

Changes in the surface topography and electronic structure of SrTiO₃ (1 1 0) single crystals heated under oxidizing and reducing conditions

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Abstract

Strontium titanate (SrTiO₃) is a promising material for resistive high temperature oxygen sensors. Unfortunately, thermal treatment results in undesirable surface reconstruction and the formation of secondary phases. Each of the three stable surface orientations ((1 0 0), (1 1 0) and (1 1 1)) shows a characteristic reconstruction of the topmost layers. To investigate these changes in more detail, SrTiO₃(1 1 0) single crystals were heated up to 1000 °C in ultrahigh vacuum and synthetic air, respectively. Atomic force microscopy (AFM) was applied to characterize the surface topography. Metastable impact electron spectroscopy (MIES) and Auger electron spectroscopy (AES) yielded information on the electronic structure and the chemical composition of the surface and the near surface region. Under all investigated conditions microfaceting of the (1 1 0) surface could be observed resulting in TiO₂-terminated ridges.

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1. Introduction

Perovskites like SrTiO₃ are of great practical concern as fast resistive oxygen sensors, materials for modern electronic devices or as substrates in thin film technology since their electrical proper-

ties vary from insulating to n- or p-type semiconducting and even metallic-like behaviour. SrTiO₃ does not exhibit a domain structure which influences the topography of the surface. It is paraelectric and maintains the perovskite crystal structure over a wide temperature range. Under certain conditions insulating islands are formed on top of the SrTiO₃ surface. Their number and size strongly depend on the heating process as well as on the nature and the concentration of the dopants. In addition, the reconstructions of the topmost surface layers strongly depend on the crystal

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orientation. The surface and the region below strongly influence the macroscopic properties of SrTiO_3 , such as the electrical conductivity [1] or dielectric behaviour at elevated temperatures [2]. It is well known that the surface region behaves drastically different as compared to the bulk of the crystal. The phenomena related to the surface region are of special relevance for technological applications. We investigated the microfaceting of the (110) surface and the formation of secondary phases under both oxidizing and reducing conditions in order to compare the changes on the surface depending on the preparation conditions. While there is an increasing number of studies on $\text{SrTiO}_3(100)$, there are only a few detailed reports

about the topographic and electronic structure of the $\text{SrTiO}_3(110)$ surface.

The ideal $\text{SrTiO}_3(110)$ surface consists of alternating positively charged SrTiO and negatively charged O_2 layers. Previous reports published a model for the ideal microfaceted $\text{SrTiO}_3(110)$ surface [3,4] shown in Fig. 1. Fig. 1a displays the pure, clean SrTiO surface before thermal treatment. The slightly reduced surface is shown in Fig. 1b; parallel roof-like structures can be seen with distances of 5.5 Å. Finally the completely microfaceted surface is illustrated in Fig. 1c with ridge distances of 11 Å. These values match the single and double spacing of the underlying SrTiO_3 lattice along $[\bar{1}10]$ ($\sqrt{2}d^2$ with $d = 3.905$

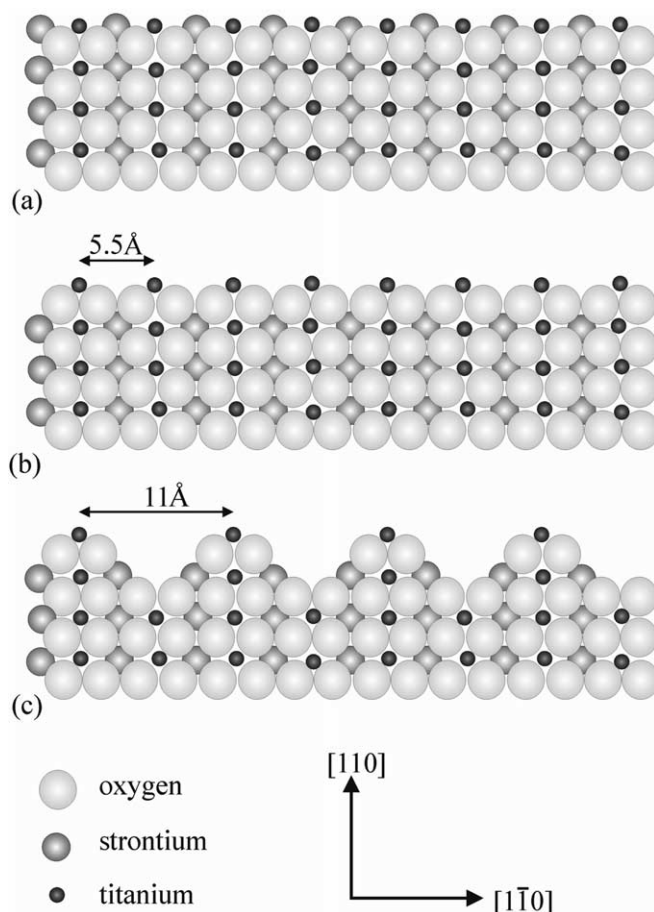


Fig. 1. Model of the surface reconstruction: (a) unheated, clean surface, (b) slightly reduced surface, (c) microfaceted surface after prolonged heating.

Å). Both surfaces are composed of $\text{TiO}_2(1\ 0\ 0)$ and $\text{TiO}_2(0\ 1\ 0)$ microfacets. This reconstruction was verified by STM, STS, LEED, as well as XPS and AES measurements [3,4]. Since these measurements only provide an indirect proof of the assumed reconstruction, we performed additional photoelectron studies (UPS and MIES) yielding information on the electronic structure of the topmost surface layer to verify the model.

2. Experimental details

Polished $\text{SrTiO}_3(1\ 1\ 0)$ single crystals ($1 \times 10 \times 10\ \text{mm}^3$) with a La concentrations of 5 and 0.1 at.% as well as nominally undoped crystals were obtained from Crystec (Germany). In order to remove surface contaminants the samples were cleaned by annealing for 24 h at 750 °C in ultra-high vacuum (UHV). During the experiments they were annealed for different durations at temperatures up to 1000 °C at ambient pressure in a flow of synthetic air (20% O_2 , 80% N_2) and in UHV (base pressure below 1×10^{-9} mbar), respectively. The sample temperature during the annealing experiments in UHV was measured using a pyrometer (Impac IGA 120). In order to monitor the surface reconstructions the samples were investigated ex situ with atomic force microscopy (AFM). The AFM measurements were conducted in ultrahigh vacuum (pressure below 1×10^{-9} mbar in the main chamber and 4×10^{-10} mbar in the microscope chamber) employing a commercial instrument (Omicron) in contact mode. To determine changes in the chemical composition the samples were studied with Auger electron spectroscopy (AES) combined with scanning electron microscopy (SEM) using a Perkin Elmer PEM 595 Auger microprobe equipped with an Ar ion sputter gun for depth profile analysis. It allows spot analysis with a lateral resolution of 1 μm . Additionally, the electronic structure of the surfaces was measured using metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS) with HeI simultaneously. MIES exclusively yields information on the topmost surface layer. A time-of-flight technique is used to separate the electrons emitted due to the

interaction of He^* atoms and HeI photons with the surface. All spectra were recorded with a resolution of 250 meV under normal emission within 100 s. The MIES spectra are displayed as a function of the binding energy E_B with respect to the Fermi level E_F . These methods were described in detail previously [5,6].

3. Results and discussion

In Fig. 2 the result of our AFM measurements for the $\text{SrTiO}_3(1\ 1\ 0)$ surface is presented. The image of $10 \times 10\ \text{nm}^2$ area shows the reconstructed surface of a sample heated in synthetic air at 900 °C for 1 h. The entire surface exhibits ridges with neighbouring rows typically 5.5 Å or 11 Å apart. A similar reconstruction is found on the samples heated in UHV as well as on less or undoped crystals. After 1 h of annealing, secondary phases could not be observed on top of the surface under both preparation conditions. Fig. 3 compares MIES spectra of surfaces obtained in both UHV and synthetic air with a TiO_x ($x \approx 1$) spectrum [7]. The SrTiO_3 spectra were both recorded after 1 h at 900 °C. Of particular importance is the prominent peak near the Fermi level at a binding energy of $E_B = 0.8\ \text{eV}$. This feature could be assigned to reduced Ti and is similarly found for all dopant concentrations. Due to the

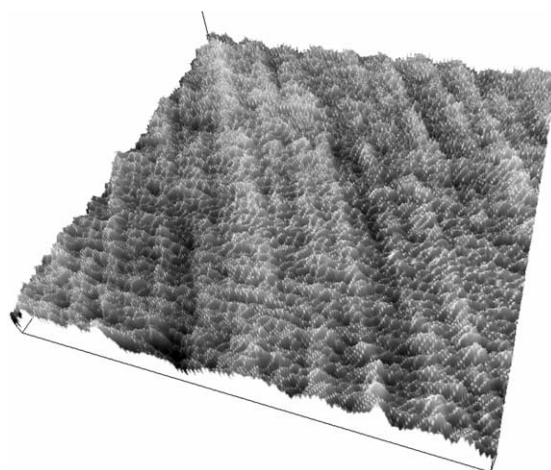


Fig. 2. AFM image of 5 at.% La-doped $\text{SrTiO}_3(1\ 1\ 0)$ heated at 900 °C for 1 h in synthetic air, visible area $10 \times 10\ \text{nm}^2$.

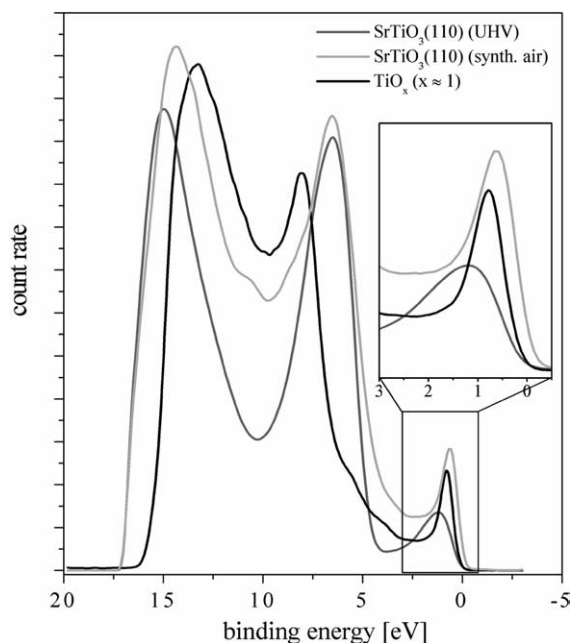


Fig. 3. MIES spectra of 5 at.% La-doped $\text{SrTiO}_3(110)$ heated for 1 h at 900°C in UHV and synthetic air compared to a MIES spectrum of TiO_x ($x \approx 1$).

good agreement between the SrTiO_3 and the TiO spectrum below $E_B > 4$ eV it is likely to assume that the surface consists of TiO_x ($x \approx 1$). The increased width of this peak for the sample heated in UHV is ascribed to the large number of oxygen vacancies produced during the experiment. Besides, the MIES spectra do not show significant changes compared to a clean, unheated $\text{SrTiO}_3(110)$ surface [8]. These results support the assumed reconstruction model (Fig. 1). Fig. 4 shows a backscattered electron image (SEM) of a 5 at.% La-doped sample after prolonged annealing in UHV. On top of the surface islands have grown which are oriented perpendicular to the SrTiO_3 $[001]$ axis. Fig. 5 shows the Auger analyses of the surface shown in Fig. 4. Between the islands (Fig. 5a) the surface does not show a significant change as compared to the unheated surface. The stoichiometry is still found to be SrTiO_3 . Fig. 5b shows the Auger analysis of an island surface. The islands consist of La, Ti, O, and a small contribution of carbon due to surface contaminations. The typical stoichiometry is found to be LaTiO_3 .

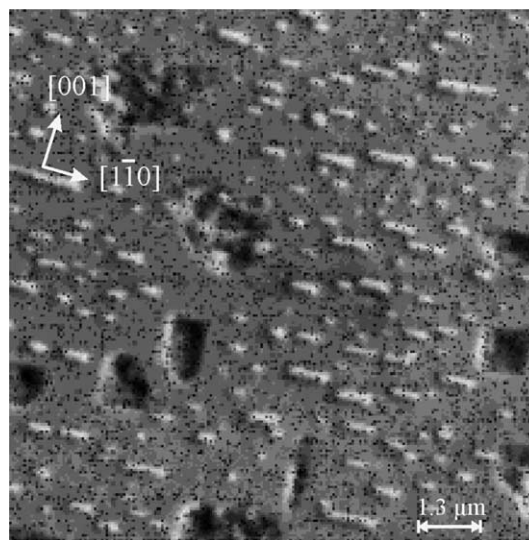


Fig. 4. SEM image of a 5 at.% La-doped $\text{SrTiO}_3(110)$ surface heated at 1000°C in UHV for 62 h.

This result confirms our findings on (100) single crystals [14]. Fig. 5c shows an AES spectrum of the same island after short sputtering. In a depth of about 1 nm, the La content is much lower compared to the surface.

Under oxidizing conditions, a comparable island formation is observed after prolonged annealing. Auger analysis reveals that these secondary phases consist of Sr and O confirming already published results of experiments at 1300°C , where SrO_x islands containing small amounts of La were found [9]. The undoped and 0.1 at.% La-doped samples also show island formation under both preparation conditions, but to a much lesser extent compared to the 5 at.% La-doped samples. This island formation was similarly found on $\text{SrTiO}_3(100)$ and could be explained using a defect chemistry model published previously [7,9–13].

4. Conclusions

$\text{SrTiO}_3(110)$ single crystals were annealed in UHV and synthetic air at temperatures up to 1000°C . The prepared samples were characterized using MIES, AFM, and AES. The SrTiO_3 crystal in $[110]$ direction consists of a sequence of alternat-

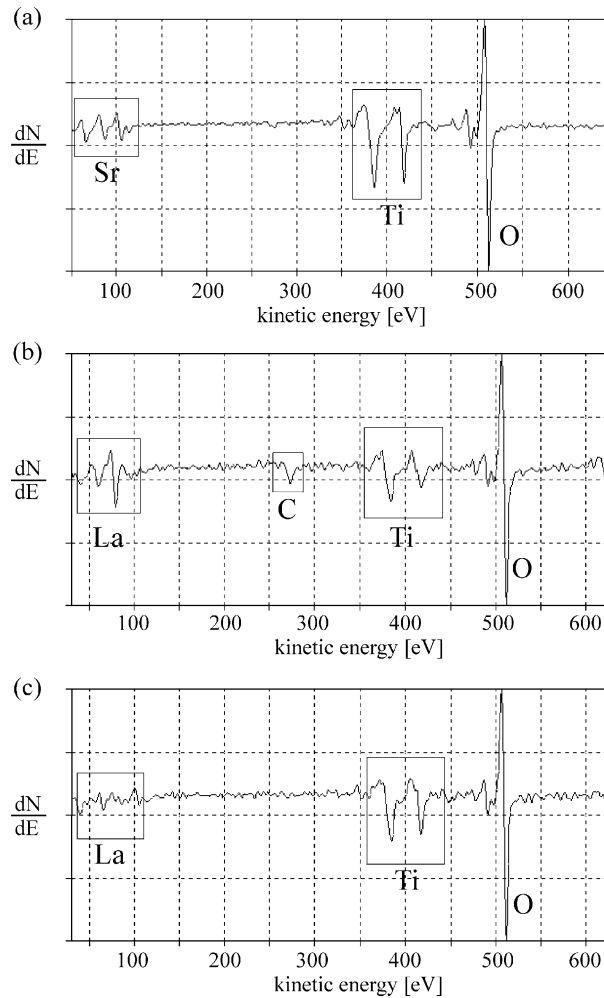


Fig. 5. AES analyses of a 5 at.% La-doped SrTiO₃(110) surface heated at 1000 °C in UHV for 62 h of the (a) area between the islands, (b) island surface, (c) island after short sputtering (≈ 1 nm).

ing SrTiO₃ and O₂ planes. Previously published reports suggest a reconstruction of the surface resulting in the formation of TiO₂(100)/(010) microfacet planes (Fig. 1). Already after short annealing we found this microfaceting of the topmost surface layer under both conditions. This is caused by a loss of Sr due to evaporation. On these surfaces a (1×1) and (1×2) periodicity of the SrTiO₃(110) surface was imaged by AFM. The MIES results show a feature next to the Fermi level that points to partially reduced titanium on top of the surface. Hence, these results give a direct evidence of the assumed reconstruction. Prolonged

heating leads to the formation of islands. The chemical composition of these secondary phases is similar to the previously published observations on SrTiO₃(100) [13,14]. The reconstruction and microfaceting model of the topmost surface layer shown in Fig. 3 corresponds well with our experiments.

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