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Nanoscale magnetoelectric coupling study in (111)-oriented PZT-Co ferrite multiferroic nanobilayer thin film using piezoresponse force microscopy: Effect of Co ferrite composition

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ABSTRACT

The perfect (111)-oriented PZT/Co$_{0.8}$Fe$_{2.2}$O$_4$ and PZT/Co$_{0.6}$Mn$_{0.2}$Fe$_{2.2}$O$_4$ bilayer multiferroic thin films were grown on Pt(111)/Si substrate using pulsed laser deposition technique. The PZT/Co$_{0.6}$Mn$_{0.2}$Fe$_{2.2}$O$_4$ bilayer showed higher magnetization and lower coercivity than the PZT/Co$_{0.8}$Fe$_{2.2}$O$_4$ bilayer film, which is due to the Mn substitution in the cobalt ferrite layer. The effect of composition of cobalt ferrite underlayer on local magnetoelectric coupling of samples was investigated using piezoresponse force microscopy under external magnetic field, showing magnetically induced evolution of piezoresponse and ferroelectric switching characteristics as a result of interfacially strain transferred from magnetostrictive cobalt ferrite underlayer. The change in piezoresponse amplitude of PZT/Co$_{0.6}$Mn$_{0.2}$Fe$_{2.2}$O$_4$ by applying the magnetic field was higher than that of PZT/Co$_{0.8}$Fe$_{2.2}$O$_4$ film and both were significantly higher than that for PZT/CoFe$_2$O$_4$, which has been discussed based on their magnetostriction properties. These results revealed that in comparison to PZT/Co$_{0.8}$Fe$_{2.2}$O$_4$, the Mn-substituted bilayer film can be used in lower magnetic fields to reach the same magnetoelectric response making it feasible to the work at lower level of magnetic field in the sensor and actuator devices.

1. Introduction

Multiferroic materials represent an attractive class of multifunctional materials with simultaneous ferroelectric and ferromagnetic properties as well as magnetoelectricity, which is of particular interest in these materials. Magnetoelectricity results from the existence of a cross coupling between the magnetic and electric orders, termed as magnetoelectric coupling. Magnetoelectric coupling is the property of a material to generate electric polarization upon exposure to magnetic field or to generate magnetization upon exposure 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 applications in the novel electronic devices such as multistate memories, sensors and actuators [1–3]. Magnetoelectricity in single phase multiferroic materials is either weak or active below room temperature which limits their applications. On the other hand, outstanding magnetoelectricity has been reported for the composite multiferroic materials composed of piezoelectric and magnetostrictive constituents, which are magnetoelectrically coupled through stress mediation [4–7]. Relatively, the composite multiferroic films provide more degrees of freedom, such as strain and/or crystallographic orientation, to tailoring the magnetoelectric behavior because of anisotropic piezoelectric and magnetostrictive properties of constituents. Most of the composite multiferroics thin films are mainly focused on oxide components, especially on lead zirconate titanate, Pb(Zr,Ti)O$_3$, and cobalt ferrite, CoFe$_2$O$_4$, because of their high piezoelectric and magnetostrictive coefficients, respectively [8–10]. Although, the research on piezoelectricity have been focused on lead free materials in the last decade, the Pb(Zr,Ti)O$_3$ has been selected in this study because of its well-known piezoelectric properties.

Cobalt ferrite shows the highest magnetostriction among all magnetic oxides. Its polycrystalline random orientation magnetostriction constant is $\lambda_s{}^R = -110 \times 10^{-6}$ to -225×10^{-6} and its

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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 [11]. The highest single crystal magnetostriction constants ($\lambda_s{}^{100} = -590 \times 10^{-6}$ and $\lambda_s{}^{111} = +120 \times 10^{-6}$) [12] were reported for $Co_{0.8}Fe_{2.2}O_4$ compound that are significantly higher than those for $CoFe_2O_4$ compound. Hence, it is expected that composite multiferroics consisting of $Co_{0.8}Fe_{2.2}O_4$ compound show higher magnetoelectricity compared to that consisting $CoFe_2O_4$. In addition, it has been clearly revealed [13,14] that the magnetostriction sensitivity ($d\lambda/dH$) of cobalt ferrite could be increased by Mn substitution. In other words, the magnetostriction of Mn substituted cobalt ferrite is higher than that of pure cobalt ferrite at low magnetic field, which promotes its application. To the best of our knowledge, there are no reports on the effect of cobalt ferrite composition (neither $Co_{0.8}Fe_{2.2}O_4$ nor Mn substituted one) on the magnetoelectric coupling in composite multiferroic.

Magnetoelectric coupling measurements in composite multiferroics have been investigated by conventional modulation of the polarization with applying a magnetic field such as measuring the dynamic change of the open-circuit voltage, capacitance or charge of the sample. The results of these methods usually accompany with the presence of parasitic effects, such as interfacial polarization leakage and the Maxwell–Wagner interfacial conductivity effect. Moreover, the electro-magnetic induction and magnetoresistance of the magnetic phase, as well as thermal effects can contribute to the measured signal [2–6]. On the other hand, characterization of composite multiferroic nanostructures such as nano-layered thin films and nanofibers suffers from size limitations. In addition, magnetoelectric composite materials are candidates of integration into microelectronic devices, which makes it important to characterize the magnetoelectric coupling at a local scale. Hence, to overcome this shortcoming and being able to characterize the magnetoelectric coupling locally, novel scanning probe microscopy (SPM) techniques have been recently developed [15–20] to examine the nanoscale magnetoelectric coupling in the multiferroic materials. These techniques map the evolution of piezoresponse as well as ferroelectric domains and switching characteristics upon applying an external magnetic field.

Our previous work showed that the perfectly (111)-oriented cobalt ferrite thin films (with different Co/Fe ratios as well as Mn-substituted one) could be grown on Pt(111)/Si substrate by pulsed laser deposition (PLD) technique [21–24] that allows growth of $Pb(Zr_x,Ti_{1-x})O_3$, PZT, top layer with perfect (111)-orientation [25–27]. The $Co_{0.8}Fe_{2.2}O_4$ thin film showed significantly improved magnetic properties compared to the $CoFe_2O_4$ film [22] and Co substitution with Mn increased the magnetization and decreased the coercivity [24]. The PZT top layer was selected as composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ because of its high piezoelectric properties among other compositions [27]. In this study, the effect of composition of cobalt ferrite underlayer in PZT/cobalt ferrite bilayer thin films are studied using magnetic-assisted piezoresponse force microscopy.

2. Experimental technique

PLD technique has been used especially to deposit high quality complex oxide films for more than a decade. The technique uses high power laser pulses to melt, evaporate and ionize material from the surface of a target. This “ablation” event produces a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablated material is collected on an appropriately placed substrate upon which it condenses and the thin film grows. The PZT and cobalt ferrite films were deposited on commercial Pt(111)-150 nm/Ti-10 nm/SiO_2-300 nm/Si(100) substrate by PLD technique, using a PZT target with $Pb(Zr_{0.52}Ti_{0.48})O_3$ composition and the cobalt ferrite targets with $CoFe_2O_4$, $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$ compositions. The details of target preparation are described elsewhere [21–27]. A KrF excimer laser (248 nm wavelength and 23 ns pulse width, Lambda Physics) with energy density of about 2 J/cm^2 was used for ablating the targets. The laser repetition rate was selected as 5 and 10 Hz for PZT and cobalt ferrite 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 4 cm distance from the target. Before deposition, the chamber was evacuated to 1×10^{-6} Torr and the cobalt ferrite and PZT films were deposited at oxygen pressure (P_{O2}) of 10 and 50 m Torr, respectively. All films were grown at substrate temperature of 600 °C. A multi target holder system was used for deposition of bilayers to avoid breaking of the vacuum and heating. After deposition, the films were cooled down to room temperature at a rate of 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) performed by synchrotron radiation (wavelength of 0.15401 nm) at 3D XRD beamline 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 the samples was observed by 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, LakeShore, Model 7407). The magnetic hysteresis loops (M-H curves) were obtained after subtracting of diamagnetic effect of sample holder as well as that of PZT/Pt/Si substrates.

All the SPM experiments were performed on Asylum Research MFP-3D atomic force microscope (AFM). AC240TM probes made of silicon with Ti/Pt (5/20) coating and tip radius of 28 ± 10 nm were used for PFM and topography imaging. The lever is coated with Al and its nominal natural frequency and stiffness are 70 kHz and 2 N/m, respectively. To confirm the local magnetoelectric coupling of samples at nanoscale, PFM analyses were carried out under in-plane magnetic fields up to 2000 Oe using an Asylum Research variable field module (VFM). This allows us to examine the evolution of piezoresponse of ferroelectric domains and polarization switching characteristics induced by the external magnetic field [16,17,20]. It is worth to note that PFM analyses were carried out at the same area under different magnetic fields.

3. Results and discussion

In this work, the cobalt ferrite and PZT films were deposited based on our optimum growth conditions [21–27]. Fig. 1 shows the XRD θ–2θ scan of $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$ single layers along with PZT/$Co_{0.8}Fe_{2.2}O_4$ and PZT/$Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$ bilayer films grown under same deposition conditions. The $Co_{0.8}Fe_{2.2}O_4$ and $Co_{0.6}Mn_{0.2}Fe_{2.2}O_4$ films were found highly oriented along the <*l l l*> directions on Pt(111)/Si substrate. No peak related to the other planes of cobalt ferrite was detected and pha. In addition, the PZT top layers were found perfect (111)-orientated perovskite single phase without any peak related to the pyrochlore phase. It is also well-known that inserting the oxide layer such as cobalt ferrite on Pt before deposition of PZT leads to the perovskite phase formation in as-deposited film as a result of suppressing the Pb deficiency on the substrate during deposition, which is reported in detail previously [25]. Furthermore, the chemical analysis by energy dispersive spectroscopy (EDS) using scanning electron microscope (SEM) in our previous works [21–27] showed the stoichiometric composi-