Journal of Physics and Chemistry of Solids 75 (2014) 1229–1233

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Piezoelectric non-linearity in $PbSc_{0.5}Ta_{0.5}O_3$ thin films

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ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form
21 May 2014
Accepted 4 June 2014
Available online 21 June 2014

Keywords:
A. Thin films
B. Epitaxial growth
D. Dielectric properties
D. Ferroelectricity
D. Piezoelectricity

ABSTRACT

Epitaxial (001)-oriented $PbSc_{0.5}Ta_{0.5}O_3$ (PST) thin films were deposited by pulsed laser deposition. Local piezoelectric investigations performed by piezoelectric force microscopy show a dual slope for the piezoelectric coefficient. A piezoelectric coefficient of 3 pm/V was observed at voltages up to 0.8 V. However, at voltages above 0.8 V, there is a steep increase in piezoelectric coefficient mounting to 23.2 pm/V. This nonlinear piezoelectric response was observed to be irreversible in nature. In order to better understand this nonlinear behavior, voltage dependent dielectric constant measurements were performed. These confirmed that the piezoelectric non-linearity is indeed a manifestation of a dielectric non-linearity. In contrast to classical ferroelectric systems, the observed dielectric non-linearity in this relaxor material cannot be explained by the Rayleigh model. Thus the dielectric non-linearity in the PST films is tentatively explained as a manifestation of a percolation of the polar nano regions.

1. Introduction

Relaxors have been instrumental in attaining several applications through the years. There has been a recent resurgence of interest in relaxor ferroelectrics because of their prospective use as actuators, switches and security systems [1-3]. Among them, $PbSc_{0.5}Ta_{0.5}O_3$ (PST) is one of the well-known ferroelectric relaxors which is a potential candidate for IR-detection due to its high figure of merit [4,5]. PST crystallizes in the perovskite structure with the compositional formula $A(B',B'')O_3$, where the A sites are occupied by Pb^{2+} cations and the B sites are statistically shared by Sc^{3+} and Ta^{+5} cations. As the devices are designed to work under the application of an applied external electric field, it is very important to understand the influence of such an external field on the piezoelectric and dielectric behavior of the relaxor material, so that the performance of relaxor-built devices can be understood completely. Piezoelectric and dielectric nonlinearities are quite well known for ferroelectrics. In this regard, several phenomenological models have been suggested, yet a full description of these nonlinear properties is still lacking [6–9]. Dielectric and piezoelectric responses of a normal ferroelectric material are due to intrinsic and extrinsic contributions. The former one comes from the deformation of the unit cell, caused by the application of the electric field [10,11]. The latter contribution is a response of the domain wall motion due to the applied electric field. The intrinsic nonlinearity can be modeled and explained by free energy equations and the Landau–Ginzburg–Devonshire theory [12,13]. However, the extrinsic nonlinearity, which has a complex physical origin such as pinning, de-pinning and re-pinning of domain walls during domain wall motion, is difficult to quantify [8]. In this paper, we report on irreversible and strong piezoelectric non-linearity well below the coercive voltage, in PLD-prepared thin PST films. The obtained results and their analysis indicate that the observed piezoelectric non-linearity is a manifestation of the percolation of polar nanoregions (PNRs) in thin PST films.

2. Experimental procedure

(001)-oriented PST thin films were deposited on $La_{0.7}Sr_{0.3}MnO_3$(LSMO)-electroded STO substrates by ablating a self-prepared PST target with KrF excimer laser pulses (wavelength of 248 nm, duration 20 ns). In order to achieve TiO_2-terminated surfaces, vicinal STO (0 0 1) substrates (0.1° offcut; from CrysTec GmbH, Berlin) were chemically treated and annealed at a temperature of 1000 °C before loading into the deposition chamber. For the electrical measurements, a 60 nm thick epitaxial LSMO layer was deposited as a bottom electrode with 5 Hz repetition rate and a fluence of 2 J/cm^2. The bottom electrode was deposited at optimized

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http://dx.doi.org/10.1016/j.jpcs.2014.06.012
0022-3697/

growth temperature and oxygen pressure of 650 °C and 0.141 mbar, respectively. PST films were deposited at 550 °C with 0.270 mbar oxygen pressure. More details on the PST growth conditions can be found elsewhere [14–18]. After the deposition, the films were cooled down to room temperature with a slow cooling rate of 5 °C/min in 1 bar oxygen pressure. In order to facilitate electrical measurements, Pt top electrodes with a size of $60 \times 60\ \mu m^2$ area were sputtered by radio frequency sputtering at room temperature through a shadow mask.

Crystallographic characterizations were performed by a Philips X'Pert MRD X-ray diffractometer with Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation. Samples for transmission electron microscopy (TEM) were prepared using mechanical and ion-beam based standard techniques. TEM images were recorded on a Philips CM20T operated at 200 kV. Surface morphology and local polarization switching were investigated by a commercial atomic force microscope (AFM) (XE-100, Park Systems), using the piezoresponse force microscopy (PFM) mode. Dielectric constants were calculated from the capacitance measured by a Hewlett Packard 4194 A impedance analyzer.

3. Results and discussions

The out-of-plane XRD pattern obtained for a PST/LSMO/STO heterostructure is shown in Fig. 1(a). Both PST and LSMO films are (001)-oriented as shown in the θ-2θ scan. The out-of-plane lattice parameter of the PST film has been calculated using the XRD diffraction pattern and it was found to be 4.08 Å which is slightly higher than the bulk lattice parameter [19]. The ϕ-scan (in-plane) scans for STO, LSMO and PST contain four peaks(Fig. 1(b)) for each material at the same azimuthal angle (φ), revealing that all the films have epitaxial cube-on-cube growth. The in-plane and out-of-plane epitaxial relationships between substrate (STO), electrode layer (LSMO) and PST thin film have been found to be (001) PST// (001) LSMO//(001) STO and [100] PST//[100] LSMO//[100] STO, respectively (cubic indexing is used for LSMO and PST). The full width at half maximum values (FWHM) of the (222) reflections for STO, LSMO, and PST were found to be ~0.29°, 0.30°, and 0.60° respectively, confirming a good crystalline growth. The surface morphology and roughness of the PST thin film were investigated by AFM measurements. The surface morphology of a PST film deposited on a vicinal STO substrate (Fig. 2(a)) is shown in Fig. 2(b), and reveals a smooth surface morphology. The PST films have a root mean square value of roughness of about 0.6 nm over an area of $4 \times 4\ \mu m^2$ signifying a flat and smooth surface of the PST film on LSMO/STO. However, due to large lattice mismatch (4.91%) between STO and PST, no step patterns were observed for PST films.

The microstructure of the PST thin films was investigated by TEM. The cross-sectional TEM image (Fig. 3(a)) and the selected area diffraction (SAED) pattern (Fig. 3(b)) (only indexed for PST) captured along the [110] direction reveal the epitaxial growth of the 30 nm thick PST film on a 65 nm thick LSMO bottom electrode. Detailed cross-sectional TEM investigations indicate a coherent growth of the LSMO layer on the STO substrate due to the very small lattice mismatch (0.6% at RT), whereas the PST film shows a columnar type of growth, possibly due to the large lattice mismatch (4.91%). The in-plane and out-of-plane lattice parameters for the 30 nm thin PST film were calculated through SAED patterns as shown in Fig. 3(c). For a cubic PST system, the ratio between AB/BC and the angle between AB and BE vectors should be 1.41 and 35.26°, respectively. The observed values of the ratio between AB/BC and the angle between AB and BE vectors were found to be 1.43 and 33.90° respectively which indicate that the PST film is tetragonally distorted.

The ferroelectric switching of the PST films has been locally investigated with a modulation voltage of 0.7 V_{rms} at 25 kHz by PFM, as shown in Fig. 4(a). A $3 \times 3\ \mu m^2$ area was poled downwards by applying a voltage of +5 V for background poling and then, at the center, a smaller area of $1 \times 1\ \mu m^2$ was switched upwards by applying a voltage of −5 V. This reveals that the films can be locally switched in either direction by applying an external voltage. The locally switched area of the films remained unchanged (Fig. 4(b)) for more than one hour for relaxor PST, suggesting that the films have decent retention characteristics. The piezoresponse of a PST film was investigated as a function of the applied ac voltage (25 kHz) using PFM measurements as shown in Fig. 4(c). When the piezoelectric coefficient primarily contributes to the amplitude of the PFM signal, the amplitude of the PFM signal is a linear function of the applied voltage for V_{ac} lower than the corresponding coercive voltage. Thus, the piezoresponse data can be linearly fitted to approximate the effective piezoelectric coefficient. However, for a V_{ac} value at and above the coercive voltage, the PFM signal drops significantly because of the change of direction of the polarization. Interstingly, even below the coercive voltage (V_c), two slopes, instead of obtaining one single slope, were observed for the PST film as shown in Fig. 4(c). The piezoelectric coefficient in the low

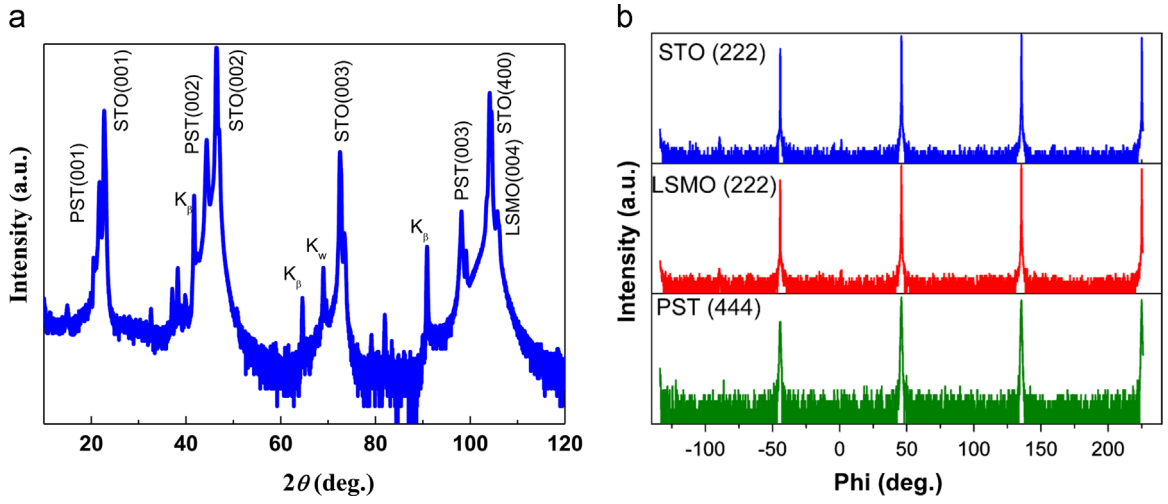

Fig. 1. (a) XRD θ-2θ scan recorded for a (001)-oriented PST/LSMO/STO heterostructure revealing that the films are in pure perovskite phase. (b) A φ-scan performed using the (444) reflections of PST, and the (222) reflection of the LSMO electrode and STO substrate confirming epitaxial cube-on-cube growth.