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Magnetic field-dependent polarization of (111)-oriented PZT–Co ferrite nanobilayer: Effect of Co ferrite composition

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ABSTRACT

The perfect (111)-oriented PZT/CFO (CFO=$CoFe_2O_4$, $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$) bilayer multiferroic thin films were grown on Pt(111)/Si substrate at 600 °C using pulsed laser deposition technique. The precision X-ray diffraction analysis (avoiding the shift of peak due to the sample misalignment) revealed that the CFO films on Pt(111)/Si substrate were under an out-of-plane contraction and deposition of PZT top layer led to more increase in the out-of-plane contraction, i.e. increase in the residual stresses. The PZT and CFO layers have significant effects on magnetic and ferroelectric properties of PZT/CFO bilayer films, respectively, leading to an enhanced in-plane magnetic anisotropy as well as increased and asymmetric polarization. The effect of composition of CFO layer on magnetic field-dependent polarization of PZT/CFO bilayer films was investigated by applying the magnetic field during *P-E* measurement. The polarization of PZT films were increased by applying the magnetic field as a result of strain transferred from magnetostrictive CFO underlayer. This increase in polarization for PZT/$Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$ was higher than that for PZT/$Co_{0.8}Fe_{2.2}O_4$ and both of them were significantly higher than that for PZT/$CoFe_2O_4$ bilayer film, which was discussed based on their magnetostriction properties.

1. Introduction

Multiferroic materials represent an attracting class of multifunctional materials that simultaneously exhibit ferroelectric and ferromagnetic properties as well as magnetoelectricity, which is the particular interest of these materials. Magnetoelectricity results from the existence of a cross coupling between the magnetic and electric orders, termed as magnetoelectric coupling. The magnetoelectric coupling is the behavior of a material to generate electric polarization when it is placed in magnetic field or to generate magnetization when it is subjected to an electric field [1]. These materials have recently attracted a great deal of attention not only from the theoretical point of view but also because of their potential practical applications in new type of electronic devices such as multistate memories, sensors and transducers [1–3]. Magnetoelectricity in single phase multiferroic materials, which is their intrinsic property, is either weak or happens below room temperature limiting their practical applications. On the other hand, the outstanding magnetoelectricity has been proposed for the composite multiferroic materials consisting of piezoelectric and magnetostrictive constituents, which can be magnetoelectrically coupled through stress mediation [4–6]. In comparison to the bulk composite multiferroics, the composite films can provide more degrees of freedom, such as strain and/or crystallographic orientation, to modify the magnetoelectric behavior because of anisotropic piezoelectric and magnetostritive properties of constituents. By survey the literature; most of composite multiferroics thin films are mainly focused on oxide components, especially on lead zirconate titanate, $Pb(Zr,Ti)O_3$, and cobalt ferrite, $CoFe_2O_4$, because of their high piezoelectric and magnetostrictive coefficients, respectively [7–11].

Cobalt ferrite has the highest magnetostriction constants among all magnetic oxides. Its polycrystalline random orientation magnetostriction constant is $\lambda_s^R = -110 \times 10^{-6}$ to -225×10^{-6} and its single crystal magnetostriction constants are $\lambda_s^{100} = -225 \times 10^{-6}$ to -590×10^{-6} and $\lambda_s^{111} = \sim -1/5\lambda_s^{100}$, depending on the stoichiometry, Co/Fe ratio, and thermal history [12]. The highest single crystal magnetostriction constants ($\lambda_s^{100} = -590 \times 10^{-6}$ and $\lambda_s^{111} = +120 \times 10^{-6}$) [13] were reported for $Co_{0.8}Fe_{2.2}O_4$ compound that are significantly higher than those for

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$CoFe_2O_4$ compound. Hence, it is expected that composite multiferroics consisting of $Co_{0.8}Fe_{2.2}O_4$ compound have higher magnetoelectricity than that containing $CoFe_2O_4$ compound. In addition, it has been clearly revealed [14,15] that magnetostriction sensitivity ($d\lambda/dH$) of cobalt ferrite could increase by Mn substituting, i.e. the magnetostriction of Mn substituted cobalt ferrite is higher than that of pure cobalt ferrite at law magnetic field, which helps to use it in lower magnetic fields. To the best of the present authors' knowledge, there are no reports on the using $Co_{0.8}Fe_{2.2}O_4$ neither with this composition nor with Mn substitution in composite multiferroic.

Our previous work showed that the perfectly (111)-oriented $CoFe_2O_4$, $Co_{0.8}Fe_{2.2}O_4$, and $Co_{0.8-x}Mn_xFe_{2.2}O_4$ films (hereafter, CFO will refer for all films) could be grown on the Pt(111)/Si substrate by pulsed laser deposition (PLD) technique [16–18] that allow to grow the $Pb(Zr,Ti)O_3$, PZT, top layer with perfect (111)-orientation [19,20]. The $Co_{0.8}Fe_{2.2}O_4$ thin film had significantly improved magnetic properties compared to the $CoFe_2O_4$ film [17] and Mn substituting for Co increases the magnetization and decreases the coercivity [18]. The PZT top layer was selected as composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ because of its highest piezoelectric properties among other compositions [20]. In this study, the effect of composition of CFO under layer on magnetic field-dependent polarization of PZT/CFO bilayer thin films is investigated.

2. Experiment procedure

The PZT and CFO films were deposited on commercial Pt(111)−150 nm/Ti − 10 nm/SiO_2 − 300 nm/Si(100) substrate by PLD technique, using the PZT target with composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ and the CFO targets with composition of $CoFe_2O_4$, $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$. The details of target preparation are described elsewhere [16–21]. A KrF excimer laser (248 nm wavelength and 23 ns pulse width, Lambda Physics) was used for ablating the target with energy density of about 2 J/cm^2.The laser repetition rate was selected as 5 and 10 Hz for PZT and CFO deposition, respectively. The laser beam was focused by optical lenses at an angle of about 45° to the rotating target. Substrate was placed at a distance of 4 cm to the target. Before deposition, the chamber was evacuated to 1×10^{-6} Torr and the CFO and PZT films were deposited at oxygen pressure (P_{O_2}) of 10 and 50 mTorr, respectively. All films were grown at substrate temperature of 600 °C. A multi target holder system was used for deposition of bilayers to avoid the breaking of the vacuum and heating. After deposition, the films were cooled down to room temperature at a rate of about 5 °C/min and at the same oxygen pressure as in the deposition.

The crystallinity and orientation of the thin films were determined by X-ray diffraction (XRD) analysis using θ–2θ scan, φ-scan, and ω-scan (rocking curve) which were performed by synchrotron radiation (wavelength of 0.15401 nm) at 3D XRD beam line of PLS-II (Pohang Light Source-II, Korea). Before each XRD analysis, the sample alignment was performed by Pt(111) peak of substrate in order to avoid the peak shift due to the sample misalignment. The cross section view of samples was observed by a field emission-scanning electron microscope (FE-SEM, Philips XL30S FEG).The magnetization of thin films was measured at room temperature under maximum applied field of 10 kOe for in-plane (magnetic field applied parallel to the film) configuration using a vibrating sample magnetometer (VSM, Lake Shore, Model 7407). The magnetic hysteresis loops (M–H curves) were obtained after subtracting of diamagnetic effect of sample holder as well as that of Pt/Si and PZT/Pt/Si substrates for CFO single layer and PZT/CFO bilayers films, respectively. For ferroelectric characterization, Pt dots with diameter of 100–200 μm were deposited at room temperature on PZT films through a shadow mask using DC sputter. Polarization-electric field hysteresis loops (P–E curves) were measured at 1 kHz using a Precision LC system (PLC0406-804 (100 V), Radiant Technologies, Inc.) assembled in an experimental set-up consists of a probe station. The probe station used for P–E measurement includes sample stage holder, micro-manipulators and pole pieces. The needle like pole pieces have a 20 μm tip and are made from tungsten alloy, which used to connect the electrodes on the film to the ferro-tester. The magnetic field-dependent polarization of the PZT/CFO bilayer films was also measured using ferro-tester, in which the samples were wire bonded in a package, connected to the probe station used for P–E measurement. The package was placed in a dc magnetic field (2 kOe) for both in-plane and out-of-plane configurations during the P–E measurements.

3. Results and discussions

In this work, the CFO and PZT films were deposited based on our optimum growth conditions [16–20]. The SEM cross section image of PZT/$Co_{0.8}Fe_{2.2}O_4$ bilayer thin films is shown in Fig. 1. As can be seen, the film has a uniform bilayer structure, which has a compacted and distinct interface. In all bilayers, the thickness of CFO and PZT layers is about 200 and 240 nm, respectively.

Fig. 2 shows the XRD θ–2θ scan of CFO single layer along with PZT/CFO bilayer films grown under same deposition conditions. The CFO films were found highly oriented along the $\langle lll \rangle$ directions on the Pt(111)/Si substrate which is indexed according to the powder diffraction pattern (ICDD PDF card no. 22-1086). No peak related to the other planes of CFO was detected. In addition, the PZT top layers were found perfect (111)-orientated perovskite single phase without any peak related to the pyrochlore phase and other perovskite planes. Degree of $\langle lll \rangle$ alignment of CFO and PZT films was examined by ω-scan (rocking curve). Full width at half maximum (FWHM) of rocking curve analysis around the [111] direction ($\Delta\omega_{(111)}$) for the PZT films is about 1.5°. The $\Delta\omega_{(222)}$ of $CoFe_2O_4$, $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}\ Mn_{0.2}Fe_{2.2}O_4$ films are 1.47°, 1.52° and 1.56° for the CFO single layer, and 1.30°, 1.38° and 1.45° for the PZT/CFO bilayers films, respectively. These values are comparable with $\Delta\omega$ of the epitaxial $CoFe_2O_4$ (100) layer in PZT/$CoFe_2O_4$/$SrTiO_3$ structure (0.986°)^{10}, and epitaxial PZT(100) thin film on $PbTiO_3$/Pt/MgO substrate (0.8°)^{21}, indicating the relatively high (111)-orientation in the films developed in the present study. In order to find the in-plane relation between films and Pt(111) underlayer, the φ-scan was taken, in which uniform intensity along 360° indicates the random in-plane orientation in our samples. Perfect (111)-orientation growth of CFO on Pt(111) and PZT on CFO(111) were discussed in details elsewhere [16–19] based on surface and interface energy minimization as well as similarity between $\{lll\}$ planes of spinel and perovskite structures. As can be seen in Fig. 2(b), the peak of CFO films have a higher 2θ than that of $CoFe_2O_4$ bulk indicating the lower lattice parameter. Since the XRD θ–2θ scan detects only the inter-planar spacing of $\{lll\}$ planes in the present samples, the higher 2θ of peaks of CFO films than that of $CoFe_2O_4$ bulk indicates the lower inter-planar spacing, i.e. the out-of-plane contraction. It has been clearly revealed in the literature [22] that the CFO film grown at high temperature on Si substrate is under in-plane residual tensile stress (after cooling from high temperature to room temperature) due to the difference between thermal expansion coefficients of film and substrate. This in-plane tensile stress may be able to induce an out-of-plane contraction which could be detected by XRD θ–2θ scan (Fig. 2). Note that the higher 2θ of peaks of $Co_{0.8}Fe_{2.2}O_4$ film compare to that of $CoFe_2O_4$ film was due to the lower lattice parameter of $Co_{0.8}Fe_{2.2}O_4$ film, which was explained based on