Interface effects on the magnetoelectric properties of (00l)-oriented Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$/CoFe$_2$O$_4$ multilayer thin films

Rueijer Lin,[a] Tai-bor Wu[a,*] and Ying-Hao Chu[b]

[a]*Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan 30013, ROC*
[b]*Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan 30010, ROC*

(00l)-oriented Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$/CoFe$_2$O$_4$ (PZT/CFO) multilayer thin films were fabricated with a change in stacking periodicity. When the periodicity increased, a size effect on both ferroelectric and ferromagnetic properties was observed. This result indicates the existence of a passive layer at the PZT/CFO interface. Consequently, the magnetoelectric coupling was significantly degraded with increasing stacking periodicity. From transmission electron microscopy analysis, in addition to slight interdifussion, a highly roughened interface structure is believed to be responsible for the formation of the passive layer.
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Multiferroic composites constructed from piezo-electric and magnetostrictive materials show strong magnetoelectric (ME) coupling through elastic interaction and are of great interest for a wide range of applications in magnetic sensors, transformers and microwave devices [1,2]. Recently, various composite systems have been fabricated, including ceramic bulk, thick laminates and thin (nanoscale) films. Of the many composite systems, the multilayer (2–2 type) ME composites displayed very large ME coupling because of the reduced leakage current and ease of poling the electric dipoles [3]. Since the ME coupling in composites is mediated by strain, the large interfacial area was expected to enhance the ME coupling. Nevertheless, for 2–2 multilayer laminates, the ME coupling coefficient was reduced with increasing stacking periodicity, which was attributed to pinning of interfacial defects, which limited the motion of domain walls [4]. Such a result suggests that the interfacial effects are key to constructing ME composites. However, for thick laminate systems, it is difficult to identify the role of the interface. In this study, multilayer composite thin films were adopted as a model system to study the interfacial effects.

Highly (00l)-oriented multilayer thin films of Pb(Zr$_{0.5}$Ti$_{0.5}$)O$_3$/CoFe$_2$O$_4$ (PZT/CFO) with three (L3),

five (L5) and seven (L7) sublayers were sequentially deposited by a dual-cathode RF sputtering system on LaNiO$_3$ (LNO, 120 nm)/Pt (150 nm)/TiO$_x$ (50 nm)/ SiO$_2$ (150 nm)/Si substrate as shown illustratively in Figure 1a. The (00l)-oriented LNO bottom electrode was chosen to grow the multilayer structure because it can promote the crystallization of perovskite thin films [5]. Moreover, compared to polycrystalline structure, the highly (00l)-oriented PZT/CFO multilayer thin films on LNO also provide assist the alignment of electric polarization and magnetic moment. The total thickness of PZT and CFO sublayers were fixed at 200 and 80 nm, respectively. Both PZT and CFO sublayers were sputtered in pure Ar at 873 K. Details of the growth conditions were reported elsewhere [6]. The crystalline structure of the films were examined by X-ray diffraction (XRD, Shimadzu LabX XRD-6000) with Cu-Kα radiation in the mode of θ–2θ scan, and the cross-sectional image of the multilayer thin film was observed by scanning transmission electron microscopy (STEM; Tecnai G2). For electrical measurement, Pt top electrodes were deposited through a shadow mask by RF sputtering. The magnetic property of the films at room temperature was measured with a vibrating sample magnetometer (VSM) and the hysteresis loops of polarization-electric field (P-E) relation were measured at 500 Hz with a TF-2000 analyzer FE module (aixACCT Co.). The dynamic ME signals at room temperature were obtained by a lock-in amplifier (Stanford Science, SR-830) under

* Corresponding author. E-mail addresses: rueijer@gmail.com; tbwu@ mx.nthu.edu.tw
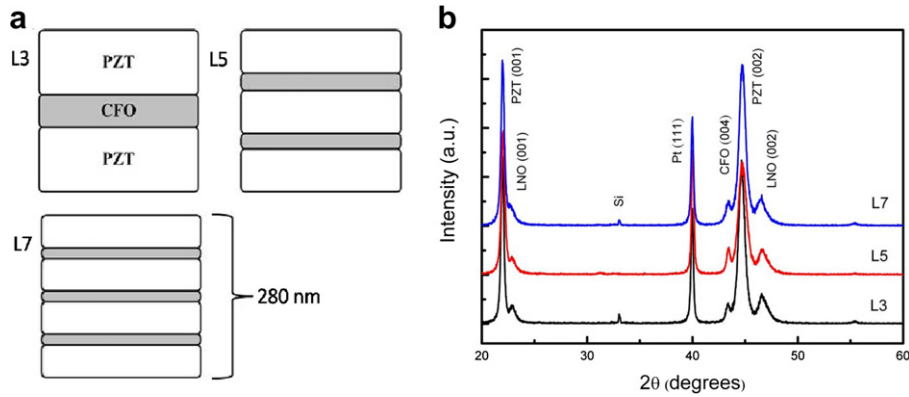
Figure 1. (a) Schematic pictures of PZT/CFO multilayer thin films. (b) X-ray diffraction patterns of the PZT/CFO/PZT trilayer thin films with different stacking periodicities.

an alternating magnetic field (H_{ac}) driven by a pair of Helmholtz coils with a function generator (Stanford Science, DS-345) imposed with a DC magnetic bias (H_{dc}) in parallel [7,8]. The in-plane ME signals were measured in samples that were bonded with Al wire on the top and bottom electrode.

In Figure 1b, the XRD patterns of the PZT/CFO multilayer thin films exhibited well-defined ($00l$) peaks of LNO, PZT and CFO without any impurity phase, which reveals the highly ($00l$)-oriented structure of PZT/CFO multilayer grown coherently on the ($00l$)-oriented LNO bottom electrode. This highly ($00l$)-oriented structure for PZT can generate a high piezoelectric coefficient [9], which is expected to induce a larger ME coupling. Moreover, regardless of the large PZT/CFO lattice mismatch (($a_{CFO} - 2a_{PZT})/a_{CFO} \sim 2.9\%$), the XRD result demonstrates that the PZT/CFO multilayer structure can be grown coherently on LNO-coated substrate.

Figure 2 shows the coexistence of FE and FM properties in the multilayer structure. The in-plane M–H loops of the PZT/CFO multilayer thin films were measured at room temperature under 15 kOe where the magnetization value was normalized to the CFO thin film volume on a 1×1 cm^2 substrate. As shown in Figure 2a, typical hard-magnetic M–H loops with coercivity of about 2100 Oe were found for the three multilayer thin films. However, the CFO magnetization was significantly reduced with increasing of the stacking periodicity, i.e. decreasing the sublayer thickness. This size-dependent magnetic property has been widely investigated, and is due to the presence of a non-magnetic layer at the ferromagnetic (FM)/non-ferromagnetic interface or free surface [10,11]. Therefore, the presence of a non-magnetic layer formed at each PZT/CFO interface is also considered in this study. PZT/CFO/PZT trilayer structures with changing CFO interlayer thickness were also fabricated to study the formation of the non-magnetic layer [6]. In the multilayer thin film of higher periodicity, more non-magnetic layers can be formed at the PZT/CFO interfaces, indicating that there would be a less effective magnetic volume ratio, and thus a diluted magnetization can be realized.

The ferroelectric (FE) properties of pure PZT (200 nm thick), L3, L5 and L7 thin films are shown in Figure 2b. A typical symmetric hysteresis P–E loop was observed

for the pure PZT thin film. To examine the space charge contribution to the polarization, P–E curves of L5 at various temperatures from 298 to 423 K are also displayed in the inset of Figure 2b. The nearly temperature-independent P–E curves of L5 indicate that the hysteresis loop mostly arises from the intrinsic FE property rather than the movement of space charge. However, the PZT/CFO multilayer thin films show tilted P–E curves compared to the pure PZT thin film, and a voltage shift to positive bias was also observed for L5 and L7. A similar voltage-shift phenomenon was reported in PZT/LSMO multilayer thin films, and was attributed to the presence of a passive layer at the PZT/CFO interface [12]. The passive layer had a non-switching behavior and the formation of this layer was complicated [13]. When the stacking periodicity was increased, the passive layer thickness ratio (d/h, where d is the thickness of passive layer and h is the thickness of the FE layer) increases, causing a decrease in the effective electric field subject to the FE layer under the same applied voltage. Thus the measured polarization would be reduced, leading to a tilted hysteresis curve. This trend is consistent with the simulated data of Tagantsev et al. [14].

Both the FM and FE results suggest the existence of a passive or non-magnetic layer at the PZT/CFO interface. To verify that, STEM investigation was employed on the specimen of L7. The cross-sectional image of L7 is shown in Figure 3a. Large columnar grains with clear interface were coherently grown across the multilayer structure. A prism-like surface and interface morphology was also formed between the columnar grains. This is because CFO tends to exhibit a pyramidal crystal form on ($00l$)-oriented PZT due to the surface anisotropy of PZT and CFO [15]. In consequence, the highly coherent growth structure results in a highly roughened interface, which is harmful to the FE and FM properties due to the increase of depolarization and demagnetization at the roughened interface, respectively. Moreover, Figure 3b shows the depth profile of the chemical composition obtained from the EDX line scan. It reveals that there is also a slight interdiffusion at the PZT/CFO interface. The slight interdiffusion at the interface would also degrade the FE and FM property in the region adjacent to the interface. Therefore, the roughened and interdiffused interface could play the role of
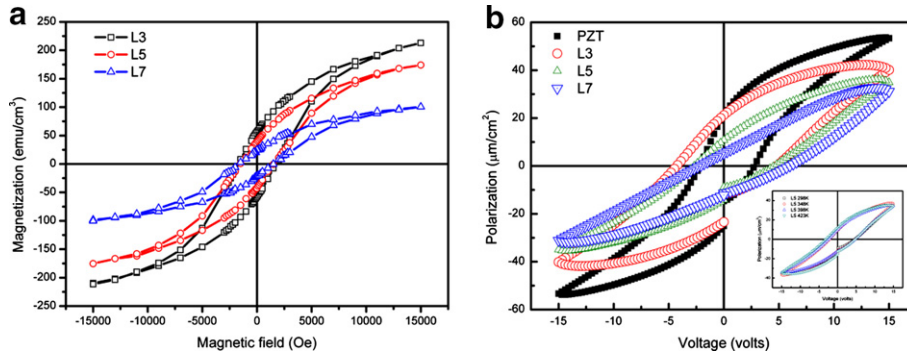
Figure 2. (a) The in-plane M–H loops of the three PZT/CFO multilayer thin films. (b) P–E curves of the pure PZT thin films and the three PZT/CFO multilayer thin films. The inset shows the P–E curves of L5 at different temperatures from 273 to 423 K.
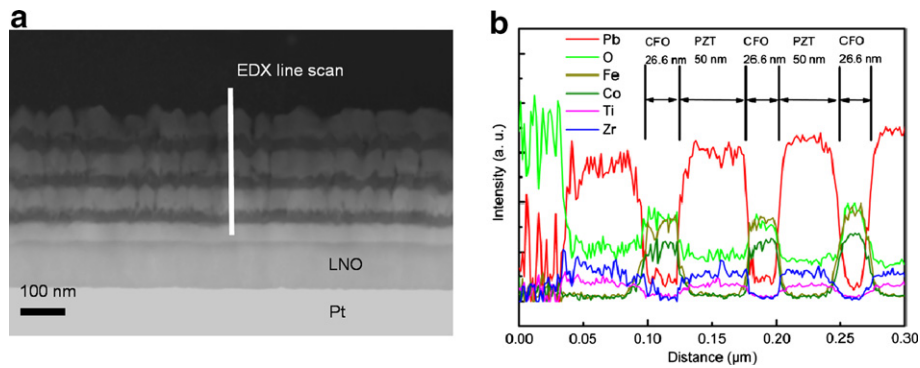

Figure 3. (a) The STEM image of L7. The solid line indicates the EDX scan line. (b) Chemical depth profile of the EDX line scan for L7.

thenon-switching layer in both FE and FM sublayers, which would seriously affect FE and FM responses for the multilayer structure with nanoscale sublayers.

The dynamic in-plane ME signals of L3, L5 and L7 were measured by a lock-in amplifier under H_{ac} (∼5 Oe) at 1 kHz imposed with H_{dc} in parallel from 0 to 7 kOe. As shown in Figure 4a, the in-plane ME coefficients ($\alpha_E = \Delta V/(H_{ac} \cdot t)$, where ΔV is the ME voltage and t is the PZT/CFO multilayer thickness) of the three multilayer thin films are insensitive to H_{dc} but strongly influenced by the stacking periodicity. The induced ME signal as a function of H_{dc} ($\delta V = \Delta V(H_{dc}) - \Delta V(H_{dc} = 0)$) is also depicted in Figure 4b. In contrast to the large ME response to H_{dc} in 3–0 type thin films [16], the induced voltage in the multilayer (2–2 type) thin films is quite weak, which is most likely related to the clamping effect inherent in the multilayer structures that limited the piezoelectric response of PZT and magnetostriction of CFO [17]. In addition, the specimen of L3 has the largest ME-coupling coefficient, but those of L5 and L7 are significantly reduced with increasing stacking periodicity. Since the ME coupling occurs via the elastic interaction of FE and FM domains, it can be supposed that the decrease in ME coupling arises from the reduction of FE and FM responses of the three multilayer thin films. Compared to the possible defect pinning effect for the ME thick laminates with different stacking periodicities [4], the passive layer at the interface in the multilayer thin films system is largely responsible for degrading the ME coupling. Consequently, instead of monotonously
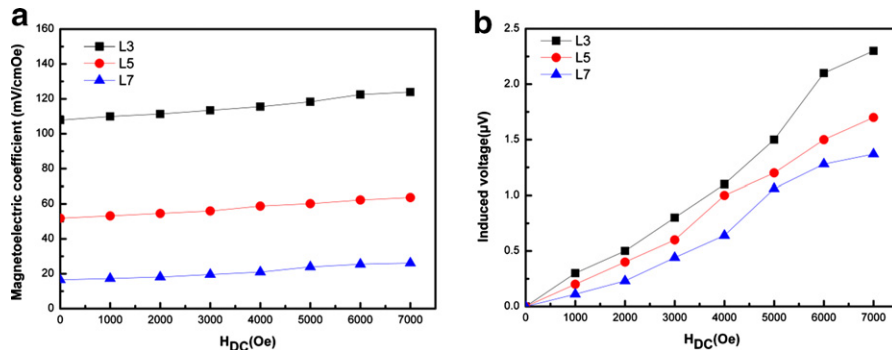

Figure 4. (a) The ME-coupling coefficient of PZT/CFO multilayer thin films. (b) The DC magnetic field-induced voltage under H_{ac} at 1 kHz measured from 0 to 7 kOe.

increasing the interfacial area, the formation of the passive nanoscale layer in FE and FM phases should be taken into consideration for multifunctional applications of ME composite thin films.

In summary, we have fabricated (0 0 *l*)-oriented PZT/CFO multilayer thin films with different periodicities on LNO-coated Si substrate to explore the interfacial layer effects. The thin films show both FE and FM characteristics. However, the FE and FM responses are reduced with increasing the stacking periodicity, which suggests the presence of a passive layer at PZT/CFO interface. The ME-coupling behavior also degrades with increasing stacking periodicity. This indicates that the volume fraction of the passive layer at the PZT/CFO interface plays an important role in the degradation of ME properties of the (0 0 *l*)-oriented PZT/CFO multilayer thin films. The cross-sectional STEM imaging reveals the formation of a highly roughened interface structure due to the coherent growth of large columnar and prism-like grains across the PZT and CFO sublayers in the multilayer thin films. An interdifussion of composition was also found at the interface between the PZT and CFO sublayers. It is believed that the roughened and interdiffused interface is responsible for the role of the passive layer in the (0 0 *l*)-oriented PZT/CFO multilayer thin films.

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