



# Manipulating the ferroelectric polarization state of BaTiO<sub>3</sub> thin films



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## ABSTRACT

Controlling the ferroelectric polarization at macroscopic or microscopic levels is crucial in the framework of the development of ferroelectric materials used in yet challenging photo-electrochemical (PEC) cells and spintronic applications. We report here on polarization methods allowing to electrically polarize prototypical samples of BaTiO<sub>3</sub> (001) films. Epitaxial single crystalline layers were grown up to a thickness of 25 nm by atomic oxygen assisted molecular beam epitaxy on 1 at.% Nb doped SrTiO<sub>3</sub> (001) single crystals. The samples were both microscopically and macroscopically polarized using Piezoresponse Force Microscopy and electrochemical poling in an electrolyte respectively. In addition we demonstrate the possibility to retrieve a quasi-native mixed ferroelectric polarization state after annealing. These polarization methods may be applied to many other ferroelectric thin films.

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## 1. Introduction

There is currently a strong interest towards developing ferroelectric materials for various applications such as their use in multiferroics systems [1–4], photoelectrochemical cells (PEC) [5–8], and heat and gas sensors [9–11]. Ferroelectricity is a particular property of non-centrosymmetric materials exhibiting a spontaneous electrical polarization that can be reversed by the application of an external electric field. In the recent years, an impressive amount of contributions have focused on the ferroelectric properties of perovskite-based oxides such as BiFeO<sub>3</sub>, BaTiO<sub>3</sub>, PZT (Lead Zirconium Titanate) [12–17]. For such crystals, in the ferroelectric state, the barycenter of cations and anions in the unit cell are slightly spatially separated, inducing an electric dipole, *i.e.* an electric polarization. Dipoles rearrange themselves to minimize the sample energy forming different ferroelectric domains wherein the electric polarization points towards a given direction. Usually in an as-grown thin ferroelectric film the polarization is not uniform and the sample exhibits several ferroelectric domains where the polarization vector is pointing towards different directions. However, it is possible to control the orientation of the domains through the application of a saturating external electric field that allows the majority of the electrical dipoles within a domain to be oriented in a particular direction. Because of the wealth of technologically important applications deriving from the inclusion of ferroelectric layers in smart devices, it is of major

importance to understand and master the manipulation of the domains electric polarization orientation in thin films, at the microscopic and macroscopic scales. Recently multiferroic BiFeO<sub>3</sub> samples were considered within this framework. M. Singh et al. have reported on the local polarization of BiFeO<sub>3</sub> samples at the microscopic scale by applying a 10 V potential on an AFM tip [18]. Cao et al. have independently demonstrated the poling of BiFeO<sub>3</sub> samples at the macroscopic scale in a solution of Lithium Chlorate (LiClO<sub>4</sub>) in propylene carbonate [19]. In the present work we consider the prototypical ferroelectric material BaTiO<sub>3</sub> that has the major advantages as exhibiting a simple perovskite crystalline structure and featuring a para- to ferro-electric transition at relatively high temperature (130 °C for bulk BaTiO<sub>3</sub> and even much higher for strained layers [20]). Here we demonstrate routes to master the manipulation of the polarization state at microscopic and macroscopic scales of BaTiO<sub>3</sub>/Nb:SrTiO<sub>3</sub> samples, as well as the possibility to erase an applied polarization state by an air annealing of the very same samples.

## 2. Experimental details

The BaTiO<sub>3</sub> epitaxial layers were deposited on single crystalline 1 at.% Nb:SrTiO<sub>3</sub> (001) (*i.e.* ~0.5 wt% Nb) substrates using atomic oxygen assisted molecular beam epitaxy (AO-MBE), a technique that makes possible the deposition of single crystalline layers of controlled morphology, stoichiometry and thickness [21]. The doped substrate is conductive enough to use it as electrode during the BaTiO<sub>3</sub> overlayer poling procedures. The oxide layers were formed by thermal

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evaporating high purity metals from Knudsen cells, while exposing the sample to an atomic oxygen plasma (RF power = 350 W) in an ultra-high vacuum vessel ( $10^{-7}$  mbar working conditions,  $10^{-10}$  mbar base pressure). In order to have a homogeneous deposition and to reach the expected stoichiometry, the samples are rotated continuously around their surface normal during the deposition while kept at a temperature of  $\sim 900$  K. The oxide deposition rate was about 0.12 nm/min. To investigate the quality and the structure of the grown epitaxial films, *in situ* reflection high-energy electron diffraction (RHEED) patterns were acquired during the film growth. The thickness of the BaTiO<sub>3</sub> layers investigated in the present work lies in-between 15 and 30 nm. In this range no influence of thickness on any measurements could be observed within the techniques used in this paper which is noticeably consistent with the previous report by Kim et al. [22] who reported a critical thickness for ferroelectricity of BaTiO<sub>3</sub> of 4 nm and very little changes of the remnant polarization with thickness above 15 nm.

*In situ* XPS spectra of the Ba 3d, Ti 2p and O 1s core levels, using Al-K $\alpha$  radiation, were systematically recorded just after deposition to check the consistency of the BaTiO<sub>3</sub> layer stoichiometry with previous reports [21]. XPS spectra were also recorded after the different polarization treatments to check eventual compositional changes in the layers.

We used Atomic Force Microscopy (AFM) and Piezoresponse Force Microscopy (PFM) to investigate the surface morphology and ferroelectric properties of our samples respectively. The images were realized with a Brüker™ scanning probe microscope and a Nanoscope V controller.

The samples were electrically poled using two major strategies as depicted schematically in Fig. 1. (i) *Local poling* (microscopic scale) was achieved using PFM, which was used in writing mode to create well defined ferroelectric domains in our samples, by poling with various positive or negative potentials applied on the tip (in the [0 V, 10 V] range), Fig. 1a and b. Since, the back of the sample was always connected to the ground, the sample surface was thus exposed to potentials in the [−10 V, +10 V] range. This poling procedure will be hereafter referred to as PFM-poling. The tip velocity was 0.4  $\mu\text{m/s}$  and the writing resolution was 20 nm. (ii) *Macroscopic poling* was realized using a non-aqueous LiClO<sub>4</sub> electrolyte (0.1 M LiClO<sub>4</sub> in propylene carbonate), with a large electrochemical window (*i.e.* a large voltage range in between which the substance is neither oxidized nor reduced), in an electrochemical cell with 2 electrodes. The sample was mounted as the working electrode and a Pt wire as the counter electrode. The geometry of the experimental setup is shown on Fig. 1c and d and a scheme of the experiment is given on Fig. 1e. This poling procedure will be hereafter referred to as EC-poling. During the EC-poling procedure, the sample was kept at 0 V. Potentials of +8 V and −8 V were applied several times alternatively (while monitoring the current) on the platinum counter electrode (during 10 s each) in order to reinforce the ferroelectric state as proposed by Roelofs et al. [23]. To obtain a remnant electric polarization pointing towards the substrate (by convention called downward polarization), the last applied potential was +8 V. Indeed,

in a previous work [5], we demonstrated that +8 V EC-poling leads to downward polarization of the BaTiO<sub>3</sub> layer. Lastly the electric current monitoring is of crucial importance during EC-poling since overcurrent appeared to be strongly detrimental to the samples as we will demonstrate later in this paper.

The PFM-poled written ferroelectric domains were observed by PFM and Low Energy Electron Microscopy (LEEM). Beyond the recognized full field morphology characterization capabilities of LEEM [24,25], it has been previously reported that surface charge changes, expected when the ferroelectric polarization orientation changes, provide a visible LEEM contrast [26]. This phenomenon was used to observe ferroelectric contrasts between polarized and unpolarized regions of the sample regions. The samples were optically patterned by laser lithography and e-beam evaporation to include metallic Au landmarks on the sample surface that allow finding the PFM polarized regions easily. The 200 nm thick Au landmarks were evaporated on top of a 15 nm thick Ti seed layer. For a broader view, one may also use Kelvin probe force microscopy [27,28] or scanning surface potential microscopy [29] to map the surface charge changes due to different ferroelectric domains polarization orientations, and DARTSPFM for P–E loops measurements [30].

The high chemical stability in air of BaTiO<sub>3</sub>, as well as of the Nb:SrTiO<sub>3</sub> substrates, allows for air annealing at high temperature without composition changes. Since annealing above the ferroelectric order-disorder temperature is easily possible in air, it appears as a method of choice to “reset” the ferroelectric domains orientation after PFM- or EC-poling. This was realized in a high temperature furnace above the Curie temperature of BaTiO<sub>3</sub> with typical rates of 14 °C/min up to 280 °C.

### 3. Results and discussion

#### 3.1. Growth

*In situ* RHEED patterns were observed and acquired during film growth to monitor the quality and the structure of the grown epitaxial samples. Upon growth, the RHEED patterns switched from features typical of the perovskite Nb:SrTiO<sub>3</sub> substrate to the ones characteristic of the BaTiO<sub>3</sub> thin epitaxial film (Fig. 2), similarly to observations reported using undoped SrTiO<sub>3</sub> (001) substrates [21]. By convention we indexed the reciprocal space using the reciprocal space unit vectors (10)\* and (01)\* to describe the primitive reciprocal surface lattice as depicted in Fig. 2e. The RHEED reciprocal space streaks remain mostly 2D rod-like with some hints of island formation for high thicknesses (intensity modulations along the streaks at high thickness). The surface lattice parameter can easily be extracted from the streaks position while the error bar is derived from the parameter dispersion obtained using several azimuths. The surface lattice parameter evolution (Fig. 2f) reveals an almost complete structural relaxation for thicknesses above 10 nm. From our RHEED observations we can conclude that the layers are mainly epitaxial, single crystalline and flat.

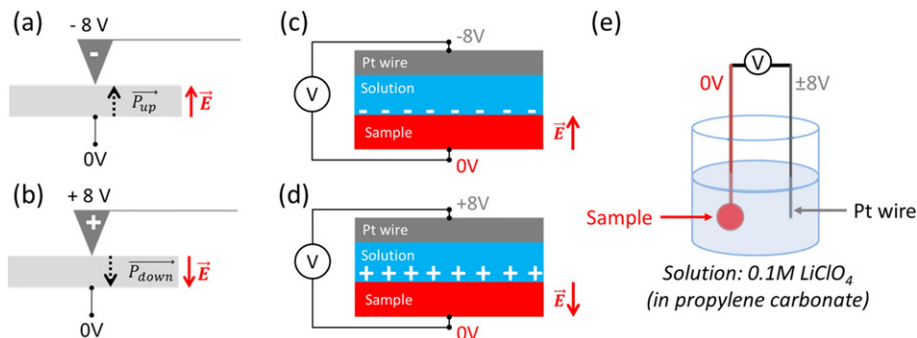


Fig. 1. (a) to (d) Geometry and expected polarization states using PFM-poling with −8 V (a) and +8 V (b) poling potentials and using EC-poling with −8 V (c) and +8 V (d) poling potentials. (e) Scheme of the EC-poling experiment.

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