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Electronic structure and topography of annealed $SrTiO_3$(1 1 1) surfaces studied with MIES and STM

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Abstract

Perovskites of ABO_3 type like strontium titanate ($SrTiO_3$) are of great practical concern as materials for oxygen sensors operating at high temperatures. It is well known that the surface layer shows different properties compared to the bulk. Numerous studies exist for the $SrTiO_3$(1 0 0) and (1 1 0) surfaces which have investigated the changes in the electronic structure and topography as a function of the preparation conditions. They have indicated a rather complex behaviour of the surface and the near surface region of $SrTiO_3$ at elevated temperatures. Up to now, the behaviour of the $SrTiO_3$(1 1 1) surfaces under thermal treatment is not sufficiently known. This contribution is intended to work out the relation between alteration of the surface topography with respect to the preparation conditions and the simultaneous changes of the electronic structure. We applied scanning tunneling microscopy (STM) to investigate the surface topography and, additionally, metastable impact electron spectroscopy (MIES) to study the surface electronic structure of reconstructed $SrTiO_3$(1 1 1) surfaces. The crystals were heated up to 1000 °C under reducing and oxidizing conditions. Both preparation conditions cause strong changes of the surface topography and electronic structure. A microfaceting of the topmost layers is found.

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Keywords: Strontium titanate; Scanning tunneling microscopy (STM); Metastable impact electron spectroscopy (MIES); Surface reconstruction

1. Introduction

Surfaces of $SrTiO_3$ single crystals are intensively investigated because of their importance for high temperature oxygen sensors, in photo-catalysis and as substrates for high-T_c superconductors [1–5]. In particular, the potential for varying the electrical properties from insulating to n- or p-type semiconducting and even metal-like behaviour makes these materials highly attractive as components for modern electronic devices. This may be achieved in a

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controlled manner by either chemical doping or high temperature treatment at different oxygen partial pressures. Most studies up to now are restricted to $SrTiO_3$(1 0 0) and (1 1 0) single crystals [6–9]. Depending on the gas atmospheres, surface orientation and dopant concentration, secondary phases with different chemical composition and orientation appear on top of these surfaces. It is well known for $SrTiO_3$ heated under oxidizing conditions that SrO-containing phases form on the surface [4,5,10–12]. In contrast, under reducing conditions TiO_x-containing islands were observed [12,13]. The composition and number of these islands depend on the oxygen partial pressure as well as on the dopant concentration. Both factors were described successfully using point defect chemistry models [12,14–17]. Furthermore, the microfaceting of thermally treated $SrTiO_3$(1 1 0) single crystal surfaces is widely known [6–9]. Haruyama et al. investigated the $SrTiO_3$(1 1 1) surface using LEED, UPS and XPS [21]. They found via UPS a clear metallic state with a sharp Fermi cut-off after annealing at 800 °C. Further annealing leads to a drastically weakening of this metallic state and the previously observed peak at 1.1 eV ascribed to oxygen vacancies is seen. The metastable impact electron spectroscopy (MIES) and UPS spectra show clearly a metallic state with sharp Fermi cut-off centred at about 0.65 eV below the Fermi level in the band gap region already after short annealing in ultrahigh vacuum (UHV) or synthetic air, respectively. Scanning tunneling microscopy (STM) measurements show an interesting microfaceting of the topmost surface layer.

2. Experimental

The samples employed in this investigation were commercially available (CrysTec, Berlin, Germany) $SrTiO_3$(1 1 1) single crystals consisting of alternating SrO_3^{4-} and Ti^{4+} layers. The crystals were grown by the Verneuil method. They were annealed at temperatures up to 1000 °C in ultrahigh vacuum (base pressure below 3×10^{-9} mbar) or ex situ in a flow of synthetic air (20% O_2, 80% N_2, ambient pressure) for different durations, respectively. For the surface analysis, we used several instruments. Metastable impact electron spectroscopy was carried out to investigate changes in the electronic structure of the surfaces. This technique was described in detail previously [13,18]. 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 with respect to the Fermi level. To detect changes in the surface topography, Scanning Tunneling Microscopy was used. The STM measurements were conducted under ultrahigh vacuum conditions employing a commercial instrument (Omicron) in the contact mode. Details were published previously [13,19].

3. Results and discussion

Fig. 1 shows several MIES spectra of $SrTiO_3$(1 1 1) surfaces. Next to a spectrum of a cleaned, unreconstructed surface, spectra recorded after annealing $SrTiO_3$(1 1 1) samples for 1 h at 900 °C in UHV and

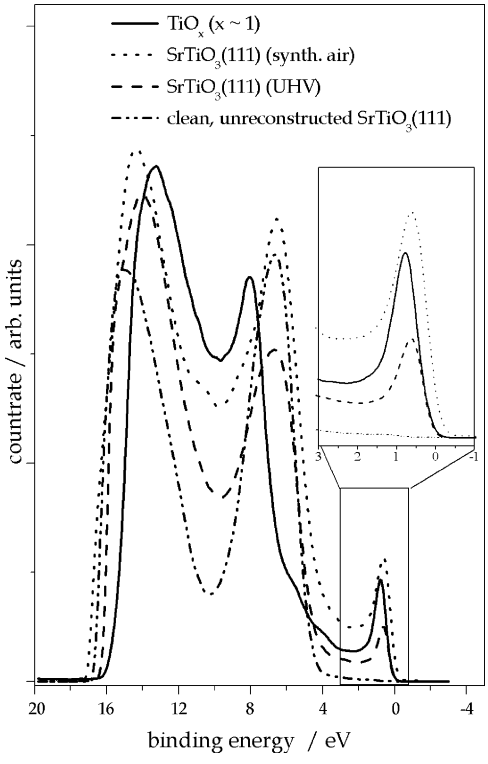

Fig. 1. MIES spectra of unreconstructed, clean $SrTiO_3$(1 1 1) (dashed and dotted line), $SrTiO_3$(1 1 1) annealed in synthetic air (dotted line) or UHV (dashed line) for 1 h at 900 °C compared to a TiO_x ($x \approx 1$) spectrum.

synthetic air are shown, respectively. Beside the other well-known structures, MIES shows after annealing a pronounced feature near the Fermi level at 0.65 eV binding energy. For comparison, a TiO_x ($x \approx 1$) spectrum is also shown [20]. TiO_x shows a metallic state at 0.8 eV below the Fermi level which is attributed to the Ti^{2+} [6]. Therefore, the sharp features in the band gap of (1 1 1) surfaces are most probably caused by reduced Ti. As the pronounced peak on $SrTiO_3$ is found at a 0.15 eV lower binding energy with respect to the feature observed on TiO surfaces, the Ti atoms on $SrTiO_3$(1 1 1) are probably onward reduced to Ti^+. These Ti^+ states found in MIES can be formed by removing Sr and O from the (1 1 1) surface, which leads to microfacets consisting of TiO_2 tetrahedrons. The peak shift could not be caused by surface charging due to the fact that the other features like O 2p do not shift. Also, other experimental artefacts could be excluded.

In Fig. 2, our STM investigations of reduced $SrTiO_3$(1 1 1) surfaces are presented. The STM image displays a 20 nm × 20 nm area. The surface is completely microfaceted. Small, regularly oriented dots are formed, with distances of $a\sqrt{2} = 5.5$ Å (with $a = 3.91$ Å being the lattice constant of $SrTiO_3$), which could be attributed to TiO_2 pyramids. The black rectangle indicates this area. The white rectangle in the STM picture indicates an area with ridges, which were similarly observed on $SrTiO_3$(1 1 0) surfaces [6–9]. The topmost Ti atom of these TiO_2 tetrahedrons is usually saturated by O atoms. Annealing in UHV removes these O atoms, formally reducing Ti^{4+} to Ti^+.

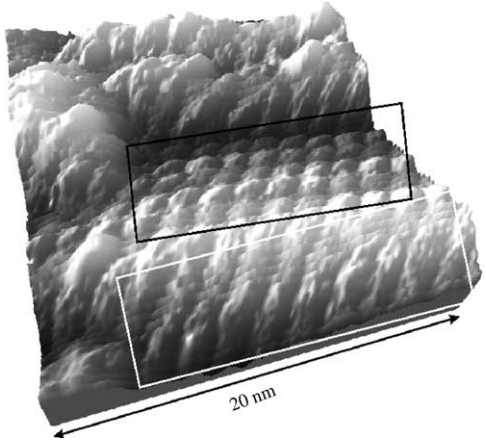

Fig. 2. 3D STM image of $SrTiO_3$(1 1 1) heated in UHV for 5 h at 900 °C in UHV (20 nm × 20 nm).

4. Summary

Changes of the surface structure and of the electronic states on the $SrTiO_3$(1 1 1) surfaces in the course of annealing in UHV and synthetic air were studied by MIES and STM measurements. Complete microfaceting of the topmost layer is found. On each terrace, an arrangement of regularly oriented TiO_2 pyramids with distances of $a\sqrt{2} = 5.5$ Å (with $a = 3.91$ Å being the lattice constant of $SrTiO_3$) is observed throughout the measurements. The recorded MIES spectra reveal a characteristic change in the electronic structure due to the thermal treatment. A broad feature in the band gap region is observed in MIES caused by Ti^+ in the topmost surface layer.

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