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The influence of *A*-site rare-earth for barium substitution on the chemical structure and ferroelectric properties of BZT thin films

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ABSTRACT

Rare-earth (*RE*) doped Ba(Zr,Ti)O_3 (BZT) thin films were prepared by rf-magnetron sputtering from a $Ba_{0.90}Ln_{0.067}Zr_{0.09}Ti_{0.91}O_3$ (Ln = La, Nd) target. The films were deposited at a substrate temperature of 600 °C in a high oxygen pressure atmosphere. X-ray diffraction (XRD) patterns of *RE*-BZT films revealed a ⟨001⟩ epitaxial crystal growth on Nb-doped $SrTiO_3$, ⟨001⟩ and ⟨011⟩ growth on single-crystal Si, and a ⟨111⟩-preferred orientation on Pt-coated Si substrates. Scanning electron microscopy (SEM) showed uniform growth of the films deposited, along with the presence of crystals of about half-micron size on the film's surface. Transmission electron microscopy (TEM) evidenced high crystalline films with thicknesses of about 100 nm for 30 min of sputtering. Electron-probe microanalysis (EPMA) corroborated the growth rate (3.0–3.5 nm/min) of films deposited on Pt-coated Si substrates. X-ray photoelectron spectroscopy (XPS), in depth profile mode, showed variations in photoelectron Ti 2*p* doublet positions at lower energies with spin-orbital distances characteristic of $BaTiO_3$-based compounds. The XPS analysis revealed that lanthanide ions positioned onto the *A*-site of the BZT-perovskite structure increasing the MO_6-octahedra distortion (M = Ti, Zr) and, thereby, modifying the Ti–O binding length. Polarization-electric field hysteresis loops on Ag/*RE*-doped BZT/Pt capacitor showed good ferroelectric behavior and higher remanent polarization values than corresponding non-doped system.

1. Introduction

Lead-free, $BaTiO_3$-based ceramics show a wide range of properties and have been extensively studied for applications in technologically relevant fields such as micro-electro-mechanical system (MEMS) devices [1]. Among various materials, solid solutions of Ba(Zr,Ti)O_3 (BZT) have been used successfully as a basis for such compounds; especially, given their high dielectric constant. On the other hand, the continued drive towards greater miniaturization of electronic components has also led to the development of thin film materials [2,3]. The deposition of BZT-type compounds in thin films has been achieved by a number of physical techniques such as the ablation laser process (PLD) [4–6] and rf-magnetron sputtering (RF) [7–10]. Applications include capacitors for multilayer ceramic capacitors (MLCCs) and ferroelectric random access memories (FRAMs) [11–13].

BZT characteristics have also been improved by inserting a lanthanide ion as dopant [14–16] because of its low leakage current behavior and low electric field. However, extensive studies are still needed on systems where the substitution of a lanthanide ion for barium requires the generation of *A*-site cationic vacancies to maintain electroneutrality in the perovskite structure. Likewise, the control of growth conditions and extensive characterization are crucial in obtaining reproducible and useful materials [17,18]. Hence, we report on the deposition and characterization of high-quality, doped BZT thin films obtained from *A*-site deficient rare-earth (*RE*) doped BZT targets. Our contribution has been focused on the influence of lanthanum and neodymium ions on the chemical structure and ferroelectric properties of *RE*-doped BZT thin films in comparison to non-doped systems. The previous analysis was performed based on X-ray photoelectron spectroscopy results, polarization-electric field hysteresis loops, and leakage current measurements on thin films deposited by RF upon Pt-coated Si substrates.

2. Experimental

Thin film samples were deposited via rf-magnetron sputtering (RF) technique in a high-vacuum system with a base pressure of

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5.0×10^{-6} Torr, RF-power of 50–60 W and a target-substrate separation of 220 mm. Ultrahigh purity oxygen was used as the processing gas with a working pressure of $1.5–3.5\times10^{-1}$ Torr. The thin films were grown on single-crystal Nb-doped $SrTiO_3$ (100) –Nb:STO–, single-crystal Si (100) –Si– and Pt(111)/TiO_2/SiO_2/Si –Pt– substrates at 600 °C for 15, 30, 45 and 60 min of deposition. Ba(Zr,Ti)O_3 (BZT) thin films were fabricated by using a target with a composition of $BaZr_{0.09}Ti_{0.91}O_3$. Rare-earth (*RE*) doped Ba(Zr,Ti)O_3 thin films were fabricated by using *A*-site deficient rare-earth doped $Ba_{0.90}Ln_{0.067}Zr_{0.09}Ti_{0.91}O_3$ (Ln = La, Nd) targets. The targets were synthesized through a soft chemistry method [19] and sintered at 1450 °C for 3 h. Films were annealed at 600 °C for 30 min in oxygen atmosphere [20].

Films deposited were structurally characterized by X-ray diffraction (XRD) technique in a Phillips MRD diffractometer with parallel optical beam, Cu$K\alpha$ radiation and Bartel-type monochromator. Micro-structural analysis was performed through high-resolution transmission electron microscopy (HRTEM) in a Phillips CM30 microscope coupled to low-energy electron diffraction (LEED) spectrometer. The morphology of the top surface of the films was examined via scanning electron microscopy (SEM) in a LEICA Cambridge S360 microscope, and cross-sections were studied by field emission SEM in an FE-SEM Hitachi S4100 microscope. Film growth was evaluated by electron probe microanalysis (EPMA) in a Cameca SX-50 microscope at 10, 12, 15, and 20 keV. The surface chemistry was analysed by X-ray photoelectron spectroscopy (XPS) in a Perkin Elmer PHI 5500—ESCA System. XPS analysis was performed in depth profile mode and the sputter was achieved by using an Ar^+ ion gun with accelerating voltage of 4 keV and emission current of 15 mA. The ferroelectric polarization and leakage current density of the Ag/*RE*-doped BZT/Pt capacitor system were measured at room temperature by a Precision LC Radiant Technologies System. Hysteresis loops were measured by using a Sawyer-Tower circuit. Silver top electrodes of 6.5×10^{-3} cm^2 area and thickness of 250 nm were deposited by evaporation technique using a shadow mask. The thickness of films grown was determined by the optical interferometry (OI) technique.

3. Results and discussion

X-ray diffraction (XRD) patterns of Nd-doped Ba(Zr,Ti)O_3 thin films deposited on three different substrates after the annealing process are shown in Fig. 1. Rare-earth (*RE*) doped BZT (*RE* = La, Nd) thin films revealed similar crystallographic behavior regardless of whether the lanthanide ion was present or the type of lanthanide.

As shown in Fig. 1a, (100) and (200) reflections, corresponding to the BZT-perovskite phase, are visible for thin films grown on Nb:STO. The diffraction peaks indicate a highly preferred orientation of *RE*-doped BZT films along the *c*-axis. Hence, thin films deposited on a Nb:STO substrate showed good epitaxial crystal growth and high crystalline quality. No second phases were detected. However, film stoichiometry with high content of zirconium was found by using Vegard's law (*Pm*3*m*; a = 4.176(1) Å). This fact could be explained as a consequence of the ideal tolerance factor (t = 1) calculated for $SrTiO_3$ and $BaZrO_3$ structures when the crystal symmetry is cubic. Nevertheless, caution should be taken because Bragg peak positions from thin-film specimens might be shifted due to intrinsic stresses and, thereby, intrinsic strains. Anyhow, these films can be useful for applications in tunable-ceramic capacitors given their possible relaxor-like ferroelectric behavior at low temperatures [21,22].

For thin films grown on Pt, the XRD pattern (Fig. 1b) showed a (111)-plane orientation because a high-purity commercial Pt-coated Si substrate with a [111]-preferred orientation was used. No additional reflection or second phases were detected. The reflection observed corresponds to the BZT-perovskite phase with a Bragg peak position similar to that observed for the powder used as target. It might indicate that the films exhibited a closer

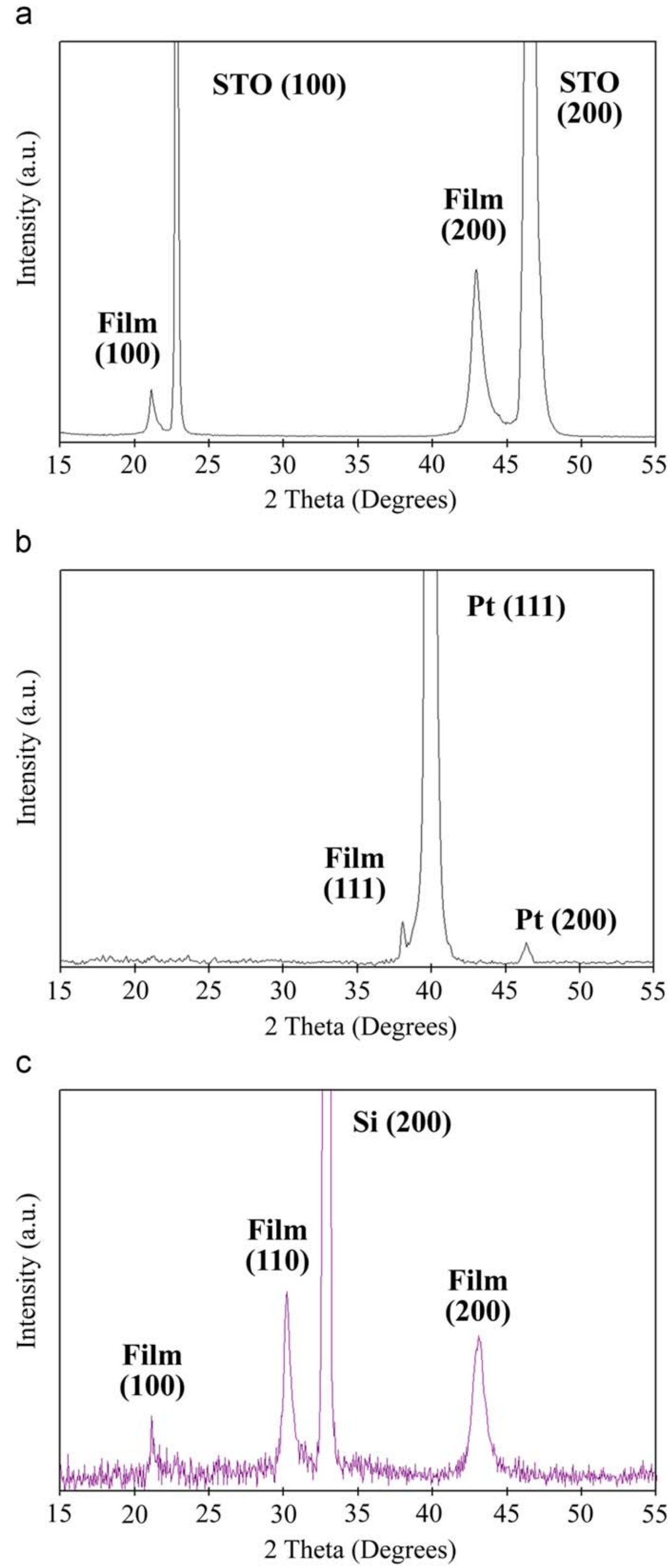

Fig. 1. XRD patterns of Nd-doped BZT thin films grown on (a) Nb:STO, (b) Pt and (c) Si substrates for 45 min of deposition.