Heterogeneous distribution of B-site cations in BaZr_xTi_{1-x}O₃ epitaxial thin films grown on (001) SrTiO₃ by pulsed laser deposition

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Abstract

The isovalent substitution of Ti⁴⁺ by Zr⁴⁺ in BaZr_xTi_{1-x}O₃ modifies the dielectric character of ferroelectric BaTiO₃ yielding different behaviours such as relaxor, polar cluster, etc. The dynamic coupling between BaTiO₃ polar nanoregions and BaZrO₃ nonpolar ones as well as microstrain between them are thought to be behind such a rich phase diagram. However, these short-range compositional variations are elusive to detect and this topic is thus rarely addressed. We have grown epitaxial thin films of BaZr_xTi_{1-x}O₃ on (001)-oriented SrTiO₃ substrates by pulsed laser deposition sweeping the entire composition range between BaTiO₃ and BaZrO₃ in increments of 0.1 in *x*. Several characterization techniques (AFM, TEM, XRD, Raman spectroscopy) were used for this research in order to understand the morphological and structural properties of the deposited films. Ellipsometric measurements allowed the calculation of the band gap energy of the films. This work demonstrates the existence of a heterogeneous distribution in the substitution of titanium by zirconium yielding relaxor and polar cluster nanoregions.

1. Introduction

The $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) perovskite shows a rich variety of dielectric properties such as conventional ferroelectricity ($x < 0.15$), diffuse phase transition ($0.15 < x < 0.25$), relaxor ferroelectricity ($0.25 < x < 0.75$) and polar cluster behaviour ($x > 0.75$) [1]. Homovalent B-site doping (e.g. Zr^{+4} , Hf^{+4} , Ce^{+4} , Sn^{+4} ...) in BaTiO_3 disrupts the long-range order of Ti^{4+} off-centre displacement [2]. This results in a broadened transition around Curie's Temperature T_C and a ferroelectric-relaxor crossover induced by composition, apart from a decrease of T_C . Relaxors present an extremely diffuse and frequency-dispersive dielectric permittivity maximum which is believed to be caused by the polarization of nanoscaled regions where permanent ferroelectric order exists [3]. In particular, ferroelectric regions in BZT are expected to be separated by non-polar Zr-rich regions [3-5] leading to an inhomogeneous cationic distribution and mechanical stress [6]. On the other hand, there are evidences [3,4,7-9] that BZT presents some singularities as compared to canonical relaxors and it may therefore represent a worth studying subclass.

Raman and dielectric permittivity studies [1,10,11] have shown that at room temperature BZT ceramics present a tetragonal to orthorhombic transition at around $x \approx 0.03$, orthorhombic to rhombohedral at $x \approx 0.08$ and rhombohedral to cubic at $x \approx 0.2$. However, the solid solution of BaTiO_3 (BTO) and BaZrO_3 (BZO) presents a nonzero enthalpy of mixing [12] and phase coexistence has been reported as well [2,13,14]. The local structures of relaxor compositions have been studied in detail by neutron pair distribution function analysis [15], neutron total scattering measurements [16] and extended X-ray absorption fine structure [5]. It was found that, clearly deviating from the cubic average BZT structure, the Zr-O and Ti-O bond distances remain close to the values of the respective end compounds and the Ti displacements are similar to those of BTO.

The eventual application in devices such as dynamic random access memories, microwave tunable devices and recently electromechanical transducers, has triggered the research on the dielectric and piezoelectric properties of BZT thin films. Nevertheless, complete structural studies including reciprocal space mapping are scarce.

Here we report on a study of the evolution of the structural properties of $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ heteroepitaxial films on (001) SrTiO_3 obtained by pulsed laser deposition (PLD) varying their composition ($x = 0, 0.1, \dots, 1$). The samples were analyzed by X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman

spectroscopy and ellipsometry. Strain relaxation mechanisms and growth mode of the films are also discussed.

2. Experimental

The BZT thin films were grown on (001) SrTiO₃ (STO) substrates by PLD using a KrF excimer laser (Lambda Physik 210i) with a fluence of 2.0 J/cm² and a repetition rate of 5 Hz. Stoichiometric targets of BaZr_xTi_{1-x}O₃ sweeping the entire composition range between BTO and BZO in increments of 0.1 in x were used (*i.e.* $x=0, 0.1 \dots 1$). The substrate temperature and oxygen pressure were set to 700 °C and 0.3 mbar respectively; 5 cm were used as substrate-to-target distance. After deposition, the samples were cooled down to room temperature under an O₂ rich atmosphere to minimize oxygen desorption. The thickness of the films presented here is 100 nm as verified by low angle X-ray reflectometry.

XRD experiments were carried out on a four circle diffractometer (PanAlytical Pro MRD) using Cu K_α radiation. Atomic concentrations were measured by wavelength dispersive spectroscopy (WDS) on a Cameca SX50 microprobe working at 15, 20 and 25 kV at five different film locations and using multi-voltage thin film analysis. AFM measurements were performed on an Agilent 5100 microscope working in either tapping or contact mode. Electrotransparent thin foils for transmission electron microscopy (TEM) examination were prepared in cross-section orientation ([010] zone axis) through conventional mechanical polishing and Ar⁺ beam milling. TEM imaging was carried out using a JEOL J2010F scanning TEM (STEM) microscope, with a hot field emission gun at 200 keV. Raman activity at room temperature was detected for all the compositions using a UV radiation source (He-Cd laser, 325 nm). The dielectric permittivity of BZT films at VIS-UV frequencies (2 to 5 eV) was obtained using a phase-modulated spectroscopic ellipsometer (SE). The spectra were interpreted by regression analysis using a multilayer model that assumes an ambient/roughness/film/interface/substrate structure. The interface and the surface roughness were modelled using the Bruggeman Effective Medium Approximation (EMA), where the dielectric permittivity was accounted by a weighted average of those of film and substrate, and those of air and film, respectively [17]. The optical properties of BZT were derived using the Herzinger-Johs parametric model.

3. Results and discussion

The BZT films showed very similar flat surfaces (Figure 1a) with roughness between 0.24 and 0.33 nm (calculated over $2 \times 2 \mu\text{m}^2$ measurement areas) which increased with the Zr molar fraction. Cross-section STEM (Figure 1b) and HRTEM images showed sharp film-substrate interfaces with edge dislocations.

Figure 2a shows the $\theta/2\theta$ diffractograms of the BZT films with different compositions. In all cases, only peaks associated to (00 l) reflections of BZT and STO are present. Therefore, the films are single phase and fully textured with (001) out-of-plane orientation. The BZT peak positions are shifted towards lower angles for increasing x , indicating an enlargement of the out-of-plane lattice parameter along with Zr content as further discussed below. The out-of-plane misalignment is low, as deduced from the narrow rocking curves of BZT (002) reflection with full width at half maximum (FWHM) around 0.15° (FWHM of STO $\sim 0.11^\circ$). Φ -scans around the (111) asymmetric reflection of BZT and STO (Figure 2b) were acquired to discern the in-plane texture of the films. In all cases, the fourfold symmetry of the unit cell diagonals without shifting between film and substrate peaks is observed. This corresponds to a single domain configuration in-plane aligned with the substrate lattice and thus, a [100]BZT(001)//[100]STO(001) cube-on-cube epitaxial relationship is derived.

In-plane and out-of-plane lattice parameters of BZT were obtained from XRD reciprocal space maps (RSMs) around (204) asymmetric reflection (Figure 3). The BZT peaks were located near to the fully relaxed positions and a broadening of the $q_{||}$ width was evidenced for films with higher Zr molar fraction. Figure 4a shows the dependence of cell parameters with the Zr molar fraction. Bezier-splines connecting the lattice parameters of bulk BZT are included as a guide to the eye. At low Zr content, $x=0$ and 0.1, the BZT unit cell is tetragonal with the elongated axis c along the out of plane direction, whereas the symmetry turns to cubic above that value. The c out-of-plane lattice parameter decreases slightly initially ($x < 0.2$) and then increases linearly, whereas the a in-plane lattice parameter raises throughout the entire composition range. The tetragonality c/a diminishes from 1.010 at $x=0$ (that of bulk BTO is 1.011) to 1.003 at $x=0.1$. The structural sequence found in the BZT films is roughly identical to that of BZT ceramics [1,10,11]. We should mention, however, that rhombohedral symmetry at $x=0.1$ could not be resolved owing to low-resolution optics, mosaicity and inhomogeneous strain [18]. Therefore, it is unclear within the dispersion of lattice parameters whether the substrate symmetry induces a tetragonal unit cell at $x=0.1$ or the rhombohedral structure of the bulk material is maintained.

The linear dependence of the unit cell volume on composition (Vegard's law, inset in Figure 4a) further reflects a solid solution scenario where Ti^{4+} and Zr^{4+} are randomly intermixed on an average BZT structure. Analysis of atomic concentrations of the films by WDS showed low statistical deviation from nominal compositions (Figures 4b and 4c), suggesting congruent stoichiometry transfer from target to film.

Figure 5 show the Raman spectra of the BZT films. The coexistence of the $A_1(\text{TO}_3)$ and the $A_1(\text{LO}_3)$ vibrational modes shows the simultaneous presence of c and a oriented domains in which the polar axis is perpendicular and parallel to the plane of the layer, respectively. The polarizability of the BZT layers decreases with increasing their Zr content, towards a disruption of ferroelectricity. In addition the mode A_{1g} appears indicating the coexistence of Ti^{4+} and Zr^{4+} at B position of the perovskite structure stating that the type of the solid solution is substitutional.

Real (Figure 6a) and imaginary (Figure 6b) spectral dielectric permittivity of the BZT films obtained by spectroscopic ellipsometry were used to calculate the bandgap energy of the films (Figure 7). The BZT indirect bandgap was conventionally obtained from square root of absorption coefficient versus photon energy plots. Deviation from parabolic dependence is caused by non ideal solid solution behaviour with tendency to clustering.

4. Conclusions

The isovalent substitution of Ti^{4+} by Zr^{4+} in $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) modifies the dielectric character of ferroelectric BaTiO_3 yielding different behaviours such as relaxor, polar cluster, etc. The dynamic coupling between BaTiO_3 polar nanoregions and BaZrO_3 nonpolar ones as well as microstrain between them is thought to be behind such a rich phase diagram.

However, these short-range compositional variations are elusive to detect and this topic is thus rarely addressed. We have grown BZT thin films on (001)-oriented SrTiO_3 substrates by pulsed laser deposition. A fully relaxed single cube-on-cube epitaxial domain with a unit cell volume proportional to the Zr content is formed across the entire compositional range, suggesting proper intermixing of Zr^{4+} and Ti^{4+} into an average BZT lattice. However, an heterogeneous distribution of B-site cations with different Ti-O and Zr-O bond distances (or local clustering) was detected by Raman spectroscopy. Furthermore, an asymmetric dependence of band gap energy on composition evidenced a non ideal solid solution behaviour with inherent tendency to the enrichment of one chemical species over another.

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Figure 1. (a) AFM topography image of the BaZr_{0.8}Ti_{0.2}O₃ film. Inset: profile extracted from the line in display. (b) Low-magnification cross-section bright field TEM image, along the [010] direction, of the same film.

Figure 2. (a) X-ray $\theta/2\theta$ diffractograms of the BZT samples. Upper labels indicate Miller indices, * stands for K_β (002) STO reflection. (b) X-ray ϕ scans around (111) reflection of BZT (top) and STO (bottom) for $x=0$.

Figure 3. Reciprocal space maps around (204) reflection of the BZT films.

Figure 4. Dependence of in-plane and out-of-plane lattice parameters and lattice volume (a), of the atomic percentage (b) and of atomic fraction (c) of BZT films on their Zr molar fraction.

Figure 5. Raman spectra of the BZT samples and of the ST0 substrate (in red).

Figure 6. Real (a) and imaginary (b) spectral dielectric permittivity of the BZT films.

Figure 7. Dependence of the bandgap energy of the BZT films on the Zr molar fraction.