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Annealing temperature dependence of local piezoelectric response of (Pb, Ca)TiO_3 ferroelectric thin films

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ABSTRACT

In this work, we have systematically investigated the piezo/ferroelectric response of (Pb, Ca)TiO_3 thin films prepared by polymeric precursor method using simultaneously topography, piezoresponse force microscopy (PFM) and local piezoelectric hysteresis loop measurements. The thin films were grown on Pt/Ti/SiO_2/Si substrates and annealed at 400, 500 and 600 °C and subjected to structural characterization using x-ray diffraction, infrared and micro-Raman spectroscopy. The ferroelectric domains structure and the piezoelectric response evolved as a function of thermal annealing temperature as well as the density of active grains (number of switchable domains) progressively increased. Another important characteristic of these films is the onset of large area showing the coexistence of active (stronger piezoresponse signal) and inactive (weak or non piezoresponse signal) grains embedded in the polycrystalline perovskite matrix. A combination of out-of-plane (OP) and in-plane (IP) PFM images revealed local features of polarization component magnitudes in samples surface. Well-defined local piezoelectric hysteresis loop was achieved on top of individual nanometer-scale grains in both samples annealed at 500 and 600 °C, and the switching behavior is evident.

1. Introduction

One of the important topics in perovskite-type ferroelectric materials technology is the knowledge the exact nature of the local piezoelectric and ferroelectric response [1,2]. Since characteristics such as size, shape, orientation, crystallization temperature, defects and doping level are recognized to modify piezo/ferroelectric properties, this topic has attracted much attention as an important issue in the nano-science field [3–6]. In particular, piezoresponse force microscopy (PFM) is a powerful tool for nanoscale investigation in piezo/ferroelectric materials. For example, the size effect indicates the disappearance of ferroelectricity in perovskite-type ferroelectric of dimensions smaller than a critical value [7]. In addition, the influence of doping type on the formation of ferroelectric perovskite materials showed that iron doping induces the disappearance of ferroelectricity in (Pb,Sr)(Ti,Fe)O_3 thin films [8]. Puli et al. [9] observed a strong domain switching response at nanoscale level by using PFM in $(Ba_{0.50}Sr_{0.50})(Ti_{0.80}Sn_{0.20})O_3$ thin films a. Furthermore, Huang et al. [10] reported PFM images in which domain boundaries are in agreement with grain boundaries in $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ ferroelectric thin films, suggesting that grain boundaries entirely confine the shape of domain boundaries. In $Bi_{0.70}A_{0.30}FeO_3$ (A=Ca, Sr, Pb and Ba) ceramic solid solution, Khomchenko et al. [11] investigated the relationship connecting piezo/ferroelectric responses and the presence of A-site dopants. They observed a reduction of the polarization due to the presence of A-site dopants which was confirmed by piezoresponse force microscopy data. Recently, piezoresponse force microscopy studies revealed an intense local polarization response in the out-of-plane direction in multi-layered structures consisting of single $Ba(Zr_{0.10}T_{0.90})O_3$ and $(Ba_{0.75}Ca_{0.25})TiO_3$ layers fabricated on Nb doped (001) $SrtiO_3$ (Nb:STO) substrates by pulsed laser deposition [12].

In this paper, we used piezoresponse force microscopy to observe

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crystallization temperature effects on local of piezo/ferroelectric properties of chemical solution deposition (CSD) prepared (Pb, Ca)TiO_3 thin films.

2. Experimental procedures

Our procedure for synthesizing $(Pb_{0.74}Ca_{0.26})TiO_3$ thin films consisted in producing a polymeric resin using a soft chemistry method (polymeric precursor route). Specific details of this synthesis is found in the literature [13]. Pt/Ti/SiO_2/Si wafers were used as substrates. The substrate was spin-coated by dropping a small amount of the precursor solution. The rotation speed and the spin time were fixed at 5000 rpm and 30 s, respectively, to ensure that the film thickness was uniform on the substrate. Each layer was dried at 150 °C after the spin coating on a hot plate for 30 min to remove residual solvents. After the pre-annealing, the films were annealed at 400, 500 and 600 °C for 2 h in air atmosphere. In addition, thicknesses of 370 nm, 315 nm, and 330 nm were obtained at 400, 500 and 600 °C, respectively.

$(Pb_{0.74}Ca_{0.26})TiO_3$ thin films were then structurally characterized by XRD in the θ−2θ scan mode (steps of 0.02°) which was recorded on a Rigaku MiniFlex600 diffractometer. Raman measurements were taken with a T-64000 Jobin-Yvon triple-monochromator coupled to a charge-coupled device (CCD) detector. An optical microscope with a 100x objective was used to focus the 514.5 nm line of the Coherent Innova 90 Argon laser onto the sample; the power was maintained at 15 mW. Infrared analyses were performed using an Equinox/55 (Bruker) Fourier transformed infrared (FTIR) spectrometer to observe variations in chemical bond densities as a function temperature crystallization. FTIR reflectance spectra were recorded at room temperature from 350 to 1200 cm^{-1} using a 30° specular reflectance accessory.

The topography, the polarization pattern of ferroelectric domain structures and the local hysteresis loops were investigated at the nanoscale level on ferroelectric thin films using a commercial AFM (MultiMode Nanoscope V, Bruker) modified to be used as a piezo-response force microscopy (PFM). The system was equipped with a lock-in amplifier (SR850, Stanford) and a function generator (33220 A, Agilent). During all PFM measurements, the conductive probe (k=42 N/m) was electrically grounded and an external voltage was applied to the bottom Pt electrode operated with a driving amplitude of 1 V (rms). The piezoresponse signal was recorded in PR = A*Cos(φ), and the piezoloops were obtained in the remnant mode.

In addition, a ferroelectric tester workstation (Radiant

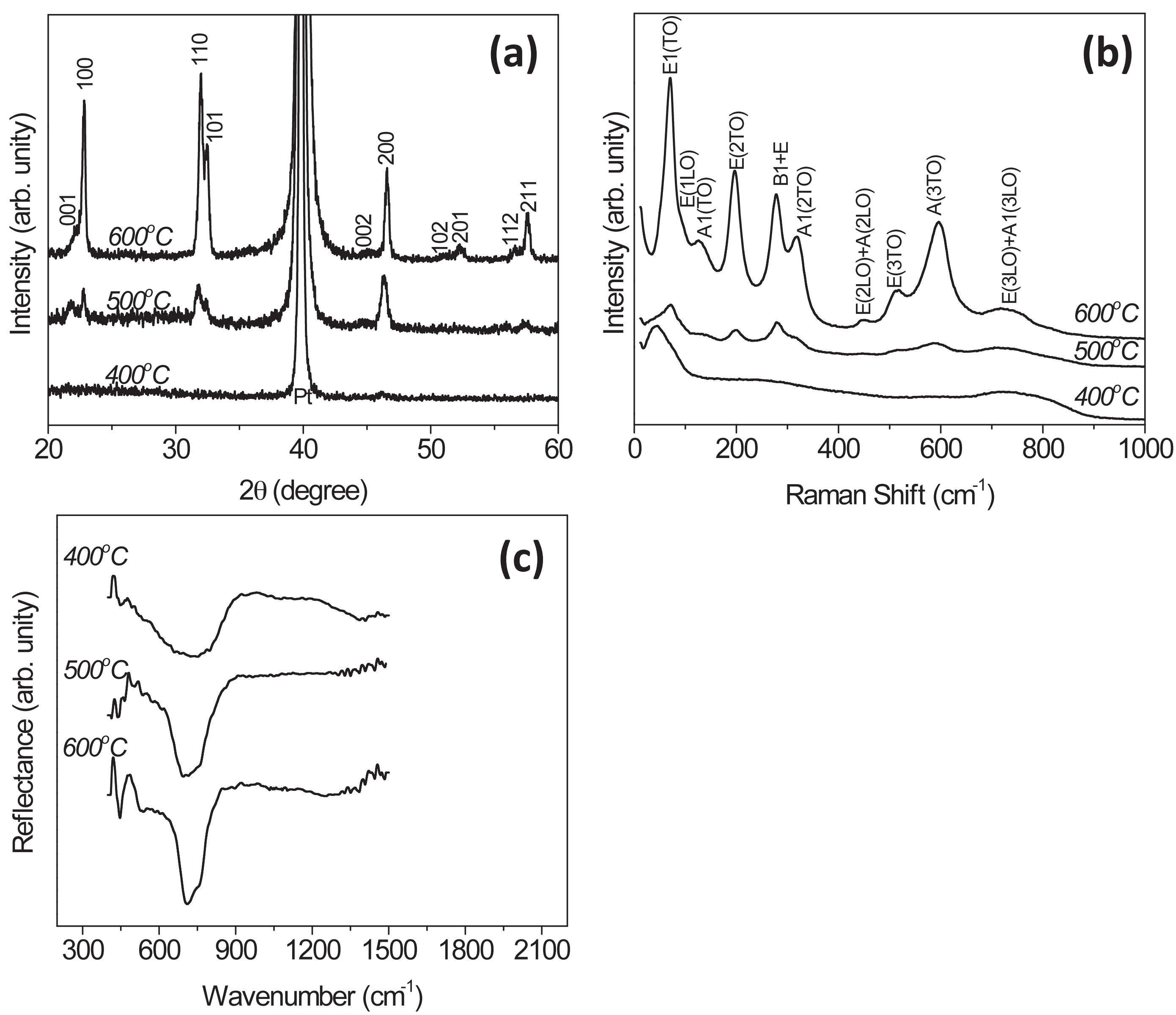

Fig. 1. (a) XRD patterns, (b) micro-Raman spectra and (c) FTIR spectra of $Pb_{0.76}Ca_{0.24}TiO_3$ thin films annealed at different temperatures.