in an octahedral oxygen configuration.¹⁶ In Fig. 1(a), for the air formed sample, the Cr *K*-edge underneath the anode (A) shows a shift toward higher energies indicating that the valence of the Cr has increased to about 4+. ¹⁶ The sample formed in H₂/Ar does not exhibit this increase in valence beneath the anode; Cr remains in its 3+ state. This proves that the valence change from Cr³⁺ to Cr⁴⁺ is not crucial for the forming process.¹⁷ Figure 1(b) shows the spectra, taken on air- and H₂/Ar-formed devices, obtained at the anode-to-crystal interface. Both show an increased intensity in the pre-edge region. This increase is indicative of the presence of oxygen vacancies in the octahedron surrounding the Cr atom.¹⁵ Based on the procedure outlined in Ref. 15 we estimate that for the air-formed device about 30% of the oxygen octahedrons surrounding Cr atoms in the interface region have a missing oxygen atom. For the device formed in H₂/Ar,

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FIG. 1. Cr K -edge μ XANES spectra on the Cr-doped SrTiO_3 memory device. (a) The Cr K -edge underneath the anode (A) taken after forming (± 10 mA) in air and H_2/Ar . (b) The Cr K -edge at the anode-to-crystal interface (AI) taken after forming in air and H_2/Ar . The reference position (R) is approximately $200\ \mu\text{m}$ away from the electrodes. The insets show schematically the positions where the spectra were collected.

which has a considerably higher intensity in the pre-edge region, approximately 60% oxygen vacancies are present. This increase indicates that there is a higher production rate of oxygen vacancies due to increased electrochemical activity in the H_2 -enriched atmosphere.

The μ XRF maps were taken at a constant x-ray energy of 6004.3 eV, which is a few eV below the main absorption edge, where higher intensity is indicative of oxygen vacancies. μ XRF maps of air- and H_2/Ar -formed memory devices are depicted in Fig. 2. In the map of the air-formed device, Fig. 2(a), the highest vacancy concentration is around the crystal-to-electrode interfaces. In contrast, the vacancy distribution in the device formed in H_2/Ar , Fig. 2(b), is fairly constant between the two electrodes. This shows that the vacancies are located at the crystal surface, whereas for memory devices formed in air, the oxygen vacancies are beneath the surface.

Figure 3 displays the μ XRF maps taken after each of the seven steps during the electrical forming in air. The pristine device is shown in Fig. 3(a). After forming the memory cell to 100 μA [Fig. 3(b)] the oxygen vacancies are distributed in a triangular shape between the electrodes with higher intensity close to the cathode and a gradual decrease toward the anode. After continuing the electrical forming to 2 mA the distribution of vacancies centers more around the cathode interface, Figs. 3(c) and 3(d). In Figs. 3(e)–3(h), the oxygen vacancies also become clearly visible at the anode interface. When the sample is fully formed [Fig. 3(h)] there is one circular vacancy-concentration spot at the anode interface and one more ellipse shaped at the cathode interface.

To characterize the behavior of the oxygen vacancies during the forming process, we integrated the intensity in

FIG. 2. (Color online) μ XRF maps at an x-ray energy of 6004.3 eV showing the distribution of the oxygen vacancies in the oxygen octahedrons surrounding Cr for fully formed devices (± 10 mA) in (a) air and (b) H_2/Ar .

FIG. 3. (Color online) μ XRF maps at an x-ray energy of 6004.3 eV showing the distribution of the oxygen vacancies in octahedrons surrounding Cr atoms. Taken in seven steps during the forming in air, (a) prior to forming, and (b)–(h) taken after the device was formed to 100 μA , 1 mA, 2 mA, 4 mA, 6 mA, 8 mA, and 10 mA, respectively. A, P, and C depict integration regions used to characterize the behavior of the oxygen vacancies.

Fig. 3 in three following regions: A is the anode-to-crystal interface; C is the cathode-to-crystal interface; and P is the region between A and C. The resulting integrated intensities are shown in Fig. 4 for increasing conductance. For the electrode-to-crystal interfaces (A,C), the intensity is generally increasing with increasing conductance. The intensity in the center of the device (P) is highest in the second point, corresponding to Fig. 3(b), and decreases with increasing conductance. This indicates that the vacancies are rearranging in the crystal during the electrical forming process.

A model for the forming was proposed based on the creation of a network of conducting filaments by the applied electric field.^{18–20} The model predicts a bifurcated structure starting on the initial filament and broadens toward the other side, independent of the used parameters. This model describes qualitatively our data in the initial forming step, as seen in Fig. 3(b). Microscopically such a percolation could arise due to creation of oxygen vacancies at the anode and a drift in these vacancies toward the cathode in the applied field, creating a triangular network as highlighted by the contour line. This model is consistent with earlier publications on electrocoloration and dc electrical degradation of SrTiO_3 single crystals.^{21,22}

As soon as a higher current flows (≥ 1 mA), Figs. 3(c)–3(h), this percolation model no longer applies. At this stage the power dissipated will heat the device. In air, this heating will lead to reoxidation of the surface. Then the low-

FIG. 4. Integrated intensities in three regions of interest, as marked in Fig. 3(a), of the air-formed sample: (A) around the anode interface, (P) around the center of the path, and (C) around the cathode interface.

est resistance will be beneath the surface, and the conducting network will in this way descend deeper into the crystal. For the device formed in the reducing H_2/Ar atmosphere no re-oxidation can occur and vacancies remain at the surface, as seen in Fig. 2(b). In the electrode-to-crystal interfaces the vacancies will contact the electrodes, making them mainly visible here for higher currents (≥ 4 mA). Between Figs. 3(c) and 3(h) only the magnitude of the oxygen vacancy concentration changes. The increasing oxygen vacancy concentration leads to increased conductivity without a change in the shape of the network. A focused ion beam (FIB) was used to mill a trench in the Cr-doped SrTiO_3 between the electrodes. This FIB experiment demonstrated that in the device the current indeed flows beneath the surface (between about 5 and 10 μm beneath the surface).

In summary the presented x-ray fluorescence maps show oxygen vacancies in the Cr-doped SrTiO_3 memory cells and how they form the conducting path. A model based on dielectric breakdown explains qualitatively that oxygen vacancies are introduced at the anode and how they percolate in a bifurcated structure toward the cathode. For the air-formed sample, 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 for the H_2/Ar -formed devices. The valence of the chromium dopant is, when comparing samples formed in air and hydrogen, considered not to be crucial for the electrical forming process.

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