



# Advanced analysis tool for X-ray photoelectron spectroscopy profiling: Cleaning of perovskite SrTiO<sub>3</sub> oxide surface using argon cluster ion source



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## ABSTRACT

This article shows the comparison between three different ionic bombardments during X-ray photoelectron spectroscopy (XPS) studies of single crystalline SrTiO<sub>3</sub> (STO) substrates. The abrasion using a “cluster argon ion source” is compared with the standard “monoatomic Ar”. The influence of the energy of the monoatomic ions used is clearly demonstrated. While the chemically adsorbed species on the STO surface are removed, such bombardment strongly modifies the surface. A reduction of part of the titanium atoms and the appearance of a different chemical environment for surface strontium atoms are observed. Implantation of argon ions is also detected. Cluster ion etching is used on oxide surface and, in this case only, due to a much lower kinetic energy per atom compared to monoatomic ions, the possibility to remove surface contaminants at the surface without modification of the XP spectra is clearly demonstrated, ensuring that the stoichiometry of the surface is preserved. Such result is crucial for everybody working with oxide surfaces to obtain a non-modified XPS analysis. The progressive effect of this powerful tool allows the monitoring of the removal of surface contamination in the first steps of the bombardment which was not achievable with usual guns.

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## 1. Introduction

Strontium titanate SrTiO<sub>3</sub> (STO) is one of the most important materials for oxide based electronics due to its unique electrical and optical properties. STO is a transparent and non-magnetic wide-band gap insulator (3.2 eV) in the bulk form. The strong interest in STO is further increased since it has been found to host a two-dimensional electron gas (2-DEG) at the interface with other oxides [1,2]. Furthermore, STO is favorably lattice-matched to many other complex oxides and is therefore a widely used substrate for epitaxial oxide growth. It is also used as a buffer layer between silicon and other functional oxides. For thin films deposition, quality of the substrate surface is crucial and it is then important to gain a greater understanding in cleaning and preparing such oxide substrates [3]. Moreover the surface termination has an essential impact on interface properties as it has been demonstrated for the conductive properties at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface [1,4]. STO surfaces have already been studied in terms of adsorption of water and other species on its surface from the point-of view of catalytic dissociation of water [5–8].

In this article, STO surface was studied by X-ray photoelectron spectroscopy (XPS) which is a powerful tool to investigate and control the chemistry of any surfaces. Unfortunately, the presence of adsorbed molecules, organic contaminants, water, and carbon dioxide, represents a real issue for many surfaces where carbon or oxygen are the elements of interest. Indeed, the number of emitted photoelectrons is attenuated by a factor  $e^{-d/\lambda}$  as a function of the depth  $d$  where  $\lambda$  is the inelastic mean free path of the considered electron. Thus, 63% of the detected electrons are coming from a depth equal to  $\lambda$ , which is typically in the range 1–3 nm for AlK<sub>α</sub> radiation [9]. Consequently, even a small amount of molecules on a surface gives important percentage of the oxygen detected when oxides are studied, leading to an incorrect XPS analysis. Furthermore, presence of adsorbed contaminants tends to decrease the signal of the material surface under study which limits the quality of the data or is time consuming.

Several strategies could be followed to get rid of these molecules. The most naive approach consists in avoiding the presence of adsorbed molecules. That could be achievable when the different processes occur in controlled environment but when chemical treatments are used for instance, molecules are always detected on surfaces. In order to remove those, annealing and sputtering [10] are the two main methods. Unfortunately, both of them involve modifications of the oxides during the cleaning processes.

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In this article, we report by XPS analysis using a dual source ion beam the comparative effects on STO surfaces of different argon bombardments using “traditional” monoatomic  $\text{Ar}^+$  ions and the polyatomic  $\text{Ar}_n^+$  cluster ion source. More especially, the removing of carbon atoms, the ion implantation and the modification of strontium and titanium peaks are studied. The effect of the traditional monoatomic argon ions with two different kinetic energies (1000 and 4000 eV) is also compared. These results are compared to the effects of bombardment using  $\text{Ar}_n^+$  cluster ions of 4000 eV. The interest of such argon cluster (3000 atoms bound with Van der Waals forces) is that the average energy per atom is much lower (few eV) and the penetration length noticeably smaller.

## 2. Experiments

We have studied commercial (SurfaceNet GmbH) single-crystal  $\text{SrTiO}_3(001)$  substrates ( $10 \times 10 \times 0.5 \text{ mm}^3$ ). Crystals were cleaned with acetone, ethanol, and demineralized water.

XPS (X-ray photoelectron spectroscopy) surface chemical analyses and depth profiles were carried out with an ESCALAB 250 Xi photoelectron spectrometer using a monochromatic Al-K $\alpha$  X-Ray source (1486.6 eV). The detection was performed perpendicularly to the sample surface, using a constant energy analyzer mode (pass energy 20 eV). Spectra were recorded with a 0.1 eV energy step size. As stoichiometric STO is an insulating material a flood gun is used to compensate the charges created by the photoelectron emission along the etchings. Charge neutralization was ensured by electron and ion beam. The sample was mounted with both rear (carbon tape) and front (clips) contacts to avoid any changes during long time experiments. The main peak of the O 1s core line at 529.3 eV is used as the reference to align the binding energies in all XP spectra. This value is fixed taking the main C 1s line at the usual value of 284.8 eV before the beginning of abrasion. (As carbon is removed along the experiment, we consider oxygen peak as the most “stable” peak in the course of the etching as its chemical state is not modified contrary to Ti and Sr). Bombardment is achieved using the MAGCIS Dual Beam ion source which enables depth profiling with monoatomic and cluster argon ions. Quantification was performed with the Thermo Fisher scientific Avantage $\text{C}$  data system.

## 3. Results and discussion

### 3.1. Carbon and argon peaks

In order to study the removing of surface contaminants, the XPS peaks related to carbon are followed. Fig. 1 shows the evolution of the intensity of the C 1s carbon peaks (C–C at 284.8 eV, C–O–C at 286.6 eV and COOH at 289.1 eV) during the different etchings. Intensities are normalized to the intensity obtained at the first spectrum before the beginning of the bombardment. Although carbon could be completely removed by the three bombardments, a clear difference is observed on the time scale. While carbon peaks disappear during the first seconds of monoatomic etching (in both cases, it completely disappear after 20–30 s etching), much longer time is needed with the cluster etching where the total disappearance of carbon peaks is obtained after 175–200 s. The removing of carbon contaminants can be described by an exponential decay (see Fig. 1) with time constants of 40 s and 4–6 s for cluster ion etching and monoatomic bombardment, respectively. Insert of Fig. 1 displays the time evolution of argon XPS ratio based on the analysis of the Ar 2p peaks. The main information here is that argon is only detected while using monoatomic argon etching whereas no traces of argon is observed with the cluster ion source in the limit of detection (meaning that less than 0.01% of argon is implanted). Conversely, a significant amount of implanted argon is observed and forms a plateau after 60 s etching for both monoatomic etchings. In the stationary regime, the XPS argon ratio reaches 2.2% at 1000 eV and 4.1% at 4000 eV. This indicates that high-energetic ions

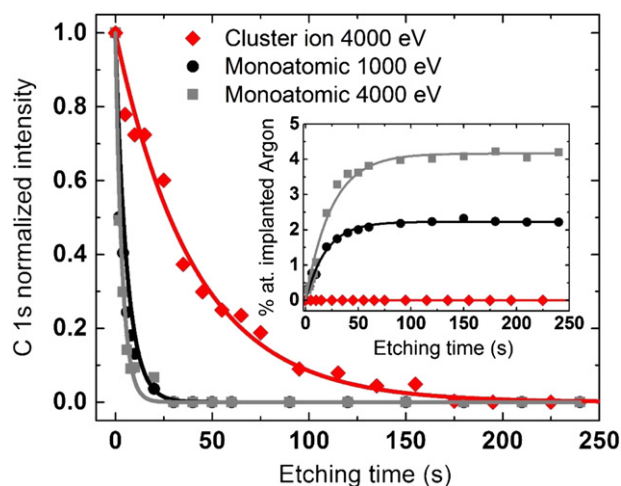


Fig. 1. Evolution of the intensities of the C 1s and Ar 2p (insert) peaks during ionic bombardment for the three different abrasions. The C 1s intensity is normalized to the intensity of the peaks at  $t = 0$  for each sample. The intensity of the argon peaks is given in XPS atomic percentage.

penetrate inside the substrate (the energy loss is typically of several hundreds of  $\text{eV}\cdot\text{nm}^{-1}$  [11]). It is worth noting that for both monoatomic bombardments, argon is detected as soon as the beginning of the etching while carbon atoms are not completely removed from the surface. Consequently, carbon cleaning is necessarily concomitant with argon implantation during monoatomic etching. At this point, the raising question is related to the effect of the different bombardments on the studied oxide.

### 3.2. Titanium peaks

In order to investigate the influence of the three argon etchings on titanium atoms, only the Ti  $2p_{3/2}$  peak was studied given that Ti  $2p_{1/2}$  is separated enough in energy ( $\Delta \approx 6 \text{ eV}$ ) to not interfere with the Ti  $2p_{3/2}$  peak. Fig. 2 (a, b and c) shows the obtained spectra at different etching times for the three bombardments. A fit is realized to display the appearance of significant low binding energy contributions for both monoatomic etchings. The arising of two low binding energy components could be associated to reduced states of titanium atoms  $\text{Ti}^{3+}$  and  $\text{Ti}^{2+}$  found at 1.6 eV and 2.9 eV from the main  $\text{Ti}^{4+}$  peak, respectively [5,10,12,13]. These contributions have been fitted assuming the same full width at half maximum (FWHM) than for the  $\text{Ti}^{4+}$  peak (see Fig. 2a and b). In STO, titanium reduction may be due to the creation of oxygen vacancies owing to the high-energetic monoatomic bombardment. After 200 s etching, the  $(\text{Ti}^{3+} + \text{Ti}^{2+}) / (\text{Ti}^{4+} + \text{Ti}^{3+} + \text{Ti}^{2+})$  ratio reaches about 37% for the 4000 eV bombardment against 27% for the 1000 eV. We note that reduced titanium peaks immediately appear after the beginning of the etching. Fig. 2c shows the evolution of the Ti  $2p_{3/2}$  region during the cluster etching. No visible contribution of reduced titanium atoms is detected all along the cluster sputtering and the data are well reproduced considering one single peak. An attempt to fit with a small contribution of  $\text{Ti}^{3+}$  is also possible and gives maximum 1% of  $(\text{Ti}^{3+}) / (\text{Ti}^{4+} + \text{Ti}^{3+})$ . Nevertheless this contribution is present even at  $t = 0$  which means that cluster abrasion does not induce noticeable reduced form of Ti, even after 315 s abrasion. By comparison with monoatomic etching, no oxygen vacancies seem to be created with the cluster projectiles leading to a very smooth abrasion without reducing the metal transition species.

### 3.3. Strontium peaks

Fig. 3 (a, b and c) show the Sr 3d region (130–137 eV) at different times for the three etchings. At  $t = 0$ , a unique doublet is observed

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