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Effective piezoelectric coefficient measurement of $BaTiO_3$ thin films using the X-ray diffraction technique under electric field available in a standard laboratory

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ABSTRACT

The structural response of piezoelectric thin films to applied electric fields is an important key for understandings the physical properties, more especially the determination of piezoelectric constants. In this context, despite low deformation, structural investigations by X-ray diffraction to obtain a fairly accurate answer represent a great interest (nondestructive, easy to use, and available in most of laboratories). Today, with the widespread use of high-resolution X-ray diffraction technique, the precision needed for such small deformations can be obtained on a conventional laboratory diffractometer and thus used to determine the piezoelectric coefficients in a thin film. This work presents an operating protocol using laboratory HR-XRD technique to determine the d_{33}^{eff} effective piezoelectric coefficient in a $LaNiO_3/BaTiO_3/Nb$ doped $SrTiO_3$-(1 0 0) thin film elaborated by Pulsed Laser Deposition. This one was determined to $50 \pm 4\,pm\,V^{-1}$. An asymmetry in the structural deformation was observed and discussed by considering the trapping charge in the interface and the clamping effect induced by epitaxial growth. Finally, it has also been shown that the study on the structural deformation monitored in temperature, allows also the determination of phase transition temperature (ferroelectric/paraelectric) in the thin film.

1. Introduction

Piezoelectric materials, such as barium titanate ($BaTiO_3$) and lead zirconate titanate (PZT), are widely used in several types of sensors (pressure, accelerometer ...) [1] and MEMs (Micro-ElectroMechanical systems) actuators [2], due to their excellent responsiveness and their high piezoelectric coefficients. Generally, this class of materials are characterized by their piezoelectric coefficients [3], namely d_{ij} and g_{ij}, but also by material constants such as S_{ij}, e_{ij} and k_{ij}.

The Electromechanical Coupling Factor (k_{ij}) represents the ability of a piezoelectric material to transform electrical energy to mechanical energy and vice versa. The first subscript denotes the direction along which the electrodes are applied and the second subscript denotes the direction along which the mechanical energy is applied or developed [4]. The dielectric coefficient (e_{ij}) determines the charge per unit area in the i-axis due to an electric field applied in the j-axis. The elastic compliance constant (S_{ij}) is defined as the strain produced per stress unit. The first subscript indicates the direction of strain and the second is the direction of stress. The piezoelectric constant (g_{ij}) represents the electric field developed along the i-axis when the material is stressed along the j-axis [5]. Finally, the piezoelectric constant (d_{ij}) is the ratio of the strain in the j-axis to the electric field applied along the i-axis when all external stresses are held constant [5]. These coefficients have a tensor form and the Voigt notation is commonly used. Indeed, the piezoelectric constant (d_{ijk}) is described as third-rank tensor with three indices (i, j, k) running through 1–3. However, this tensor is symmetric in j and k which reduces the number of independent coefficients to (3×6) matrix, where two indices (instead of three) are used to access all 18 independent piezoelectric constants [6]. So, the suffices j and k are usually replaced by single suffix (new j) running from 1 to 6 ($11 \rightarrow 1$; $22 \rightarrow 2$; $33 \rightarrow 3$; $23 \rightarrow 4$; $13 \rightarrow 5$; $12 \rightarrow 6$). Thus, the indexes refer to different directions within the material coordinate system

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such as the numbers 1, 2 and 3 are associated with the coordinates *x*, *y* and *z* directions and the numbers 4, 5 and 6 are associated with shear around *x*, *y* and *z*, respectively [3].

The determination of these piezoelectric coefficients is therefore an essential element to characterize a new piezoelectric material and more specifically, the piezoelectric constant (d_{ij}), if the materials is intended to be used in electromechanical systems [7]. This coefficient can be determined by different methods, either direct or converse piezoelectric effect. Among the first category, one can measure the charge induced when a stress is applied (such measures can be found inter alia in the Berlincourt method [8]), the impulse method with the mini force hammer [9] or the sample flexure technique [10]. The d_{ij} coefficient can also be determined by converse piezoelectric effect, where the deformation is measured by applying external electric field. This method of measurement is used, among other for techniques of Double Beam Laser interferometry [11], Laser Doppler Vibrometer (LDV) [12] and Atomic Force Microscopy (AFM) in piezoresponse mode [13].

X-ray diffraction is already widely used to study the polarization switching, phase transitions or structural deformations in piezoelectric materials either in the form of single crystal or as ceramic ones. X-ray studies make use of the deformation of the lattice and the resulting shift of Bragg reflections. This shift induced by an external electric field enables a direct measuring of the piezoelectric effect in the material. The first studies concerning influence of the electric field on the shape and angular position in Laue films go back to the 30's by Němejcová and Brož [14]. But, to the best of our knowledge, we had to wait the mid-70's to see the first theoretical study aiming to determine the piezoelectric coefficient from XRD measurements [15] followed by experimental studies on a quartz crystal [16]. The deformation of the crystal can be easily observed for materials with a significant piezoelectric coefficient and/or on single crystals giving very fine reflections and thus well-defined peaks positions. However, in other cases, we need to accurately determine the angular position and its small changes under the influence of an external electric field to obtain the value of the strain with a good enough definition. Nowadays, the High-Resolution Synchrotron X-ray Diffraction (HR-XRD) technique provides very high accuracy on the angular position (≈0.0001°), which allows a precise measure of the effective piezoelectric coefficient. Many studies have been carried out on single crystals or ceramics as $LiNbO_3$ [17], $AgGaS_2$ [18], KD_2PO_4 [19], KH_2PO_4 [20], $KTiOPO_4$ [21], lead zirconate titanate [22,23], $Li_2SO_4{\cdot}H_2O$ [24], $Ca_3TaGa_3Si_2O_{14}$ [25]. The time-resolved stroboscopic X-ray diffraction technique presents also a great interest for the study of piezoelectric materials [26,27]. Among all studies and to the best of our knowledge, the studies performed on thin films are scarce and require the use of synchrotron diffraction [28,29].

This work aims to measure the structural deformation experienced by a $BaTiO_3$ thin film under an electric field using a conventional laboratory X-ray diffractometer. It will allow us to determine the value of the "effective" piezoelectric coefficient, that can be, more particularly in the case of an epitaxial film, different from the intrinsic bulk one. In a second step, we will also study the deformation of the film following the direction of the applied electric field highlighting a clamping effect due to the epitaxial growth and attributed to the presence of charge trapping at the electrode–BTO interface. Finally, we will also determine the effective Curie temperature by performing HR-XRD measurements in temperatures.

Synthesis methods commonly used for the preparation of thin films of $BaTiO_3$ are the sol–gel way [30,31], spray pyrolysis technique [32], hydrothermal method [33], magnetron RF sputtering [34], Chemical Vapor Deposition (CVD) [35,36], Pulsed Laser Deposition (PLD) [37–39] or Molecular Beam Epitaxy (MBE) [40]. These preparation techniques, allow to control the crystal growth of the thin film according to the nature of the substrate and thus to obtain a better piezoelectric coefficients when compared to ceramic. In this work, we use the PLD technique to obtain epitaxial heterostructures with good crystallinity and low mosaicity.

2. Experimental

In order to apply the electrical field, it is necessary to have lower and upper electrodes. In this approach, Nb doped $SrTiO_3$ (conductive substrate while the non-doped is an insulator) will act as the lower electrode and $LaNiO_3$ (conductive oxide) as an upper electrode. The following hetero-structure: $LaNiO_3/BaTiO_3/SrTiO_3$:Nb-(1 0 0) will realized via PLD technique.

Nb doped (1.4% at.) $SrTiO_3$-(1 0 0) (also named STO:Nb) substrates (Crystal GmbH, Germany) were first ultrasonically cleaned in acetone then in ethanol for 5 min and finally attached to a heater plate using silver paste.

$BaTiO_3$ target was synthesized by sol–gel method using Titanium (IV) t-butoxide $Ti(OC_4H_9)_4$ (Strem Chemicals, 99.95%) and barium acetate $Ba(CH_3COO)_2$ (Strem Chemicals, 99.9%) as starting precursors [41]. A first solution is realized by mixing the Titanium (IV) t-butoxide with glacial acetic acid and absolute ethanol at room temperature (molar ratio used is 1:3:6, respectively). It is worth to note that titanium (IV) t-butoxide is known to be hydrolyzed rapidly in the presence of water [42]. With this constraint, the employment of glacial acetic acid is important to avoid hydrolysis of the titanium precursor in the first step. Separately, a second solution is produced independently by dissolving the barium acetate solution in acetic acid (6 mol L^{-1}). This solution is added to the first solution under vigorous stirring and with a Ba/Ti molar ratio 1:1. A translucent gel is formed after 2 h. Then, the gel was dried at 120 °C during 8 h to obtain a xerogel. Finally, the xerogel is calcined at 700 °C during 4 h to obtain $BaTiO_3$. Note that $BaCO_3$ impurities can be observed if a portion of the titanium is hydrolyzed. We can remove these impurities by washing the powders with distilled water. Then, the powders were re-ground and placed in the uniaxial press to produce PLD targets (1 in. diameter). Finally, these targets were sintered at 1300 °C during 10 h. X-ray patterns, realized on the targets, confirmed the presence of the expected tetragonal phase, without detectable impurities.

$LaNiO_3$ target was synthetized by co-precipitation method [43]. Initially, a solution containing the La^{3+} ($La(NO_3)_3{,}6H_2O$ Strem Chemicals, 99.9%) and Ni^{2+} ($Ni(NO_3)_2{,}6H_2O$, Strem Chemicals, 99.9%) ions was prepared with a molar ratio of 1:1. In a second step, a solution of sodium carbonate (Na_2CO_3, Strem Chemical, 99+%) was also carried out. The two solutions were rapidly mixed by introducing the first solution in the CO_3^{2-} solution prepared with a large excess. The solution turns a pale milky green color corresponding to the co-precipitation of lanthanum and nickel carbonates. After Buchner filtration and drying at 120 °C, the resulting powders were then calcined at 700 °C for 10 h to obtain the $LaNiO_3$ powders. Finally, a target of 1 in. in diameter is prepared after unixal pressing and sintering at 900 °C for 15 h.

Thin films were synthesized from the PLD technique using a Compex Pro 102 Laser (KrF excimer laser operating at a wavelength of 248 nm). For $LaNiO_3$ and $BaTiO_3$ films, the synthesis conditions are: 2 J/cm^2 for the energy density, 4.5 cm for the target-substrate distance, 2 Hz for pulse repetition rates and 700 °C for substrate temperature.

The films were synthesized under dynamic conditions with O_2 pressure of 10^{-2} mbar, then rise to 200 mbar at the end of deposition. Cooling was achieved with a ramp of 10 °C/min. The deposition conditions were: 3000 pulses for each $LaNiO_3$ (LNO) electrode (0.17 Å/pulse) and 8000 pulses (0.19 Å/pulse) for $BaTiO_3$ (BTO).