

Significant enhancement of magnetoelectric output in multiferroic heterostructural films modulated by electric polarization cycles

Yujie Wu,^{1,2} Jian-guo Wan,^{1,a)} Jun-ming Liu,¹ and Guanghou Wang¹

¹Department of Physics, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

²Department of Physics, South China University of Technology, Guangzhou 510640, People's Republic of China

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The Pb(Zr,Ti)O₃/CoFe₂O₄/Pb(Zr,Ti)O₃ heterostructural film was prepared and the variation in its magnetoelectric output with the cycling electric polarization was investigated. The giant magnetoelectric output, which was about one order enhancement in magnitude compared with the original film, was observed after the film was subjected to the cycling electric polarization with the strength of 45 MV/m and cycling number of $\sim 2.2 \times 10^8$. We consider that both oxygen vacancy migration in the heterostructure and the polarized electric charges in the CoFe₂O₄ layer play important roles in such significant magnetoelectric enhancement. © 2010 American Institute of Physics. [doi:10.1063/1.3394008]

The multiferroic magnetoelectric (ME) materials consisting of both ferromagnetic and ferroelectric orderings have attracted tremendous interest due to their multifunctionality. Based on the coupling between the ferromagnetic and ferroelectric orderings in the ME materials, magnetic-field control of electric polarization or electric-field control of magnetization can be achieved, which provides an opportunity for the development of next-generation storage devices with higher storage density and lower power consumption.¹⁻⁴ For actual applications, it is crucial to pursue giant ME effect in the multiferroic materials. At present, an available strategy is to synthesis the multiphase composite by combining piezoelectric and magnetostrictive components. Strong ME effect can be achieved through the interfacial strain-mediated transferring and coupling between piezoelectricity and magnetostriction.⁵ Unfortunately, unlike the bulk composite, the heterostructural film shows quite weak ME coupling because of the substrate constraint effect.⁶ In order to enhance the ME output, significant effort has been made on controlling the morphology of the component phases in the heterostructural films, e.g., the preparation of the multiferroic vertical nanostructured film consisting of the ferromagnetic pillarlike phase which is epitaxially embedded into the ferroelectric matrix.^{7,8} Another available avenue is to deposit the ME heterostructural film onto the substrate with a buffered bottom-electrode layer.⁹ In spite of these effort, the ME output of the heterostructural film is not sufficient for the practical uses.

On the other hand, the periodic electric field modulation may be promising for the enhancement of the ME output in the multiferroic heterostructural film. The periodic electric field is an energetically higher perturbation, enough to cause the microstructure change in the material, e.g., the migration of the oxygen vacancies,^{10,11} which could consequently lead to the great change in the physical properties. In this letter, we report the significant enhancement of ME output in the ferroelectric-ferromagnetic heterostructural film upon the

modulation of the cycling electric field. We observe that, after undergoing the electric polarization cycles the heterostructural film shows giant ME output enhanced by one order in magnitude, which is sufficient for the practical applications. We reveal that such ME modulation is attributed to the formation of the additional polarized electric charges in the ferromagnetic layer, introduced by the oxygen vacancy migration from the ferroelectric layer to ferromagnetic layer during the electric polarization cycles.

In this work, a sandwich-structural film of Pb(Zr_{0.52}Ti_{0.48})O₃(PZT)/CoFe₂O₄(CFO)/PZT was grown on the Pt/Ti/SiO₂/Si(100) wafer by the sol-gel process and spin-coating technique. The PZT layer was first deposited on the Pt/Ti/SiO₂/Si(100) wafer and annealed at 650 °C for 5 min under the oxygen atmosphere. And then the CFO layer and another PZT layer were in sequence deposited and annealed by the same process. The thickness of the whole film is ~ 220 nm, and each PZT and CFO layer was ~ 80 nm and 60 nm in thickness, respectively. The XRD phase structure characterization confirmed that there existed no additional phases in the film apart from the PZT and CFO phases. The field dependent in-plane magnetization measurement at room temperature showed that the film possessed evident ferromagnetism with saturation magnetization of $M_s \sim 70$ emu/cc. For dielectric measurement, Au electrodes with diameter of 200 μm were deposited onto the film surface. The films exhibited a well-defined ferroelectric loop with remanent polarization of $P_r \sim 28$ $\mu\text{C}/\text{cm}^2$.

The ME coupling characterization of the film was subsequently performed in a self-built device. A magnetic bias (H_{bias}) together with a small alternating magnetic field ($H_{\text{ac}} = 5$ Oe) with fixed frequency of 1.0 kHz was applied parallel to the film plane. The induced ME voltage V_{ME} under both H_{ac} and H_{bias} was measured using a lock-in amplifier (SRS Inc., SR830). Before the cycling electric polarization treatment ($N=1$), the film exhibited the weak ME coupling, as shown in Fig. 1. The induced ME voltage increment (ΔV_{ME}) was only ~ 4.0 μV when the saturated H_{bias} of 5.0 kOe was applied.

^{a)}Author to whom correspondence should be addressed. Electronic mail: wanjg@nju.edu.cn.

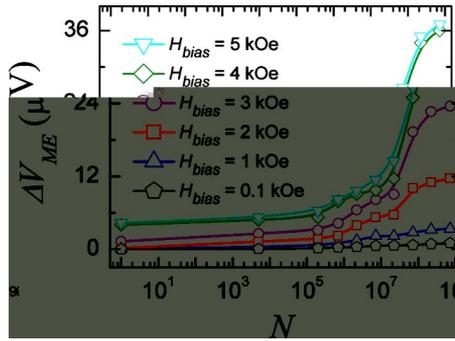


FIG. 1. (Color online) Induced ME voltage increment ΔV_{ME} of the film as a function of N at various H_{bias} .

The cycling electric polarization treatment on the film was carried out on a RT66 ferroelectric testing unit. The 50 kHz bipolar square pulse with field strength of ~ 45 MV/m was applied to the film, which was beyond the ferroelectric coercive force of the film so that the ferroelectric domain in the PZT layer can be reversed adequately. It is surprising that, the ME coupling behavior of the film greatly changed after it was subjected to the cycling electric polarization. Figure 1 presents the induced ΔV_{ME} as a function of cycling number N at various H_{bias} . The ΔV_{ME} value increases with increasing N . When the N value increases to $\sim 10^7$, ΔV_{ME} has an abrupt rise, and increases continuously until it reaches the saturation value near $N \sim 10^9$. The enhanced ME output was giant. Typically, when $N = 2.2 \times 10^8$ the induced ΔV_{ME} value was enhanced to as large as $36 \mu\text{V}$ (measured at $H_{bias} = 5.0$ kOe), almost being a factor of ~ 10 times higher than that of the virgin film.

It is well known that the ME output of the multiferroic material is closely related to the capacitance C and the induced electric charge Q ($V_{ME} = Q/C$). In order to understand the origin of such giant ME enhancement, it is necessary to explore the variation in these two parameters with the cycling electric polarization. We first examined the capacitance variation in the film on an impedance analyzer (HP4294A), as shown in Fig. 2, in which the capacitance decreases continuously with increasing N in the measured frequency range. It is seen that, after subjected to the cycling electric polarization with $N = 2.2 \times 10^8$, the film has a capacitance decrease of $\sim 17\%$ when the measurement frequency is $f = 1.0$ kHz (the inset of Fig. 2). Evidently, the degree of the capacitance decrease is not enough to cause the giant ME enhancement by one order in magnitude, indicating that the enhanced ME

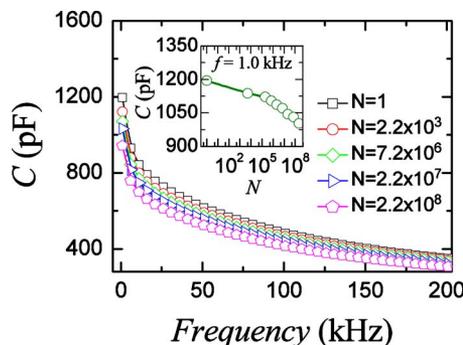


FIG. 2. (Color online) Frequency dependence of the capacitance of the film after subjected to the cycling electric polarization with various N values. The inset is the capacitance vs N at the frequency of 1.0 kHz.

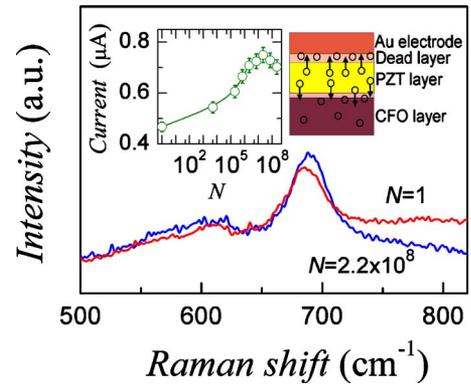


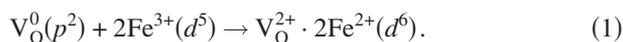
FIG. 3. (Color online) Raman spectra of the film subjected to the cycling electric polarization with $N=1$ and $N=2.2 \times 10^8$. The left inset is the leakage current as a function of N . The right inset is the schematic diagram of the oxygen vacancy migration in the film. The hollow dot represents the oxygen vacancy and the arrow represents its migration direction.

output should be caused by the other factor, i.e., the induced electric charges. For a common PZT/CFO/PZT film without cycling electric polarization treatment, the induced electric charges under the external magnetic bias generally originates from the ferroelectric polarized charges in the PZT layer. However, according to our experimental results (not shown here), the ferroelectric polarization strength of the film almost had no change even after it was subjected to the cycling electric polarization with $N \sim 2.2 \times 10^8$. This suggests that the induced electric charges which cause the significant ME enhancement could not come from the ferroelectric polarized charges in the PZT layer. Accordingly, it implies that the cycling electric polarization treatment must bring about the additional induced electric charges that attribute to the giant ME output.

In order to find the origin of the additional induced electric charges, we then studied the microstructure change in the film subjected to the cycling electric polarization. It was reported that the long-range diffusion of oxygen vacancies was one of the important process in pure ferroelectric oxide film (e.g., PZT) when it was subjected to the cycling electric polarization.¹⁰ However, if PZT is combined with the other oxide (e.g., CFO) to form a heterostructure, the interior electric field distribution of the heterostructure will become non-uniform, and thus the long-range diffusion of the oxygen vacancies will change due to the existence of interface between PZT and CFO. Therefore, in addition to the normal oxygen vacancy diffusion from PZT layer to electrode layer which results in the formation of the dead layer,¹² the oxygen vacancy also has a chance to diffuse from PZT layer to CFO layer since the Schottky barrier in the PZT/CFO interface is so small. Meanwhile, the CFO oxide produces the shallower charge traps and acts as a sink for oxygen vacancies,¹³ which further facilitates the oxygen vacancy diffusion into the CFO layer. The schematic diagram of such oxygen vacancy migration in the heterostructure film is presented in the right inset of Fig. 3. To confirm whether the oxygen vacancy migration happened in the PZT/CFO/PZT film during the cycling electric polarization, we performed the cofocusing microarea Raman spectra measurement, as shown in Fig. 3. The Raman peak located at $\sim 693 \text{ cm}^{-1}$ was observed, which corresponds to the E (LO_3) phonon mode associated with the Ti-O bond in PZT.¹⁴ Before the film was subjected to the cycling electric polarization ($N=1$), the Raman peak was

suppressed to a degree because of the existence of the oxygen vacancies in PZT.¹⁵ After the film was subjected to the cycling electric polarization with $N=2.2 \times 10^8$, the Raman peak intensity increased as a result of the reduction in the oxygen vacancy concentration in PZT, indicating that the oxygen vacancies diffused from PZT layer to CFO layer. Furthermore, we made the leakage current measurement on the film to evaluate the degree of the oxygen vacancy diffusion at various N values, as shown in the left inset of Fig. 3. With increasing N , the leakage current of the film rapidly increases, till reaches the maximum value near $N \sim 10^7$, and then drops. Obviously, the maximum leakage current corresponds to the saturation state of the oxygen vacancies diffused into the CFO layer.¹⁶

By further comparison between the ME coupling characteristic (Fig. 1) and the leakage current characteristic (the left inset of Fig. 3), we find that the leakage current dependence on N is very similar to the ΔV_{ME} dependence on N , and the maximum ΔV_{ME} value is almost corresponding to the N value of $\sim 10^8$ at which the leakage current is maximum. That is to say, the maximum ME output is corresponding to the maximum oxygen vacancy concentration in the CFO layer, indicating that the giant ME enhancement is related to the oxygen vacancy migration which further causes the generation of the additional induced electric charges. This ME enhancement process can be further understood as follows. During cycling electric polarization, the oxygen vacancies diffused into the CFO layer are pinned in the ferromagnetic domain, resulting in the formation of the complexes composed of oxygen vacancy (V_{O}) and metal ion (e.g., Fe^{3+}).¹⁷ This process can be described by the electric charge transfer reaction



Accordingly, the additional ferromagnetic orders are generated due to the superexchange between the $[V_{\text{O}}^{2+} \cdot 2\text{Fe}^{2+}]$ complexes where the Fe^{2+} ions exchange electrons via empty vacancy level,¹⁷ which has been experimentally proven in a transitional-metal-doped dielectric oxide by Griffin *et al.*¹⁸ So, when an external magnetic bias is applied to the heterostructural film, the response of these additional ferromagnetic orders to the magnetic bias will certainly cause the electric charges in the complexes to deviate from their symmetry center, consequently leading to the generation of the induced polarized electric charges.

Different from the conventional ME coupling process which is generally attributed to the ferroelectric polarization in the ferroelectric PZT layer, the present enhanced ME output originates from a nonconventional ME coupling process, i.e., the polarized electric charges in the ferromagnetic CFO layer. Moreover, we found that, after the film was subjected to the cycling electric polarization, even if it was kept for several months, the enhanced ME output was almost unchanged and the situation could be repeated. This is important for the actual application, implying that the combination

of the oxygen vacancies with the metal ions in the CFO oxides is tight enough to maintain the generation of the polarized electric charges under the magnetic bias. We consider that this cycling electric polarization modulation is promising to be a universal method, not only efficient for the ME enhancement of the multiferroic heterostructures, but also applicable for the other functional oxide systems to modulate their physical properties which is related to the oxygen vacancies.

In summary, the PZT/CFO/PZT heterostructural film exhibits significant enhancement of the ME output after it is subjected to the cycling electric polarization. The cycling electric polarization causes the oxygen vacancy migration from the PZT layer to CFO layer. The giant ME output of the film originates from the polarized electric charges in the CFO layer induced by the magnetic field.

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