



SrTiO₃ surface modification upon low energy Ar⁺ bombardment studied by XPS



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ABSTRACT

Segregation processes occurring in the vicinity of the SrTiO₃ (100) single crystal surface induced by low energy Ar⁺ ion etching was studied with the use of X-ray Photoelectron Spectroscopy (XPS). The etching is selective and after the process the near surface region is depleted in both oxygen and strontium relative to titanium. However, photoemission data show an unexpected effect: the surface of the treated crystal after its exposure to air was re-enriched not only in oxygen but also in strontium. The preferential sputtering leads to formation of titanium oxides with lower oxidation states and insulator to metal transition in the surface vicinity of strontium titanate crystals. XPS data indicate that the process of conductive layer formation is less effective when ion sputtering of the crystal takes place at an elevated temperature. The effect is explained by the enhanced oxygen diffusion rate and the process of self-oxidation in the heated sample.

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1. Introduction

Ion bombardment can lead to the removal of surface atoms of the sample as a result of collisions with striking ions (ion etching, ion sputtering). The ion etching can take place in a selective manner and for different atoms the yield of etching can be various (selective etching, preferential sputtering). Theory of ion bombardment can be found elsewhere [1].

Interesting results were achieved during ion bombardment of strontium titanate SrTiO₃ (STO) which is often treated as a model perovskite structure material. It was observed that ion sputtering of this insulating material generate energy states in the energy gap of STO. In addition, ion etching was accompanied by changes in the relative concentration of Sr/Ti and Ti in the 3 + oxidation state appears on the sample surface [2]. The oxidation level of titanium can be even lower during long lasting sample treatment [3]. However, the Ti “surface states” disappeared when the sample was exposed to oxygen or simply to air. Moreover, it was shown recently for another perovskite single crystals of STO:Nb or KTaO₃ that oxygen induced depopulation of the band gap states (generated by ion etching) is much more efficient at higher temperature [4,5]. STO

crystal surface bombardment using argon ions causes also remarkable changes in the electronic structure of strontium ions. Photoelectron spectroscopic study shows that after ion bombardment, there is an extra doublet in the Sr 3d core spectrum, shifted by about 0.7 eV towards higher binding energies with respect to the main doublet attributed to the perovskite lattice [3,6]. The location of the additional peaks in the Sr 3d line is usually attributed to the Sr-O complexes present in the vicinity of the surface [3,7], although it is possible also to find an interpretation that it comes from evolved metallic strontium [6]. Interestingly, the return of the lower Ti oxidation state to the initial (+4) state appears as a result of not only the exposition of the etched surface to oxygen conditions, but also deposition of a metal layer such as Pt [8] or Ni [9]. A surprising result, interesting for optoelectronic device applications, was published by Reagor and Butko [10] where bombarding with argon ions of STO lead to a stable, conductive and moreover transparent surface layer. However, electrical measurements were possible only when electric contacts were deposited on the surface directly after ion etching. It was found, that the most favorable energy of bombarding argon ions to form the conductive nanolayers is about 300 eV. It is worth to add that the ion etched (Ar⁺, 300 eV) STO sample was able to emit the blue light [11].

The aim of this paper is to shed some light on the stability of the conductive layer exposed to atmospheric conditions in the context of the reported requirement to deposit the electrodes directly after

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ion bombardment. Another purpose is to extend the observation of STO ion etching to the non-ambient temperature.

Our study is based on X-ray Photoelectron Spectroscopy (XPS) measurements of STO single crystal treated by ion beam at various temperatures and exposed of the treated sample to air. Additionally, formation of a conducting layer upon the ion bombardment was tested in-situ in the XPS chamber.

2. Experimental

Single crystals of STO from Crys Tec with the (100) surface obtained by epipolishing were investigated. XPS measurements were done with the use of Physical Electronics PHI 5700 spectrometer with monochromatized Al K_{α} radiation. The XPS spectra were collected at different angles of analysis (take-off angle to the sample surface plane). The analysis of the spectra and calculation of atomic concentration were done with the use of MultiPak software (ver. 9.01) by Physical Electronics.

The position of the core level spectra on the binding energy scale was determined before sputtering process relative to the lines of carbon C 1s (285.6 eV) [12]. After ion sputtering the spectra (maximum of line intensity) were adjusted to the same positions as before the process. However, in our analysis the precise position of the core level spectra was of minor importance. The main focus was on the changes in the spectra shape, which allows to observe the appearance or disappearance of additional energy states under certain conditions. Charge neutralization during XPS measurement was achieved by using low energy electron beam. The XPS chamber is equipped with the ion gun and Ar⁺ ion bombardment was performed *in situ*. The surface of the samples was bombarded by ions with the energy of 300 eV and the density of flux was about 0.02 mA/cm², at the pressure of about 1×10^{-7} mbar. The base pressure in the vacuum chamber during XPS measurements (and generally except during ion sputtering process) was about 5×10^{-10} mbar. The maximal pressure during annealing (described below) did not exceed the range of 10^{-9} mbar. The XPS analysis area has a diameter of 0.8 mm and the sputtering beam was raster scanned over a square 2×2 mm². The angle of the impinging Ar ions to the sample surface was 45°. The ion sputtering procedure was performed not only at room temperature but also at lower and elevated temperature (ca. 183 K and 673 K respectively). The measurements were made using the sample holder equipped with the thermocouple.

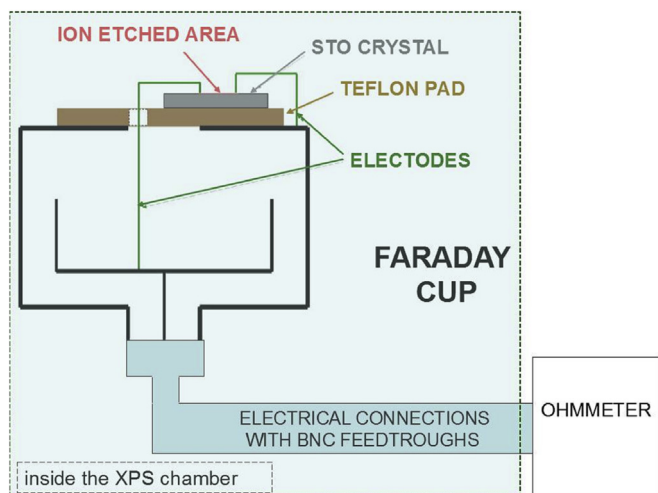


Fig. 1. Scheme of the in-situ electrical measurements inside the XPS chamber.

The in-situ electrical resistance was measured using a sample holder based on a Faraday cup (normally used to calibrate the ion beam), as schematically presented in Fig. 1. The electrical measurements were provided by two-point method with the use of the commonly available ohmmeters. The platinum electrodes were glued to the crystal with the silver paste. The distance between them was about 2 mm. The potential deposition of the electrode material during sputtering was tested by monitoring the platinum and silver XPS lines.

Lowering of temperature during the test was performed by construction of the sample holder which was thermally coupled to the tank filled with liquid nitrogen (standard equipment of the XPS apparatus). Increase of the temperature was achieved due to the resistance heater built in the sample holder.

3. Results and discussion

3.1. Brief introduction to analysis of XPS spectra of SrTiO₃ single crystal

The detailed analysis of the structure of the Ti 2p and Sr 3d lines directly after ion bombardment together with the fitted spectra components coming from various compounds is given in our earlier article [3]. For clarity, in the present discussion only general remarks related to the changes in the spectra will be recalled. In the ion treated sample, both Ti 2p and Sr 3d spectra show additional doublets formed beyond the main doublets assigned to STO. The additional Sr 3d doublet shifted towards higher binding energy indicates presence of the SrO complexes in the perovskite structure matrix and possibly also metallic Sr. The presence of additional Sr states is easily visible as an increase of the intensity between the main components of the spin-orbit split doublet (Fig. 2). In the Ti 2p spectrum the additional doublets assigned to a lower oxidation states of titanium relative to +4 state characteristic for STO matrix are shifted towards lower binding energy (Fig. 2). The presence of the lower Ti oxidation state can be easily seen as an enhancement of the spectral region at the lower binding energies side of the Ti 2p_{3/2} main peak. It is accompanied by the appearance of the additional electronic states in the energy gap (Fig. 3) which can be related to the improvement of the electrical conductance of the

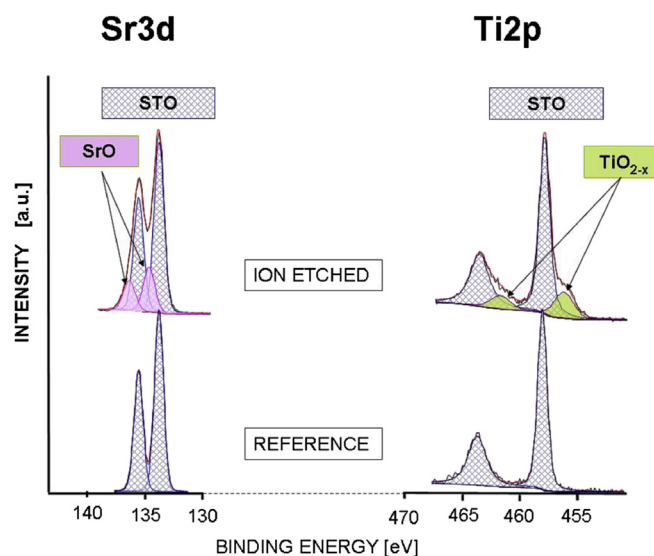


Fig. 2. Formation of the new electronic states in the Sr 3d and Ti 2p XPS spectra of SrTiO₃ upon Ar ion bombardment. The doublet described as TiO_{2-x} represents Ti compounds with lower oxidation states in general (angle of analysis 45°).

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