In situ reduction of (100) SrTiO₃

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Abstract

Low energy electron diffraction (LEED) and photoelectron spectroscopy (PES) have been employed to study the (100) SrTiO₃ surface annealed in ultra high vacuum. The annealing was performed up to 830°C. After annealing at 830°C, we have observed from PES spectra the appearance of the conduction band and from LEED patterns the ($\sqrt{5} \times \sqrt{5}$)R 26.6° superstructure. Both features seem to have the same origin: the ordering of oxygen vacancies.

Keywords: Strontium titanate; Reduction; PES; LEED; Ordered oxygen vacancies

1. Introduction

Strontium titanate, a perovskite with band-gap energy of 3.2 eV at 25°C [1], is a ‘classic’ in Solid State Science because of its interesting properties. Basically an insulator, it becomes semi- and even superconducting upon reduction [2], i.e. oxygen extraction. Yet, this is not the only reason why the surface of SrTiO₃ is lately the focus of interest. Also, and depending on the stoichiometry, it becomes ferroelectric, in contrast to the pristine SrTiO₃. It is one of the few stable materials that can decompose water into hydrogen and oxygen with the assistance of light (photoelectrolysis) [3], although with a relatively low yield. Moreover, SrTiO₃ has been found as one of the most suitable substrates for the epitaxial growth of high T_c superconducting YBa₂Cu₃O_{7-x} films. Nevertheless, its reduction process is still unclear [4,5]. In the present work we have tried to understand such a process.

2. Experimental

The photoelectron spectroscopy (PES) experiments were performed in an ultrahigh vacuum (UHV: $P < 10^{-10}$ mbar) chamber equipped with an angle-resolved hemispherical analyzer mounted in a goniometer and with a high-precision manipulator. The experiments were carried out using synchrotron light from the Spanish–French beam line (SU8) of the Super-Aco storage ring in Orsay. The measurements were performed using linear polarised light with an overall energy resolution better than 100 meV. The low energy electron diffraction (LEED) patterns were recorded at different energies by a video camera connected to a computer. In the present experiment, single crystalline samples (5 × 5 × 1 mm) of SrTiO₃ (100) (Crystal-GmbH) were fixed on a silicon resistive heater. They were annealed

at different temperatures in subsequent thermal treatments (300, 640, 750, 830°C) under UHV conditions for different periods of time (see Table 1).

Table 1. SrTiO₃ (100) heat treatment in 10⁻⁷ mbar

Sample	Temperature (°C)	Time (min)
A	—	—
B	300	30
C	640	60
D	750	20
E	750	70
F	830	120

Fig. 1. Photoemission overview of SrTiO₃ (100) surface, treated at different temperatures in UHV. Photon energy 130 eV.

Temperatures were measured with an optic pyrometer. In all the cases, the pressure in the preparation chamber during the thermal treatment was of the order of 10^{-7} mbar. Then, they were cooled down at room temperature and, afterwards, LEED and PES were used to examine the structure and composition of the surface at pressure $\approx 10^{-10}$ mbar. The PES spectra were measured at 130 eV for every temperature and the LEED patterns were taken at 167, 133, 106, 98 and 42 eV. The position of the Fermi level (E_F) has been determined by comparison with the measured Fermi edge of a copper film mounted besides the sample.

3. Results and discussion

3.1. Photoelectron spectroscopy

As is well known, the heating of SrTiO_3 at temperature $\geq 500^\circ\text{C}$ in ultra high vacuum generates n-type conductivity due to the reduction process ($\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$) that accompany the oxygen vacancies produced [6,7]. Also, according to previous studies, when the sample is heated to temperatures higher than 600°C in ultra high vacuum, (10^{-10}) carbon and water contamination disappear from the surface [8,9]. This allows us to study the samples by two different surface probes: PES and LEED, since the sample presents enough conductivity to be studied by these techniques.

Fig. 1 shows an overview of the sample surface at different temperatures as seen by PES spectra. The spectra obtained without any previous thermal treatment has an 18.42 eV shift with respect to the others. This is due to the insulating characteristic of the pristine SrTiO_3 . The shift disappears when the sample is being annealed up to 300°C . This is indicative of the sample becoming conducting.

In this same spectrum of Fig. 1, without treatment, apart from the valence band (VB), and the Ti, Sr and O core level peaks, the presence of other bands can also be observed; these can be indexed as due to some impurities (see Table 2; quality suggested by the supplier: Crystal-GmbH). Therefore, impurities like Si, Al, Fe, Ca, Na, and K are present on the surface, while Ba must be in the bulk. As the temperature of the thermal treatment increase the crystal darkens and, as can be observed in Fig. 1, some of these impurities peaks start to disappear.

After an 830°C annealing, some of the impurity bands (Al, Fe and Na) completely disappear, while others like Ca nearly do so. This means that the surface is becoming free of them. Nevertheless, the same cannot be said for the Si band, because it overlaps with the background of the inelastic electrons produced during the photoemission.

Furthermore, these are not the unique important changes in the spectrum: the Ti, Sr and O core levels also change and a new band, meaning the Fermi level, starts to appear at 830°C : the conduction band. All these peaks are directly related to the reduction process. For this reason it is worth studying them in some detail.

The PES spectrum of the Ti (3p) level (Fig. 2) shows that when SrTiO_3 is heated at high temperature ($>640^\circ\text{C}$) a new band starts to appear. This new component (observed on the right side of the peak) appears during annealing. In this way, the Ti (3p) core level spectrum shows at smaller energies the consequences of the elimination of oxygen. To preserve the electrical neutrality of the lattice some Ti^{4+} is transformed in Ti^{3+} . Moreover, at 830°C an

increasing of the Ti^{3+} peak relative to Ti^{4+} is observed and another new component appears. Due to its position, it can be attributed to the presence of Ti^{2+} . Consequently, titanium seems to be in three different oxidation states, Ti(II), Ti(III), Ti(IV).

Fig. 2. PES spectra of SrTiO_3 (100) surface, treated at different temperatures in UHV. Core level of Ti (3p). Photon energy 130 eV.

Another region of the PES spectrum, which shows an important change, is close to the Sr core level (Fig. 3). This emission seems to be quite complicated since it includes the contributions of Ca, Sr, O and K. At 830°C the peak corresponding to the Ca (3p) and K (3p) core levels have mostly disappeared (Fig. 3). This means that the surface is becoming free of them. Moreover, at 830°C a decreasing of the O peak relative to the Sr one is observed (from 1/2 in the spectrum for the sample without treatment to 2/5 at 830°C). This indeed means that, when heating oxygen is going out of the sample. The oxygen band position is in good agreement with that suggested by See et al. for stoichiometric SrTiO_3 [10].

Fig. 3. PES spectra of SrTiO₃ (100) surface, treated at different temperatures in UHV. Core levels of Ca (3p), Sr (4p), O (2s) and K (3p). Photon energy 130 eV.

Table 2. Chemical analysis of the SrTiO₃ single crystals and its binding energies

Element	Concentration (ppm)	Binding energy (eV)	
Al	10	2p _{1/2}	72.9
		2p _{3/2}	72.5
Ba	19	4d _{3/2}	92.6
		4d _{5/2}	89.9
Ca	14	3p _{1/2}	25.4
		3p _{3/2}	25.4
Fe	< 2	3p _{1/2}	52.7
		3p _{3/2}	52.7
K	2	3p _{1/2}	18.3
		3p _{3/2}	18.3
Na	< 2	2p _{1/2}	30.4
		2p _{3/2}	30.4
Si	< 2	2p _{1/2}	99.8
		2p _{3/2}	99.2

The reduction of SrTiO₃ also originates the appearance of a new band between the Fermi level (E_f) and the VB: the conducting band (see Fig. 4). This new band is generated by the reduction of $Ti^{4+}=(Ar)3d^0$ to $Ti^{3+}(Ar)3d^1$, so that the promotion of electrons, from the VB to the conduction, does occur. The gap observed at 830°C is 3.2 eV.

Fig. 4. VB for different temperatures. Photon energy 130 eV.

3.2. LEED results

Fig. 5 shows the LEED diagrams for each temperature at 98 eV. Until 640°C LEED was not detected. At 640°C the patterns exhibit sharp spots over a low background, indicating a smooth and well ordered surface: a typical P(1x1), characteristic of a (100) orientation of a cubic perovskite. The oxygen vacancy concentration is neither high enough to produce conductivity nor to produce a surface reconstruction. It is worth mentioning that shell model calculation [15] and STM [11–14] works have shown that the (100) SrTiO₃ surface is Ti–O-terminated. The same pattern was detected up to 740°C (see Fig. 5). Nevertheless, after the annealing at 830°C during 2 h, a new superstructure is found. In Fig. 6, patterns taken at different voltages are shown and they can be described in k-space, as fractional spots, based on the primitive crystal structure perovskite in two dimensions $\approx 3.9 \times 3.9 \text{ \AA}$. They appear at $(2/5, 1/5)$, $(4/5, 2/5)$, $(1/5, 3/5)$ and $(3/5, 4/5)$ for the first group, and $(1/5, 2/5)$, $(3/5, 1/5)$, $(2/5, 4/5)$ and $(4/5, 3/5)$ for the second group with respect to the P(1x1) pattern; the two sets can be transformed into each other by rotating 36.87° and correspond to two domain sets (Fig. 7). The vectors of the primary unit cell in k-space are $[2/5, 1/5]$; $[1/5, 3/5]$ for the first domain set and $[3/5, 1/5]$; $[1/5, 2/5]$ for the second one. Transforming into real space and taking into account that the most favorable top layer is the titanium–oxygen one, we find that the LEED pattern corresponds to a $(\sqrt{5} \times \sqrt{5})R 26.6^\circ$ reconstruction. The ordering of the oxygen vacancies in two intergrown domain sets, at the top layer of SrTiO₃, it seems to be responsible for it rather than the presence of impurity aggregation in the crystal surface as other authors have proposed [16]. The corresponding model is illustrated in Fig. 8. Up to now, this reconstruction in SrTiO_{3-x} had only been detected by techniques like STM and RHEED [17–19] when SrTiO₃ is heated at 1200°C in vacuum for several minutes. Other types of reconstruction have been observed in this material [15], for example SrTiO_{3-x} (3x2) by Tomashpol'skii et al. [20].

Fig. 5. LEED patterns from SrTiO₃ (100), E_p 98 eV at different temperatures. (a) 640°C for 60 min, (b) 750°C for 20 min, (c) 70 min, and (d) 830°C for 120 min, in accumulative thermal treatment.

Fig. 6. LEED patterns from SrTiO₃ (100), at different photon energy (167, 133, 106 and 42 eV) after 830°C annealing in vacuum.

Fig. 7. Reciprocal unit cell. It is the result of two $(\sqrt{5} \times \sqrt{5})R 26.6^\circ$, intergrown domain sets rotated 36.87° from each other.

Fig. 8. A model in the real space of $\text{SrTiO}_3 (\sqrt{5} \times \sqrt{5})R 26.6^\circ$, the oxygen vacancies are ordered along the $\langle 120 \rangle$ direction in the TiO_2 top layer.

4. Conclusions

The annealing in UHV produces enough conductivity (n-type) to allow electron spectroscopy and diffraction using synchrotron radiation to be performed in SrTiO_{3-x} . Impurities like Al, Fe, Na, Ca disappear from the surface when the sample is heated at 830°C in UHV. The elimination of oxygen from SrTiO_3 originates a new band between the Fermi level and the VB: the conduction band. This new band is related to the presence of Ti^{3+} in the surface. After 830°C annealing in vacuum for 2h, a superstructure is observed by LEED. It can be scribed as two $(\sqrt{5} \times \sqrt{5})R 26.6^\circ$ intergrown domain sets rotated 36.87° from each other.

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