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Short communication

# Band bending at free Pb(Zr,Ti)O$_3$ surfaces analyzed by X-ray photoelectron spectroscopy

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## ARTICLE INFO

## ABSTRACT

This paper analyses in detail the core levels evolution of Pb(Zr,Ti)O$_3$, i.e. Pb 4f, Zr 3d, Ti 2p, O 1s in various conditions: absolutely freshly prepared sample, sample stored under air, and the effects of in vacuum annealing. The aim of the study is to quantify separately the chemical reactivity at the surface and the band bending effects due to the ferroelectric polarization. It is found that freshly prepared samples present mostly inwards (↓) polarization. This phenomenon is mostly revealed by the Ti 2p and O 1s spectra, manifested as a distinct component with 1.8 eV lower binding energy in the O 1s binding energy and by 1.1 eV in the Ti 2p binding energy. Sample aging under air suppresses the inwards polarization, and most signal comes from surfaces not presenting ferroelectric permanent polarization perpendicular to the sample surface. This process conducts also to the formation of Pb(CO$_3$)$_2$ on the surface. Annealing to temperatures up to 400 °C stabilizes a surface composed by a main part of surface without polarization perpendicular to the surface, and with some areas presenting outwards (↑) polarization. These areas have, most probably, different terminations, the polarized area being (Ti,Zr)O$_2$ terminated.

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## 1. Introduction

Ferroelectric thin films are widely studied nowadays, owing to a tremendous number of applications [1,2]. To date, however, the details of charge distribution near the surface in presence of a polarization perpendicular to the surface is not yet elucidated. Charge accumulation near surfaces induces surface depolarization in the films and the relaxation of the tetragonal distortion, responsible for the occurrence of ferroelectricity. The interplay between the two phenomena (charge accumulation and lattice relaxation toward the cubic geometry) is still subject of debates, since most older experiments were performed on polycrystalline samples, where grain boundary effects intervene in a complicated manner. At the same time, modern synthesis methods, such as pulsed laser deposition, allow the controlled growth of single crystal ferroelectric films with well-defined stoichiometry and minimum surface roughness [3,4]. Such samples are well suited for the detailed study of the afore mentioned phenomena. In this work, we will use a model developed by Pintilie and Alexe [5] and applied to Pb(Zr,Ti)O$_3$ (PZT) with several compositions [6]. Briefly, the 'apparent built-in potential' at a ferroelectric interface is modified owing to a polarization $P$ perpendicular to the surface of the ferroelectric by the value $eP\delta/\epsilon$, where $\delta$ is the distance between the polarization charge sheet and the physical termination of the ferroelectric. The parameter $\delta$ may be viewed as a typical length on which the band bending at the surface of the ferroelectric occurs. Fig. 1a and b depicts the two situations, with polarization outwards (↑), or $P^{(+)}$, i.e. oriented from the ferroelectric to the vacuum, or inwards (↓), or $P^{(-)}$, i.e. oriented from the vacuum to the ferroelectric. $\epsilon = \epsilon_0 \epsilon_r$ is the permittivity of the ferroelectric, and $e$ is the elementary charge.

An open question remains about how charge carriers from the crystal re-distribute to compensate this band bending. For instance, in the derivation of the correcting factor for the built-in potential, a constant charge distribution was assumed in the depleted region, governed by ionized impurities. Interestingly, by taking into account usual values for PZT, i.e. $\epsilon_r = 180$, $P = 1$ C/m$^2$ [7], $\delta = 3$ nm [6], a band bending of about 1.88 eV is obtained, which is near half of the PZT bandgap, 3.4–3.9 eV [2,5,6]. From Fig. 1 it may be inferred that, in case of strong polarization or low dielectric constants, the band curvature will be eventually quenched as soon as one of the bands (conduction or valence band) approaches the Fermi energy; in this case, free carriers (electrons for the $P^{(+)}$ case, holes for the $P^{(-)}$ case) will stabilize in the neighborhood of the free surface, with consequences opposite to that of the static polarization charge. Also, more complicated phenomena might occur, such as space charges, partial screening, and misfit strain [8]. Moreover, all usual electrical measurements (IV curves, CV characteristics, ferroelectric hysteresis loops) influence the surface of the ferroelectric via the metal contacts [6,9].

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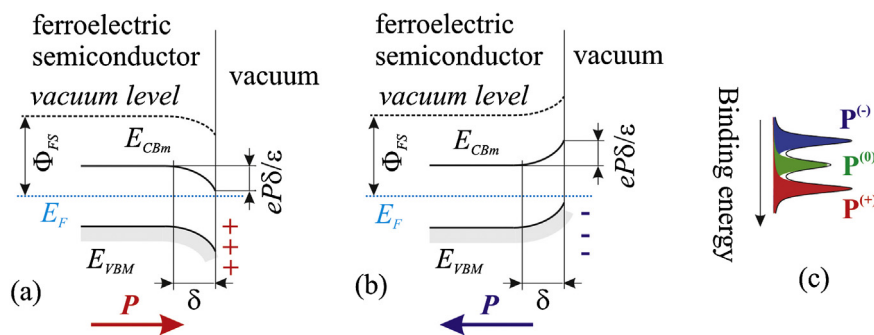
**Fig. 1.** (a) Represents the band bending at an ideal ferroelectric surface with outwards (↑) polarization; (b) the similar case, for a ferroelectric with inwards (↓) polarization; (c) the way such polarization may be detected as distinct components in X-ray photoelectron spectroscopy. $E_{CBm}$ represents the energy of the conduction band minimum, $E_{VBM}$ the energy of the valence band maximum, $E_F$ the Fermi energy, $\Phi_{FS}$ the work function of the ferroelectric semiconductor, $P$ the polarization (positive when pointing outwards), $\delta$ the depth where one may find the polarization charge sheet according to Refs. [5,6], $\varepsilon$ is the permittivity of the ferroelectric, and $e$ the elementary charge.

Therefore, it is desirable to find a method to derive experimentally the band bending of free ferroelectric surfaces. Not only this method may be used to infer model parameters such as $\delta$, but such information may also be used to gain more insight into the intimate characteristics of charge re-distribution, screening, surface states, etc. High resolution X-ray photoelectron spectroscopy (XPS) is a highly recommended method for such investigations. Firstly, it is an element specific method, consequently eventually separate shifts on different kind of atoms may be outlined. Secondly, its high surface sensitivity (1–2 nm [10]) makes it the ideal techniques to investigate surface core level shifts. It has been recently shown how in situ poling of $BaTiO_3$ samples revealed a measurable relative core level binding energy shift of about 1 eV when the samples are poled $P^{(+)}$ and $P^{(-)}$ [11]. Nevertheless, such shifts are dependent on the nature of the contact used to polarize the ferroelectric film. It seems that in the absence of such a contact, by a technique such as mirror electron microscopy (a version of low energy electron microscopy), a much lower shift is observed between $P^{(+)}$ and $P^{(-)}$ regions of a PZT sample [12]. This is intriguing, since it is to be expected that this shift will be even larger for PZT, owing mainly to its higher ferroelectric polarization (100 μC/cm$^2$ [7]), to be compared with ∼25 μC/cm$^2$ for $BaTiO_3$.

Consequently, more data on high resolution photoemission spectra for PZT are needed. These data should be accompanied by a special care to eliminate all charging effects occurring in photoelectron spectroscopy, in order to highlight specific core level shifts intimately connected to the ferroelectric polarization of the sample. Also, chemical reactivity must also be taken into account and the stoichiometry analysis should isolate all possible interface compounds (e.g. carbonates [3] or oxides [4]); finally, the band bending analysis should be performed only to those XPS components belonging to the ferroelectric surface. This is the main purpose of this study.

This work is part of an integrated work on interfaces formed between ferroelectrics and various metals [4]. In the framework of this comprehensive work, one had the opportunity to work on various PZT substrates, with different ages: either they were stored under air a given time, either they were introduced immediately after preparation into the photoemission analysis chamber, and some of them were annealed into vacuum. By summarizing all these data, we aim to find some common features of these samples and also to evidence the effect of aging under air and of the thermal treatments on these samples.

## 2. Experimental

Single crystal 200 nm thick $PbZr_{0.2}Ti_{0.8}O_3$ films are grown by pulsed laser deposition (PLD) on $SrTiO_3$ with a $SrRuO_3$ buffer layer. The PLD setup (manufactured by Surface, Germany) uses KrF radiation (with 248 nm wavelength), pulses of 0.7 J energy with 20 ns duration. The repetition rate was 5 Hz, and the laser fluence 2–3 J/cm$^2$. During the PZT growth, the substrate was heated at 575 °C and the partial $O_2$ pressure was 0.2 mbar [4]. The samples are introduced afterwards in the XPS chamber. Therefore, the samples experience air exposure (from several minutes to several months) between preparation and XPS analysis. The XPS machine (manufactured by Specs, Germany) operates with monochromatized Al K$_{\alpha1}$ radiation (1486.74 eV) and a 150 mm hemispherical electron energy analyzer. The best experimental resolution achieved is 0.35 eV, whereas in the conditions for the actual experiments (pass energy 30 eV), the estimated resolution (total full width at half maximum) on Ag 3d core level is 1.0 eV, including the excitation line width and the core hole lifetime of the analyzed level (Ag $3d_{5/2}$).

The experiments described here are performed on the following samples: (a) a 'fresh' sample, loaded into the XPS machine immediately (within ten minutes) after preparation; (b) the '1 week old' sample; (c) the '1 year old' sample. This sample was annealed under ultrahigh vacuum at 200, 300, 400 °C. The base pressure in the whole surface science cluster (basically composed by an XPS analysis chamber and a molecular beam epitaxy chamber) is in low $10^{-10}$ hPa vacuum range. During the first heating of the samples (2 h at 200 °C), the pressure increased into mid $10^{-8}$ hPa vacuum range for 20–30 min, whereas during the subsequent annealing (also 2 h at 300 °C and at 400 °C), the pressure in the preparation chamber did not exceed mid $10^{-10}$ hPa.

As mentioned in the Introduction, special care was undertaken to compensate all possible charging effects due to the photoemission process. By several trial-and-errors, it was found that, by operating with 250 W anode power and with a flood gun set at 1 eV beam energy and 100 μA electron current, the core levels are quite stable in time, and, also, the main component of the C 1s peak does not move from the 'standard' value of 284.6 eV accredited in the XPS community. These C 1s core level spectra are collected in the Supplementary information.

The data are analyzed by fits with Voigt profiles and their integrals, computed by using Ref. [13]. The software analysis routines are written by one of the authors. More details on the core levels involved in PZT samples are explained in Ref. [4]. Let us just emphasize that we identified a Pb Auger line ($M_5N_2N_2$) lying in the same region as the Ti 2p core level, therefore, in addition to the two doublets used in this deconvolution, we had to add a singlet to simulate this Auger line. Since all results presented here are obtained with monochromatized Al K$_{\alpha1}$ radiation, it was difficult to get rid of this Auger line e.g. by switching the anode to Mg K$_\alpha$ (unmonochromatized). This introduces satellites in the XPS spectra and, also, the