AIP Applied Physics Letters

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Citation: Applied Physics Letters **91**, 142910 (2007); doi: 10.1063/1.2798054
View online: http://dx.doi.org/10.1063/1.2798054
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/91/14?ver=pdfcov
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Magnetoelectric coupling of [00*l*]-oriented $Pb(Zr_{0.4}Ti_{0.6})O_3-Ni_{0.8}Zn_{0.2}Fe_2O_4$ multilayered thin films

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(Received 25 July 2007; accepted 20 September 2007; published online 5 October 2007)

Multilayered thin films consisting of alternatively stacking $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZFO) layers were fabricated to exploit a strain-mediated coupling of piezoelectricity and magnetostriction. The 450-nm-thick PZT/NZFO multilayer fabricated by pulsed laser deposition showed magnetodielectric effects upon applying a static magnetic field. The magnetoelectric (ME) susceptibility values estimated using these magnetodielectric responses were in the range of 15–30 mV/cm Oe at a zero magnetic-field strength and were comparable to those obtained using a more commonly employed "dynamic" ME method. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2798054]

Multiferroic ferroelectromagnets that possess simultaneous ferroelectric and ferromagnetic orders have attracted intense scientific and technological interest.[1–4] However, the rareness of room-temperature multiferroics[2] has led many workers to combine ferroelectric materials with ferromagnetic phases, for example, bulk laminates,[5,6] multilayer structures of thick films,[7,8] and nanoparticulate film structures.[9,10] In these two-phase systems, magnetoelectric (ME) coupling effects can be considered as arising from the interfacial strain-mediated coupling of piezoelectricity and magnetostriction.

Recently, Zheng *et al.*[11] reported the fabrication of three-dimensional-nanopillar structure, where $CoFe_2O_4$ spinel ferromagnetic nanopillars were embedded in a ferroelectric $BaTiO_3$ matrix. According to their assertion, a multilayer structure on a certain substrate, in general, cannot show the ME coupling because the clamping effect by a substrate suppresses the magnetostriction or piezoelectricity at the interfaces. On the contrary, their nanopillars were vertically aligned and thus, the interfacial ME coupling was not hindered.[11] However, epitaxial misfit strains are fully relaxed above a certain critical distance from a substrate.[12] Thus, one would expect a multilayer structure with reasonably strong ME coupling by making the first layer thick enough to relieve the strain from the substrate. Here, we report the ME coupling properties of a piezoelectric-magnetostrictive multilayer structure fabricated by alternatively stacking $Pb(Zr_{0.4}Ti_{0.6})O_3$ (PZT) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZFO) layers with a periodicity of 30 nm.

Pulsed laser deposition was used to fabricate a PZT/NZFO multilayer structure on a (001) plane of $SrTiO_3$ (STO) single-crystalline substrate buffered with a $SrRuO_3$ (SRO) bottom-electrode layer. All the multilayer films were grown at 650 °C under P_{O_2} of 100 mTorr. To effectively reduce the clamping effect, a 100-nm-thick SRO layer was deposited on STO (001) and the first PZT layer was deposited on the SRO layer to a thickness of 150 nm. Then, 30-nm-thick NZFO and PZT layers were alternatively stacked for five times one after another. Thus, the present multilayer consists of 11 alternating layers, and the total film thickness is 450 nm $(150+60\times5)$. For dielectric measurements, a Au(100 nm)/Ti(30 nm) top electrode with a diameter of 200 μm was deposited on the top PZT layer.

We first fabricated a PZT/NZFO bilayer (180 nm) and a PZT/NZO/PZT trilayer (210 nm) to examine the growth pattern of these stacking layers. As shown in the θ-2θ x-ray diffraction (XRD) patterns of bi- and trilayers [Fig. 1(a)], both PZT and NZFO layers exhibit a highly (00*l*)-oriented growth. Φ-scan spectra further indicate a coherent epitaxial growth of the PZT/NZFO bilayer on (001) STO [Fig. 1(b)]. The observed fringes around the SRO (002) peak indicate that the SRO layer is fully strained. Therefore, this bottom-electrode layer does not contribute to the reduction of clamping effect. A broad peak centered at $2\theta=44.57°$ (marked with an asterisk) in the multilayer suggests the formation of *a*-axis ferroelectric domains in the PZT layers.

One interesting conclusion can be deduced by examining the peak positions of PZT (002) and NZFO (004). The *c*-axis lattice parameter of PZT decreases with increasing number of the stacking layers: 4.122 Å for a bilayer, 4.115 Å for a trilayer, and 4.102 Å for a multilayer. The corresponding in-plane *a*-axis lattice parameters are 4.021, 4.028, and 4.041 Å, respectively. Since the *c*-axis and *a*-axis lattice parameters of the bulk unstrained $Pb(Zr_{0.4}Ti_{0.6})O_3$ are 4.100 and 4.043 Å, respectively,[13] one can conclude that the clamping effect by the STO substrate is effectively removed in the PZT layers of the 450-nm-thick film. Similarly, the in-plane lattice parameter of NZFO increases gradually with increasing number of the stacking layers: 8.356 Å for a bilayer, 8.362 Å for a trilayer, and 8.364 Å for a multilayer. Since the cubic lattice parameter of the bulk unstrained NZFO is 8.365 Å,[14] the epitaxial misfit strain is fully relaxed in the NZFO layers of the 450-nm-thick film. Thus, the PZT/NZFO structure consisting of 11 alternating layers satisfies the prerequisite for the interfacial ME coupling of piezoelectricity and magnetostriction.

The remanent polarization (P_r) and the coercive field (E_c) of the 450-nm-thick multilayer are 26 $\mu C/cm^2$ and 500 kV/cm, respectively, under the maximum applied electric field (E_{max}) of 1500 kV/cm [Fig. 2(a)]. Compared with the polarization-field (*P*-*E*) hysteresis loop of the trilayer

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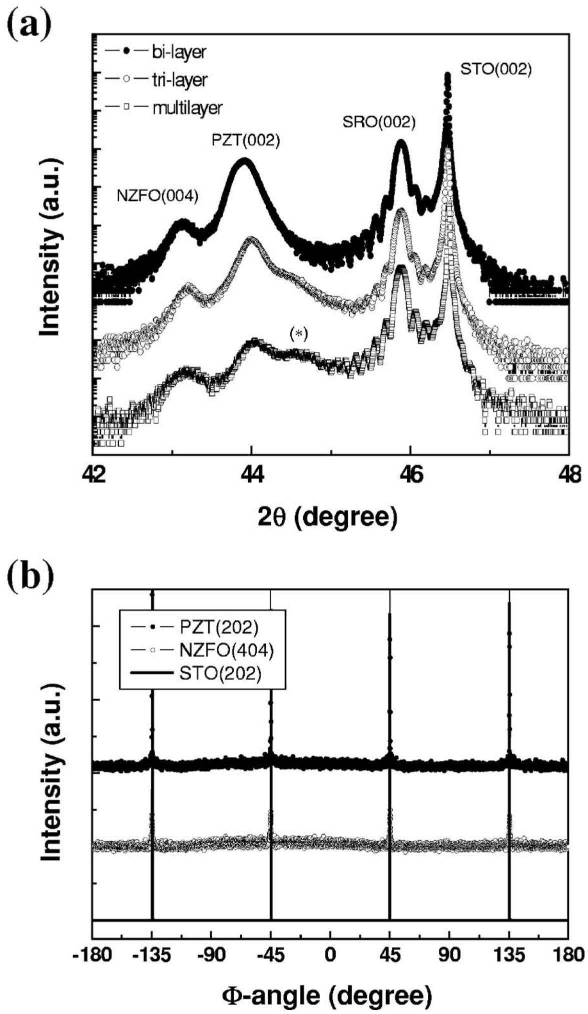

FIG. 1. (a) θ-2θ XRD patterns of three distinct layered structures in descending order: a PZT/NZFO bilayer (180 nm), a PZT/NZFO/PZT trilayer (210 nm), and a PZT/NZFO multilayer structure consisting of 11 alternating layers (450 nm). (b) XRD Φ-scan spectra of the 180-nm-thick PZT/NZFO bilayer.

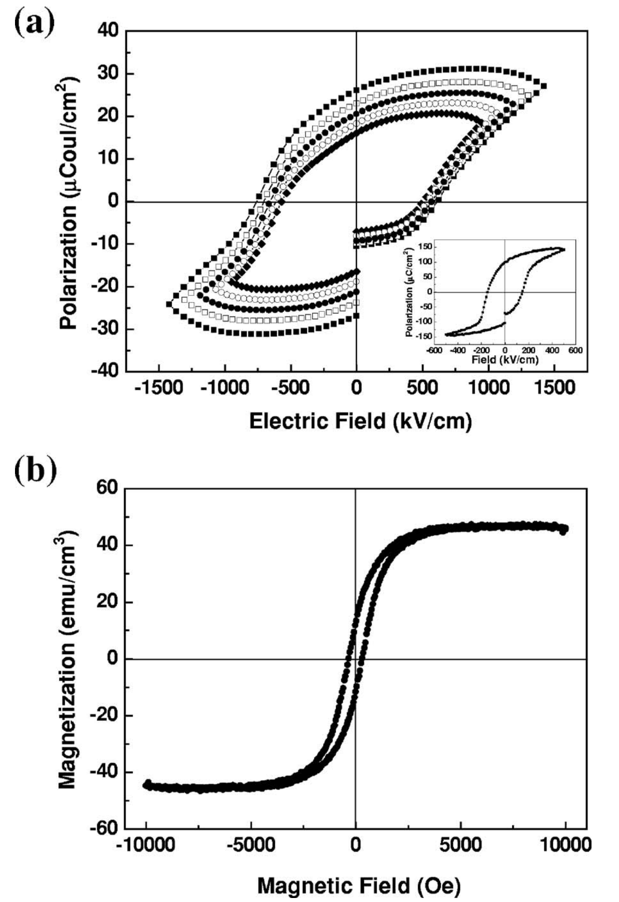

FIG. 2. (a) P-E hysteresis loops obtained at 1 kHz and (b) M-H hysteresis curve of the PZT/NZFO multilayer structure consisting of 11 alternating layers.

[$P_r \approx 100\ \mu\mathrm{C/cm^2}$, inset of Fig. 2(a)], the P-E curves of the multilayer tend to be electrically leaky near $E_{\max}$ and show significantly reduced P_r. This smaller value of P_r seems to be closely related to the increasing fraction of the a-axis domains with increasing number of the stacking layers [Fig. 1(a)]. As presented in Fig. 2(b), the saturation magnetization and the coercive field of the 450-nm-thick multilayer are 46 $\mathrm{emu/cm^3}$ and 300 Oe, respectively, for the static magnetic field applied parallel to the stacking plane.

Figure 3(a) presents the percent change in the real part of dielectric permittivity ($\Delta\varepsilon \equiv \Delta\varepsilon'_{33}$) as a function of the applied static magnetic field along the longitudinal direction (ΔH_3). The result clearly shows pronounced magnetodielectric (MD) effects of the present PZT/NZFO multilayer. The amplitude of the measuring ac electric field (E_0) was 2.22 kV/cm. Similar results, i.e., pronounced MD effects with their measuring frequency dependence, were also observed in a sol-gel-processed Sc-modified $BiFeO_3$ film.[15] The observed MD effect (magnetocapacitance) can be explained in terms of the magnetically induced polarization. The application of a longitudinal bias field (ΔH_3) induces a magnetostriction in the NZFO layer along the direction 3. This magnetostriction then induces a piezoelectric strain in the neighboring PZT layers, thereby producing the magnetically induced polarization (ΔP_3). The induced polarization is proportional to the change in the relative dielectric susceptibility under the bias field ΔH_3 by the following relation: $\Delta P_3 e^{+i(\omega_p t-\delta)} = \varepsilon_0 \Delta\eta_{33} E_0 e^{+i\omega_p t}$, where E_0 is the amplitude of the measuring ac electric field with the frequency ω_p and δ is the phase lag between the induced polarization and the ac field.

Considering the magnetically induced polarization or voltage, one can establish the following relation for the frequency-dependent longitudinal ME susceptibility $\chi_{E,33}$:

$$\chi_{E,33} \equiv \frac{\Delta V_{\mathrm{ind},3}(\omega_p)}{\Delta H_3} = \frac{E_0}{\eta'_{33}} \frac{[(\Delta\eta'_{33})^2 + (\Delta\eta''_{33})^2]^{1/2}}{\Delta H_3}, \qquad (1)$$

where $\Delta V_{\mathrm{ind},3}(\omega_p)$ denotes the voltage induced along the direction 3 (i.e., direction vertical to the electrode plane) under various ac-field frequencies. $\Delta\eta'_{33}$ and $\Delta\eta''_{33}$ represent the change in real and imaginary parts of the dielectric susceptibility ($\eta_{33} = \varepsilon_{33} - 1$) which is induced by the bias magnetic field (ΔH_3). Figure 3(b) shows $\chi_{E,33}$ estimated using Eq. (1) and magnetocapacitance data ($\Delta\eta'_{33}$ and $\Delta\eta''_{33}$). Except for a weak static field up to 2000 Oe, $\chi_{E,33}$ tends to decrease steadily with increasing ΔH_3. The inset demonstrates an instantaneous response of the relative dielectric permittivity ($\Delta\varepsilon'_{33}$) to ΔH_3 at 1.0 T.

To compare the above estimated $\chi_{E,33}$ with the ME susceptibility obtained under a "dynamic" condition, we also measured the ME output by applying an oscillating magnetic

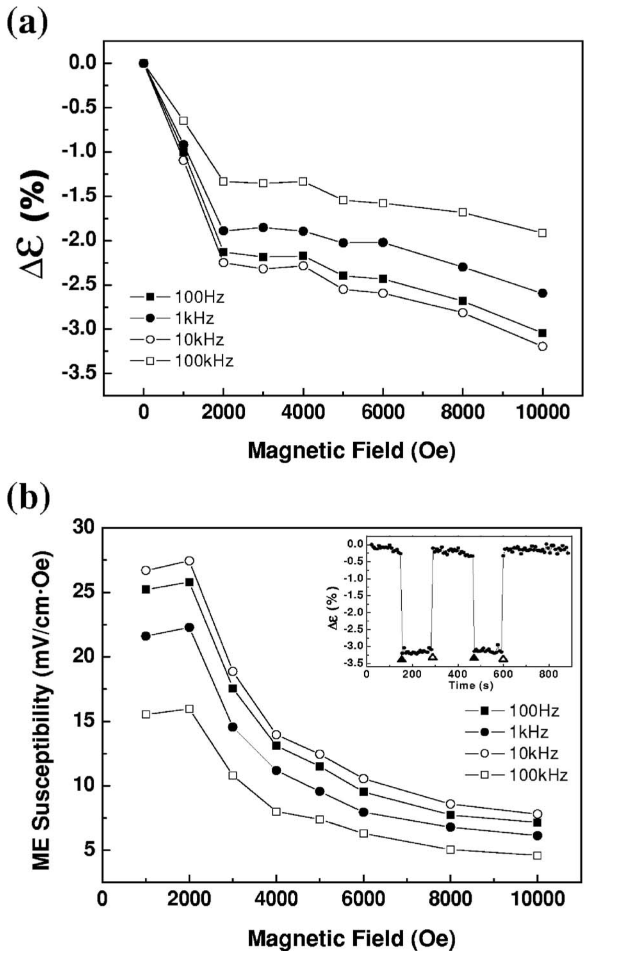

FIG. 3. ME coupling characteristics of the 450-nm-thick PZT/NZFO multilayer consisting of 11 alternating layers. (a) Percent change in the real part of dielectric permittivity at various measuring ac electric-field frequencies. (b) Longitudinal ME susceptibility plotted as a function of ΔH_3.

field of a small amplitude ($\delta He^{-i\omega_m t}$) under a static bias field (H_0). A homebuilt dynamic ME setup was used to determine the time-dependent induced voltage.[16,17] Figure 4 reveals the dynamic ME voltage susceptibility at two different frequencies for the longitudinal magnetic field applied parallel to the direction 3. According to theoretical analysis by Srinivasan *et al.*,[8] the longitudinal dynamic ME voltage coefficient ($\chi^d_{E,33}=\delta V_3/\delta H_3$) is proportional to $-d^p_{31}(\delta\lambda^m_{13}/\delta H_3)$, where d^p_{31} denotes the piezoelectric voltage response along the direction 3 by the magnetostriction along the in-plane direction, and $\delta\lambda^m_{13}$ denotes the variation of the magnetostriction along the direction 1 by δH_3. According to Srinivasan *et al.*,[8] $q^m_{13}(\equiv\delta\lambda^m_{13}/\delta H_3)$ of the 406-μm-thick PZT-NFO laminate is essentially constant, independent of the bias H field. If this result also applies to the present PZT-NZFO multilayer having 20 at. % Zn-substituted NFO layers, the longitudinal ME voltage susceptibility ($\chi^d_{E,33}$) is expected to show a nearly constant plateau behavior with respect to the variation of the bias magnetic field. The dynamic ME results presented in Fig. 4 are basically consistent with this prediction.

In summary, the 450-nm-thick PZT/NZFO multilayer fabricated on a STO substrate buffered with a SRO bottom-electrode layer showed MD effects upon applying a static magnetic field. The ME susceptibility values estimated using these MD responses are in the range of 15–30 mV/cm Oe at

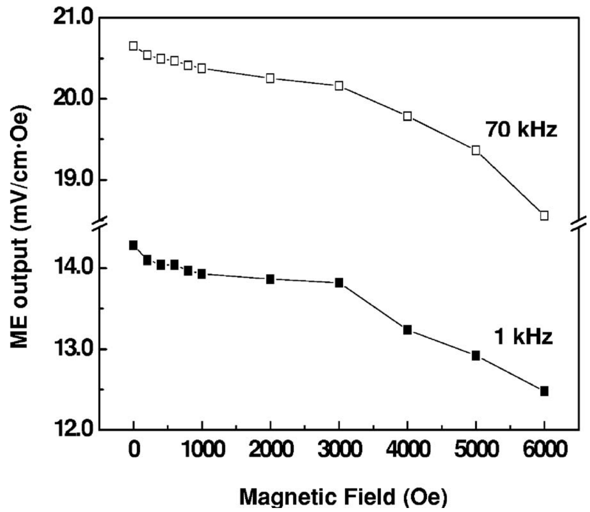

FIG. 4. Longitudinal ME voltage susceptibility values obtained by "dynamic" ME measurements at $\omega_m=1$ and 70 kHz with the amplitude of an oscillating magnetic field (δH) of 10 Oe. Both the bias H field and the oscillating field (δH) are parallel to the direction 3.

a zero magnetic-field strength and are comparable to those obtained using a more commonly employed dynamic ME method.

This work was supported by the Korea Research Foundation under Contract No. KRF-2004-041-D00329.

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