Scripta Materialia 150 (2018) 125–129

Contents lists available at ScienceDirect

Scripta Materialia

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

Regular article

Room temperature magnetoelectric and magnetodielectric properties of 2–2 bilayer 0.50Pb $(Ni_{1/3}Nb_{2/3})$ O_3–0.35$PbTiO_3$–0.15$PbZrO_3$/$CoFe_2O_4$ thin film

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ARTICLE INFO

Article history:
Received 3 January 2018
Accepted 6 March 2018
Available online xxxx

Keywords:
Thin films
Interfaces
Dielectrics
Magnetic properties
Magnetoelectric effect

ABSTRACT

A 2–2 bilayer composite 0.50Pb$(Ni_{1/3}Nb_{2/3})O_3$–0.35$PbTiO_3$–0.15$PbZrO_3$(PNNZT)/$CoFe_2O_4$ (CFO) thin film has been fabricated using a pulsed laser deposition technique. Due to the coexistence of ferromagnetic (FM) order in the CFO layer and ferroelectric (FE) order in the PNNZT layer, the product property, i.e., the magnetoelectric (ME) coupling has been realized with a ME voltage coefficient (α_E) of ~500 mV/cm.Oe and a magnetodielectric response (MD(%) of 0.27 at room temperature. The present new composite thin film with its enhanced ME and MD properties could be a useful material for developing ME-based devices.

Multiferroic systems, i.e., systems with at least two ferroic orders such as spin and charge lead to magnetoelectric (ME) properties [1,2]. Devices from such multifunctional systems operating at traditional operating temperatures (−50 to 150 °C) are being extensively studied in recent times [3,4]. Despite the discovery of several single-phase multiferroic materials [5–8], the applications of these materials are limited due to weak coupling between the ferroic orders. With a view to improve the ME properties as well as coupling, a new relaxor piezoelectric material, 0.50Pb$(Ni_{1/3}Nb_{2/3})O_3$–0.35$PbTiO_3$–0.15$PbZrO_3$ (PNNZT), has been developed. It exhibited good electrical properties such as high dielectric constant (~4500), high piezoelectric voltage coefficient (900 pm/V) and remnant polarization (~20 μC/cm^2) [9,10]. In order to fabricate ME composite, $CoFe_2O_4$ (CFO) has been chosen as the magnetostrictive phase due to the higher magneto-crystalline anisotropy [11,12] and magnetostriction [13] and the ME properties have been studied for different composite architectures such as 0–3 bulk particulate and 2–2 thick film laminate forms in our previously reported works [9,10]. Amongst these, PNNZT- CFO bulk (0–3) particulates and PNNZT/CFO thick film (2–2) laminates showed a maximum ME voltage coefficient (α_E) of ~13 and 26 mV/cm. Oe respectively [9,10]. However, these ME voltage coefficient values are lower than required for device application. ME device application requires device miniaturization with a large ME response (~1 V/cm.Oe) at room temperature. To achieve this, several advanced thin film growth processes have been developed to engineer the ME devices with different architectures at the nanoscale [6]. Amongst these thin film architectures, 2–2 bilayer structure is found to be favorable because of the ease of its thin film growth and displayed large ME responses. The enhanced ME response in 2–2 bilayer thin films is ascribed to the strong interfacial coupling between the magnetostrictive and ferro/piezoelectric layers [1,2]. Hence, it is anticipated that PNNZT and CFO in the 2–2 bilayer thin film form would exhibit substantially large ME properties owing to their favorable piezo/ferroelectric and magnetostrictive properties of their respective layers. In view of this, a new 2–2 bilayer PNNZT/CFO thin film is fabricated using pulsed laser deposition (PLD) system and its room temperature ME and magnetodielectric (MD) properties are studied.

The 2–2 bilayer PNNZT/CFO composite thin films were deposited on Pt/Ti/SiO_2/Si substrate. A KrF laser of wavelength 248 nm, operating at a frequency of 5 Hz with the energy density of

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https://doi.org/10.1016/j.scriptamat.2018.03.008
1359-6462/

2.0 Jcm^{-2} was used to ablate highly dense pure PNNZT and CFO targets. A substrate temperature of 800 and 750 °C was maintained during the deposition of PNNZT and CFO layers respectively, while maintaining an oxygen partial pressure of 0.30 mbar in the deposition chamber. In order to promote the perovskite phase and to avoid pyrochlore phase formation in the PNNZT layer, $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin film (with an optimized thickness of ~250 nm) deposited from an LSCO target is used as a seed/nucleating layer [14].

X-ray diffraction (XRD) patterns were recorded by using PANalytical Xpert-Pro diffractometer equipped with a Cu K_α ($\lambda = 1.5406$ Å) radiation. Fig. 1(a) represents the XRD patterns of PNNZT, PNNZT/CFO and CFO thin films. It is evident from the XRD patterns that there are two sets of peaks in the composite thin film corresponding to perovskite PNNZT phase [9,10,15] and spinel CFO phase [16]. Thus, the XRD results confirm the 2–2 bilayer composite structure formation on a global scale. Raman spectroscopy is well known to study the structural phases on a local scale. Therefore, Raman scattering spectra were recorded using Horiba Jobin Yvon (Japan) spectrometer equipped with an excitation laser source of 532 nm at an operating power of 5 mW.

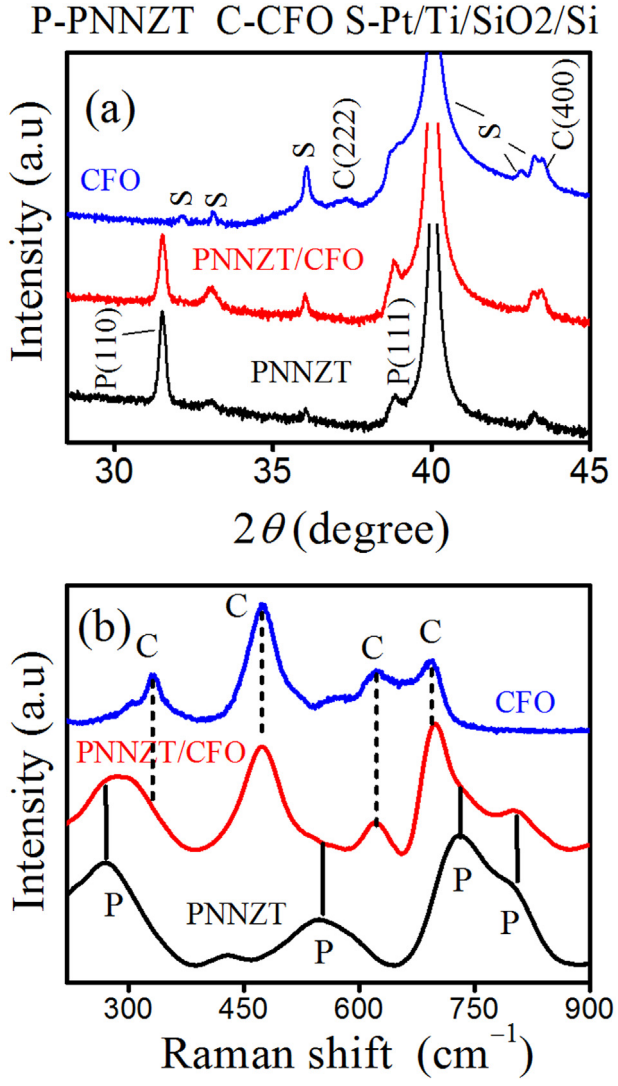

Fig. 1. (a) X-ray diffraction patterns and (b) Raman scattering spectra of PNNZT, PNNZT/CFO and CFO thin films grown on Pt/Ti/SiO_2/Si substrate.

Fig. 1(b) shows the Raman scattering spectra for pure PNNZT, PNNZT/CFO and CFO thin films recorded in the range from 200 to 1000 cm^{-1}. Raman spectra of PNNZT/CFO thin film clearly shows major phonon modes corresponding to both PNNZT(solid lines) and CFO (dotted lines) phases centered at 265 cm^{-1}, 550 cm^{-1}, 733 cm^{-1}, 810 cm^{-1} [15] and 335 cm^{-1}, 485 cm^{-1}, 575 cm^{-1}, 702 cm^{-1} respectively [17]. This feature strongly confirms the PNNZT/CFO 2–2 layered composite formation, without any other secondary phase formation an account of any chemical reactions at the interface.

Microstructural analysis was carried out using field emission scanning electron microscope (FE-SEM) (JSM-7600F). The cross-sectional micrographs for PNNZT/CFO thin film in the scanning electron (SE) and back-scattered electron (BSE) mode are shown in Fig. 2 (a) and (b). The cross-sectional image in BSE mode indicates a clean interface between PNNZT and CFO layers. The measured thickness of the individual PNNZT and CFO layers is found to be ~300 and ~100 nm respectively. Surface morphology of PNNZT and CFO and their corresponding grain size distribution are shown in Fig. 2(c), (d) and (e), (f) respectively. Surface micrographs show dense and crack-free microstructure for both thin films, which indicates the quality of the films. However, a distinct grain size distribution and surface morphology between PNNZT and CFO are observed, which could be due to the surface energy difference between these two materials [18].

Dielectric constant (ε'), dielectric loss ($\tan\delta$), ac conductivity (σ_{ac}) and magneto-dielectric ((MD) %)) properties were measured using an alpha-A high resolution frequency analyzer (Novocontrol GmbH, Germany). Electrical measurements were performed using Au/Cr (*sputtered using a shadow mask*) and Pt as a top and bottom electrodes respectively. Fig. 3(a) shows ε' versus f plots measured in the frequency range from 100 Hz - 1 MHz. For PNNZT thin film, dielectric constant depicts almost a plateau kind of behavior in the measured frequency region. In the case of PNNZT/CFO thin film, dielectric constant decreases slightly as compared to PNNZT thin film, in the frequency range between 10^3 and 10^6 Hz. However, below 1 kHz, a large increase in dielectric constant along with dielectric loss (see inset of Fig. 3(a)) are observed for PNNZT/CFO thin film. These features can be attributed to the dominance of space charge polarization as well as relatively higher conducting behavior of CFO as compared to the PNNZT [10]. The effect of CFO layer on the electrical conductivity is further investigated and as shown in Fig. 3(b). The ac conductivity versus frequency plots are fitted according to Jonscher's universal law [19] to estimate the dc conductivity of thin films using the following equation

$$\sigma_{ac} = \sigma_{dc} + A\omega^n \quad (1)$$

where σ_{ac} is the electrical ac conductivity (at a given frequency) and σ_{dc} is the dc conductivity, ω is the frequency. From the fitted data, the estimated σ_{dc} values are found to be 1.58×10^{-9} S/cm and 9.80×10^{-7} S/cm for PNNZT and PNNZT/CFO respectively. The observed increase in σ_{dc} value for PNNZT/CFO thin film indicates the effect of the conductivity of CFO layer in PNNZT/CFO bilayer thin film.

The ferroelectric properties of both PNNZT and PNNZT/CFO films are measured at a switching frequency of 1 kHz using a standard ferroelectric loop tester (aixACCT GmbH, TF 2000). Polarization (P) versus applied electric field (E) plots for PNNZT and PNNZT/CFO thin films are shown in Fig. 3(c). The remnant polarization (P_r) is ~26 and 30 μC/cm^2 and coercive field (E_c) is ~70 and 88 kV/cm for