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# Study and characterization of SrTiO<sub>3</sub> Surface

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**Abstract.** Two-dimensional electron gas (2DEG) at an oxides interfaces and surfaces has attracted large attention in physics and research due to its unique electronic properties and possible application in optoelectronic and nanoelectronic. The origin of 2DEG at oxide interfaces has been awarded to well known "polar catastrophe" mechanism. On the other hand, recently 2DEG has been also found on clean SrTiO<sub>3</sub>(001) surface due to the creation of oxygen vacancies. However, these 2DEG systems have been until now found mostly on an atomically perfect crystalline samples usually grown by pulse laser deposition or molecular beam epitaxy e.g. samples which are difficult to be prepared and require specific experimental conditions. Here, we report on the fabrication of SrTiO<sub>3</sub> thin films deposited by magnetron sputtering which is suitable for mass-production of samples adapted for nanoelectronic applications. The characterization of their structural and electronic properties were studied and compared to those of SrTiO<sub>3</sub> single crystal. XRD patterns and SEM micrography showed that the deposited films are amorphous and their structure changed to polycrystalline after heating at 900°C. Photoemission spectroscopy (XPS and UPS) were used to study the electronic properties of the films and crystal. In both, we observed the 2DEG system at Fermi level and the formation of Ti<sup>3+</sup> state when the surface was heated at 900°C.

## INTRODUCTION

The demand for improving efficiency in solar cells was always one of the top goals in photovoltaic applications and has enhanced the studies on perovskite thin films. Transition metal oxides having perovskite structure had attracted the attention of researchers because of their powerful properties such as high dielectric constant, magneto-electric coupling, chemical stability and photo-activity. Indeed, SrTiO<sub>3</sub> is one of the titanates that is considered as a good candidate for dielectric and photoelectric applications. SrTiO<sub>3</sub> thin films can be found in a wide range of applications as well, in particularly solar cells.

According to previous studies, it has been shown that the intrinsic and fundamental properties of transition metal oxides are strongly related to the experimental conditions of growth and surface treatment. This is due to the role that defects play in these materials since they cause disorder and affect the functionality of the hosting system. Moreover, despite the insulating nature of SrTiO<sub>3</sub>, this latter has shown the possibility to create a 2-dimensional electron gas (2DEG) system on its surface and at the interfaces with other oxides.

One example is the famous crystalline LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterostructure discovered for the first time by A. Ohtomo and H. Y. Hwang [1]. They reported the formation of 2DEG at this interface and the resulting properties such as superconductivity and magnetism. Others also revealed that a large number of electrons were confined at the heterojunction of LaAlO<sub>3</sub> and SrTiO<sub>3</sub> layers due to the well-known polar catastrophe mechanism [2] in the origin of 2DEG. Thus, series experimental findings had been performed and theoretical investigations as well for a better understand on the 2DEG formation at LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interfaces [4, 5, 6, 7, 8, 9, 10].

Another type of 2DEG systems is the one found at an amorphous/crystalline interface [3]. These two types have a similar physical properties in term of superconductivity, potential-well depth, etc. [11, 12, 13], but also many differences as well, i.e. the a-2DEG has less lattice strain at the interface, higher interface carrier density and fewer requirements for growth.

Oxygen vacancies are considered as another possible origins of electron sources at the interfaces [14, 15] and the main reason in the formation of 2DEG system at the surface of SrTiO<sub>3</sub> [16, 17]. Considerable studies on the origins of oxygen vacancies and their role in the formation of 2DEG have been reported [11, 18, 19]. However, according to literature, almost all the studies that carried out the formation of 2DEG at SrTiO<sub>3</sub> surface have been done on perfectly crystalline samples generally grown by Pulsed Laser Deposition (PLD) or Molecular Beam Epitaxy (MBE). Yet, all these techniques require specific growth conditions such as high temperature ( 600°C), crystalline substrate etc, they are time-consuming and expensive as well which is not suitable for applications from the economical point of view. Starting from these reasons, many researches have carried out the properties of SrTiO<sub>3</sub> thin films by using other growth techniques. Dubourdiou has reported the dielectric properties of SrTiO<sub>3</sub> thin films deposited by MOCVD with respect to thickness and composition [20], S H Nam et al discussed the electrical properties of SrTiO<sub>3</sub> thin films deposited on Si(100) substrate by RF magnetron sputtering [21]. In this work, we aim to study the quality of SrTiO<sub>3</sub> films deposited on crystalline Si substrate terminated with amorphous SiO<sub>2</sub> layer by RF magnetron sputtering, their structure and composition by comparing them with the surface state of single SrTiO<sub>3</sub>(100).

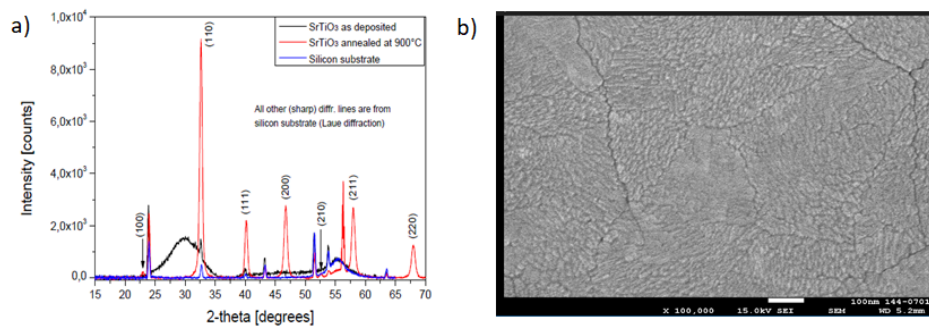
## EXPERIMENTAL METHODS

The films were prepared by the RF (13.56 MHz) magnetron sputtering using BOC Edwards TF 600 coating system. Before films growth, the deposition chamber was evacuated to a base pressure of  $2.10^{-4}$  Pa. Substrates were cleaned by ion etching in argon plasma by applying RF power of 200 W for 15 minutes at 0.2 Pa. A pure target of SrTiO<sub>3</sub> was placed on a magnetron connected to RF power supply. The deposition was kept under constant discharge RF power (400 W). The films were deposited on amorphous Si substrate at 400°C in argon atmosphere at constant pressure 0.6 Pa. Thickness of the films was in the range of 70 to 100 nm.

The structure of the films was studied by X-Ray diffraction (XRD) using an automatic powder diffractometer XPert Pro with CuK $\alpha$  radiation. XRD patterns were collected using the asymmetric  $\omega$ - $2\theta$  geometry with  $\omega=0.5^\circ$  from 15 to 70 degrees in  $2\theta$  scales [23]. A line profile analysis of the strongest lines was performed in order to calculate the crystallite sizes of the films by procedures based on Voigt function [24, 25].

The surface morphology of the films was carried out using a scanning electron microscopy JOEL JSM 7600F operated at 30 kV (field emission (Schottky) with a resolution of 1 nm at 15 kV) with an Energy Dispersive X-ray (EDX) SDD detector Oxford Instruments X-Max attached.

We characterized electronic properties by photoemission. Core levels were measured by X-Ray photoemission spectroscopy (XPS) using Mg K $\alpha_{1,2}$  radiation ( $\hbar\nu=1256$  eV) and the valence band by Ultraviolet Photoemission Spectroscopy (UPS) with HeII radiation ( $\hbar\nu=40.8$  eV). In the photoemission experiment one needs to distinguish between two different approaches. Angle-resolved measurements are required for single crystal samples because they allow to accede to the  $k$ -vector of the initial state. Angle integrated measurements are used for polycrystalline samples [22], as in this case  $k$ -vector information is blurred by integration over all electronic states in the Brillouin zone.



**FIGURE 1.** a) XRD patterns of STO thin film as deposited (black), after a heating treatment at 900°C (red). The blue represents the patterns of Silicon substrate. b) SEM micrograph of STO thin film

## RESULTS AND DISCUSSION

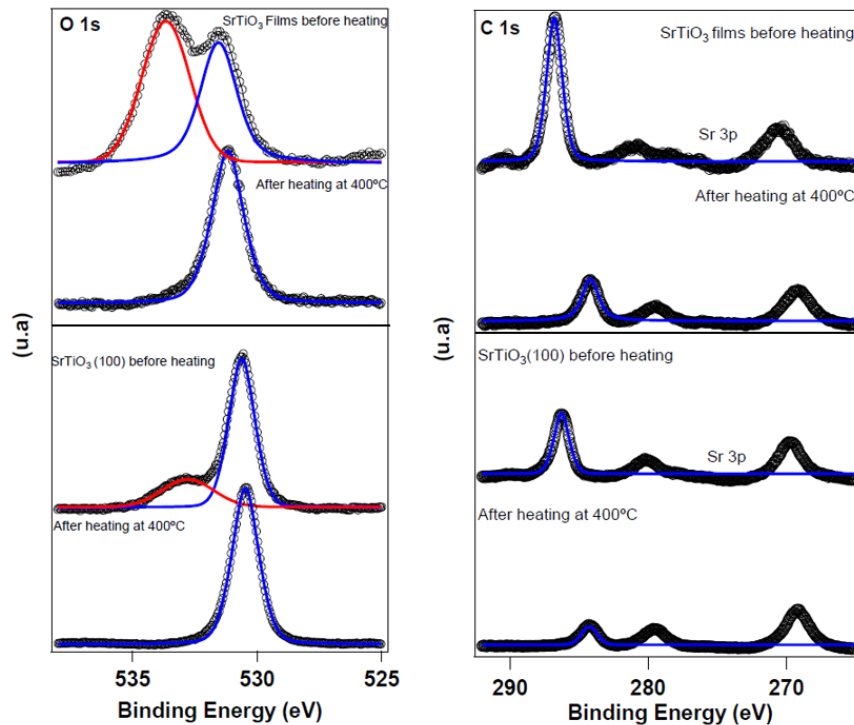
### 1. Structural and Surface Properties

The XRD patterns of the as-deposited and annealed SrTiO<sub>3</sub> films are represented in Figure 1(a). The broad lines of as-deposited SrTiO<sub>3</sub> show that the films are amorphous. The amorphous nature of the as-deposited films is due to the growth method and the experimental conditions during the deposition, considerably low growth temperature. After the heating treatment at high temperature (900°C), these lines changed to sharp lines of SrTiO<sub>3</sub> having a polycrystalline structure with a preferred orientation in the (110) direction. The average dimension of the diffracting domains (crystallites) is about 50 to 60 nm. Figure 1(b) illustrates the SEM micrography of the annealed SrTiO<sub>3</sub> films. It can be seen that the surface of these films which have polycrystalline structure is rough with grain boundaries. The SEM image also confirm the size of crystallites obtained from the XRD data.

### 2. Electronic Properties

Due to a short mean free path of photoelectrons (typically 1 nm), the photoemission measures only top most layers of the sample. So, a cleaning procedure is to be applied to remove a contamination film sitting on the surface. We applied the same approach of surface preparation for both, polycrystalline films and the crystal:

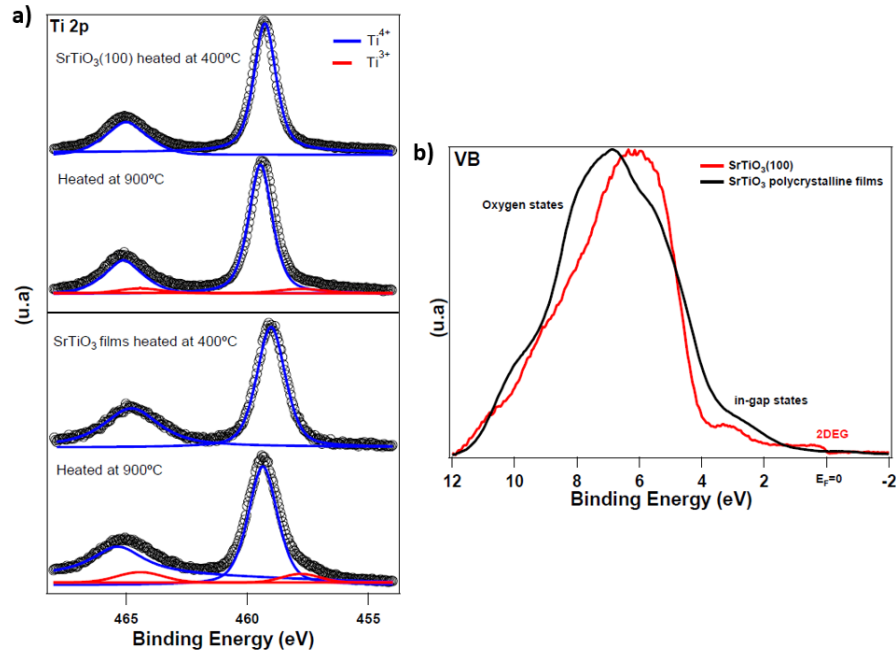
- i. After the transfer in the vacuum the samples were cleaned by heating at 400°C (that is the same temperature as used during the films deposition) at a base pressure of  $2 \cdot 10^{-9}$  mbar for 3 hours,
- ii. Samples were then heated at 900°C in vacuum ( $P=5 \cdot 10^{-9}$  mbar) for 5 hours.



**FIGURE 2.** a) O 1s and b) C 1s core levels of SrTiO<sub>3</sub> films and crystal before and after they were heated at 400°C in the vacuum, respectively.

O 1s and C 1s core levels were first measured, after introducing the films and the crystal samples in the vacuum and after heating at 400°C. The resulting spectra are represented in Fig.2(a) for O 1s and Fig.2(b) for C 1s, respectively. Before the cleaning procedure described above, O 1s spectra (Fig.2(a)) show two peaks around 531 eV and 533 eV while only the main peak at 531 eV was observed after the cleaning in both, films and crystal samples. In Fig.2(b),

C 1s spectra show an intense peak at 286.5 eV for films and crystal after introducing in the vacuum. The intensity of the peak is considerably reduced and the peak is shifted to 284.8 eV after the cleaning procedure at 400°C. When samples are exposed to the air, the main contamination is build by hydrocarbons and by C-O, C=O radicals. The heating procedure removes a majority of the contaminants. Clearly, only one component of O 1s is detected and corresponding to oxygen in SrTiO<sub>3</sub>. This is corroborated by the reduced C 1s signal. However, a presence of residual and shifted carbon signal is still detected on the cleaned surface. It testifies that the carbon atoms are presumably forming sp<sup>3</sup> and/or sp<sup>2</sup> bonds, a signature of graphitic-like compound. In the case of SrTiO<sub>3</sub> films, carbon can be present in the bulk of the samples, as the preparation is performed in rather low vacuum (2.10<sup>-4</sup> Pa) conditions.



**FIGURE 3.** a) Ti 2p core levels of SrTiO<sub>3</sub> films and crystal before and after they were heated at 900°C in the vacuum. The corresponding fits of the spectra describe different valence states: Ti<sup>4+</sup> in blue for and for Ti<sup>3+</sup> in red. b) Valence band of SrTiO<sub>3</sub> polycrystalline films (blue) and crystal (red) after they were heated at 900°C in the vacuum, representing the 2DEG at Fermi level, in-gap states and oxygen bands.

Figure 3(a) shows Ti 2p core levels measured by XPS for SrTiO<sub>3</sub> films and single crystal respectively, heated in the vacuum at 400°C and then annealing at 900°C for 5 hours with corresponding fit data. In the following, Ti 2p<sub>3/2</sub> will be discussed since the spectrum is more intense than the one for Ti 2p<sub>1/2</sub>. As it can be seen in the figure, for both films and crystal, after heating at 400°C, Ti 2p<sub>3/2</sub> shows a single peak at 459.5 eV which corresponds to the Ti<sup>4+</sup> valence state existing in SrTiO<sub>3</sub>. By reaching high temperature (900°C), a low binding energy shoulder appears in the Ti 2p<sub>3/2</sub> spectra at 457.7 eV in case of polycrystalline films and single crystal as well. The energy difference between these two states is about 1.8 eV which is equal to the chemical shift between Ti<sup>4+</sup> and Ti<sup>3+</sup> valence states. The same result was reported by many previous studies on SrTiO<sub>3</sub> single crystal. According to references [18, 26] the formation of Ti<sup>3+</sup> represents a clear signature of a reduced surface, consistent with the formation of a metallic-like Fermi edge. To test this hypothesis on polycrystalline films, we measured the valence band at the surface of films and single crystal SrTiO<sub>3</sub>(100) after they were heated at high temperature of 900°C in vacuum.

Figure 3(b) shows valence band spectra measured with photon energy of 40.8 eV. The main structure between 4 and 8 eV represents the O 2p states and the band gap is about ≈3.2 eV as confirmed, for example, by [16, 18]. Other important features in these spectra are the 2DEG peak at Fermi level clearly observed only on the surface of the crystal and the in-gap state between 1.5 and 3.5 eV formed on both films and crystal surfaces. According to previous experimental findings, in-gap states are related to oxygen vacancies and are detected between 1 and 1.5 eV for samples measured at low and room temperature [16, 18, 19]. Theoretical models predict these states at binding energies between 2 and 4 eV [27]. The distribution of these states and their origins depend strongly on the growth

method, the structure and the surface state of the sample, which can lead to different binding energies and/or intensities. As deduced from XRD patterns and SEM images, the films evolve to polycrystalline structure after they were heated at 900°C with a preferred orientation along (110) direction. Since the size of crystallites is relatively small (60 nm) compared to the diameter of photons beam (0.5 mm), during the photoemission measurement we are integrating over a large number of crystallites, mostly in the (110) direction. Y. Aiura et al. in reference [28] have reported the formation of 2DEG at Fermi level and some states in the gap for SrTiO<sub>3</sub>(110) heated at 800°C. The intensity of this 2DEG system becomes drastically weak after they heated up to 1000°C and only one state at 1.1 eV has been seen in the gap. They related this difference in the spectra directly to the surface structural change. In our experiments, the polycrystalline films were heated up to 900°C and all the crystallites have not the same orientation. This may explain a very weak intensity at Fermi level, corresponding to the 2DEG peak, in our spectrum.

## CONCLUSION

Our observations show that the structure of SrTiO<sub>3</sub> films deposited by magnetron sputtering is amorphous and changes to polycrystalline when the films are heated at high temperature (900°C). We have used photoemission to observe the formation of 2DEG at the surface of SrTiO<sub>3</sub> polycrystalline films and of the single crystal at room temperature after they were annealed at 900°C. Our experimental findings indicate that the structure and electronic properties of SrTiO<sub>3</sub> surface are highly dependent on experimental preparation conditions. Namely, they determine formation of oxygen vacancies which are considered to be an important factor in the formation of 2DEG at the SrTiO<sub>3</sub> surface. We found in gap states on polycrystalline films, probably referred to oxygen vacancies, similarly to those of single crystal.

## ACKNOWLEDGMENTS

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