Electric-field tuning of non-volatile magnetization modulation in NiZn ferrite/PZT multiferroic heterostructure

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ABSTRACT

Electrical-field tuning of non-volatile magnetization modulation in a multiferroic NiZn ferrite/lead zirconate titanate (PZT) heterostructure was investigated at room temperature. The heterostructure was fabricated by spin-spray deposition of Ni0.27Zn0.1Fe2.63O4 ferrite on a specific PZT substrate that possessed residual strain states without voltage support. The biaxial residual strain caused the non-volatile deviation of magnetic moment in the ferrite film via strain-mediated magnetoelectric coupling effect. This phenomenon ultimately led to the non-volatile modulation in ferromagnetic resonance (FMR) and magnetic hysteresis characteristics. The proposed method provides a promising approach for reducing energy consumption in magnetization modulation and can be potentially applied in many non-volatile tunable RF/microwave devices.

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1. Introduction

With the increasing demand for compact, fast, and low-power-consumption RF/microwave devices in the past decade, many researchers have attempted to realize an electric-field (E-field) or voltage control of magnetism as an alternative to magnetic-field (H-field) [1,2]. Recently fabricated composited multiferroic heterostructures achieve strong magnetoelectric coupling because optimal ferroelectric and magnetic-component phases, rather than single multiferroics, are utilized. Many studies have extensively investigated such heterostructures, serve as a promising avenue for achieving large magnetic tunability as a result of converse magnetoelectric (CME) coupling effects at room temperature [3–12]. The CME effect can be realized in multiferroics composites through a strain/stress-mediated interaction; such interaction enables an effective energy transfer between the E-field and the H-field, thereby facilitating the development of important functionalities and the creation of voltage-controlled magnetic devices [13–16]. Unfortunately, the majority of voltage-tunable magnetization switching or ME devices are limited by their volatility; thus, a constant applied E-field, rather than a short-term voltage impulse, is required for tuning and operation. Z. Wang et al. recently realized non-volatile magnetic easy-axis rotation in CoFe2O4 film/PMN-PT heterostructures [17]. Liu et al. achieved voltage-impulse-induced and non-volatile ferroelastic switching of ferromagnetic resonance in FeGaB/PMN-PT(011) (0.71Pb(Mg1/3Nb2/3)O3–0.29PbTiO3) heterostructures [18]. Yang et al. obtained similar non-volatile magnetization switching in CoFeB/PMN-PT heterostructures [19]. In their studies, non-volatility was derived from E-field-induced structural phase transitions in single-crystal PMN-PT substrates. However, single-crystal PMN-PT is very costly, and some PMN-PT substrates can realize nonvolatile “strain memory” effect, some cannot even with the same composition. Nan et al. realized bistable and non-volatile magnetization switching in a FeGaB/PZT heterostructure and found that non-volatility might be derived from hysteresis in the strain–E loop at E < Ec (electric coercive field of the PZT) [20]. However, the non-volatility could only be realized when Ec < E < Ec. Under this condition, the strain was relatively small, and the difference between the two residual strain states was even smaller (less than 150 ppm). It is known that microwave ferrites have more applications in RF/microwave devices than metal alloy thin films. However, very few reports existed on magnetization modulation in ferrites by E-field [3], particularly non-volatile...
modulation. In the present study, we realized continuously non-volatile magnetization modulation in a NiZn ferrite/PZT heterostructure. The ferrite film was produced by spin-spray technique at 90 °C. The polycrystalline PZT substrate adopted in this study was specific, given that the defect dipoles were inside through acceptor doping. Capable of realizing stable and repeatable non-volatile magnetization modulation by voltage-impulse-induction, this heterostructure has potential applications in non-volatile RF/microwave ME devices.

2. Experiments

The PZT substrate selected in this experiment was made by Shanghai Institute of Ceramics, Chinese Academy of Science (based on type: 5m–32c) with negative d33 = d32 = 340 pC N−1. The substrate was poled along the thickness direction, aged, and polished for film deposition. The substrate adopted in this study was specific because of its defect dipoles through acceptor doping. Acceptor doping refers to the use of low valence state metal ions to partially substitute quadrivalent Zr4+/Ti4+, thereby creating oxygen vacancies in the unit cell. For example, choosing Mn2+/Mn4+ to partially substitute quadrivalent Zr4+/Ti4+ is a typical acceptor doping method, and oxygen vacancies will be introduced by the compensation. The two sides of the 10 mm × 10 mm × 0.5 mm PZT substrate was first coated with 100 nm Au electrode by magnetron sputtering. Then, a 5 mm × 5 mm × 5 μm Ni0.27Zn0.73Fe2.63O4 ferrite film was manufactured by spin-spray process on the surface of the PZT substrate. An amount of 1 L oxidation solution containing 2 mM NaNO2 and 17.5 mM CH3COONa, and 1 L precursor solution containing NiCl2, ZnCl2, and FeCl3 were spin sprayed simultaneously onto a heated plate at 90 °C. The growth rate was approximately 40 nm/min. The detailed description of the spin-spray deposition process is reported in other papers [21,22]. Field sweeping FMR measurements were conducted by utilizing our homemade FMR test unit. Magnetization measurement of the heterostructure was performed by using a vibrating sample magnetometer (VSM, Lakeshore 7400). The in-plane strain–E characteristic of the PZT substrate was tested by bonding a resistance strain gauge to the top electrode of the PZT substrate, and detection was conducted using a strain gauge (WSMCM-1, Sigmar Corporation). All tests were performed at room temperature.

3. Results and discussion

Fig. 1(a) shows the schematic of the ferrite/PZT heterostructure. Fig. 1(b)–1(d) display the magnetic hysteresis loops of the heterostructure in the x-, y-, and z-directions, The loops in the x- and y-directions were nearly the same and easy to be magnetized. However, in the z-direction, the heterostructure required a much higher field, that is, nearly as large as 1 T, for magnetization to saturation. These characteristics facts were due to that the demagnetizing field in the out-of-plane direction was much higher than that in the in-plane direction, when the thickness of the film was much smaller than the width of the film [23,24]. To lower free energy, the magnetic moment in the Ni0.27Zn0.73Fe2.63O4 ferrite film preferred to align in the in-plane direction. Therefore, In-plane direction was the easy axis and out-of-plane was the hard axis of magnetization in this study. Furthermore, In view of the symmetry in the x- and y-directions (including the characteristics of ferrite film and PZT substrate), the orientation of the magnetic moment in the x- and y-directions was the same and the VSM testing results were also almost the same in these two directions.

The PZT substrate in our experiment was specific with interior defect dipoles through acceptor doping. Thus, we first tested the in-plane strain–E loops of the PZT substrate by cycling the E-field between ±12 kV/cm. As shown in Fig. 2(a), the testing was executed in two cycles, and the strain curves matched well except for the initial polarization curve (curve 1). A strong asymmetric loop can be found, indicating that the strain exhibited a “memory” effect. Even without an E-field, a residual strain was maintained, and the PZT substrate cannot return to its initial state. When the E-field was decreased from +12 kV/cm to zero E-field, the substrate still retained a residual strain in the range of −410 ppm to −430 ppm. When the E-field was decreased from −12 kV/cm to zero E-field, the residual strain was in the range of −71 ppm to −80 ppm. The strain began changing its direction at approximately ±4 kV/cm. The appearance of the asymmetric butterfly-shaped curves was due to the preferential orientation of the defect dipoles along the poling direction in the PZT substrate [25–27]. According to the symmetry-conforming principle of point defects, oxygen vacancies generated by defect dipoles may hop onto adjacent energetically preferred oxygen sites during the aging process. The defect dipoles are then gradually aligned to create an internal bias field parallel to the poling direction. The internal bias field can shift strain-E loop along the field axis. A similar phenomenon was observed in Ref. [25]. The mechanism of this kind of strain–E asymmetry is completely different from the reported single-crystal PMN–PT and can be easily repeated [17–19]. Furthermore, if the E-field was changed between −4 (slightly less than the negative coercive field) and 12 kV/cm (the maximum positive E-field), the strain–E field curve would present a hysteretic loop characteristic and would have two stable negative residual strain states (states A and B) under zero E-field. This loop is well reversible and stable, as shown in Fig. 2(b). By using this loop, an arbitrary residual strain between A and B can be theoretically realize by changing the amplitude of the E-field between −4 and 12 kV/cm and subsequently removing the E-field. All residual strains were in contractility states.

We tested the magnetization modulation effects of the PZT substrate on the ferrite film in the heterostructure. Fig. 3(a) shows the in-plane E-field dependence of the FMR spectra in field sweeping mode at 9.3 GHz. Upon the application of an E-field of 12 kV/cm on the heterostructure, the resonance field notably increased from 1204 Oe to 1281 Oe. When an E-field of −4 kV/cm was applied, the resonance field slightly decreased from 1204 Oe to 1194 Oe. In this layered magnetoelastic heterostructure, an E-field-induced effective in-plane H-field, ΔHeff, can be expressed as [13]

ΔHeff = 3λs × Y × d eff × E H0M s,

(1)

where λs is the saturation magnetostriction constant of the ferrite film, Y is the Young’s modulus, Ms is the saturation magnetization, deff is the piezoelectric coefficient of the PZT substrate, and E is the E-field applied on the PZT substrate. This field can manipulate FMR as described in the Kittel equation below [13].

f = γ H r + ΔHeff H r + ΔHeff + 4πMs ,

(2)

where γ is the gyromagnetic ratio ~2.8 MHz Oe−1, and Hr is the net in-plane H-field at zero applied bias E-field. The details are described in a previous report [26]. Given the positive magnetostriction of the NiZn ferrite and negative d eff (d eff = d33 − d32 < 0) of the PZT substrate, an E-field of 12 kV/cm on the PZT produced a contractility in the in-plane direction and tensility in the out-of-plane direction. Formula (1) states that ΔHeff was also negative. According to Formula (2), when the resonance frequency was fixed at 9.3 GHz, a higher Hr was required to realize ferromagnetic resonance. Both magnetic moment in the x- and y-directions were inclined to switch from the in-plane to the out-of-plane direction to
decrease the free energy via the CME effect. This phenomenon resulted in the increased resonance field in the x-direction. By contrast, an E-field of $-4$ kV/cm caused an opposite effect, and a smaller resonance field was therefore required. Furthermore, when decrease the free energy via the CME effect. This phenomenon resulted in the increased resonance field in the x-direction. By contrast, an E-field of $-4$ kV/cm caused an opposite effect, and a smaller resonance field was therefore required. Furthermore, when
the E-field applied on the heterostructure was removed, the resonance field could not return to its initial value and changed based on the different E-field applied over time, as shown in Fig. 3(b). When the applied 12 kV/cm E-field was removed, the resonance field moved to 1249 Oe. When the applied –4 kV/cm E-field was removed, the resonance field changed to 1208 Oe. Further investigation revealed that the resonance field could also present a “hysteresis loop” characteristic against the applied E-field.

As shown in Fig. 4(a), two stable and reversible residual states A and B would facilitate the realization of non-volatile resonance field tuning by reversing the applied E-field. The residual FMR resonance field states A and B exactly corresponded to the residual strain states A and B in Fig. 2(b). Therefore, the non-volatile tuning of FMR in the heterostructure was attributed to the stable and reversible residual strain states in the specific PZT substrate. Furthermore, after E-field was removed, the PZT could present different residual constriction strain states between A and B, as shown in Fig. 2(b). Therefore, the FMR resonance field can be non-volatile and continuously modulated between A and B states, as shown in Fig. 4(b), when the PZT was subjected to an impulse of 12 kV/cm, the remnant strain state A resulted in a maximum FMR resonance field of approximately 1249 Oe. When an impulse field of –4 kV/cm was applied, the FMR resonance field was reduced to the minimum value of approximately 1208 Oe, indicating that the strain state was switched to the remnant state B. Apart from the non-volatile switching of the FMR resonance field between the maximum and minimum values, any resonance field between them can also be reached by the selection of the appropriate electric impulse. For example, by applying an impulse field of 4 kV/cm, the FMR resonance field of 1230 Oe can be realized (state C).

We examined the non-volatile variation of the magnetic hysteresis (M-H) loops. Fig. 5(a) shows the normalized M-H loops in x-direction after removing E-field from 12 and -4 kV/cm. Due to the symmetry of the x- and y-directions, state A was more difficult to be magnetized to saturation in the x-direction compared with state B. This fact also meant that some magnetic moment left the in-plane direction to the out-of-plane direction when changing states from A to B. However, due to the large demagnetizing field led by the shape anisotropy in the out-of-plane direction (z-direction), if magnetizing the heterostructure to saturation in the z-direction, the difference in hysteresis loops of states A and B was imperceptible. As shown in Fig. 5(b), state A could obtain a slightly bigger magnetic moment and be easier to be magnetized in the z-direction compared with state B. This trend was opposite to the trend in Fig. 5(a). More specifically, as $d_{31} = d_{32} < 0$ of the PZT substrate, the residual contraction strain in the x-direction also caused the biaxial contraction strain in the in-plane direction, leading to the magnetization deviation from the in-plane to the out-of-plane direction. States A and B presented different residual strains; as such, the effects on magnetization deviation also varied. Consequently, M-H loops and residual magnetization states differed. In this study, given the relatively small magnetostriction constant of the NiZn ferrite (~18 ppm), the non-volatile modulation effects on FMR and
M-H loops were not very significant. However, this method provided a promising approach for realizing continuous non-volatile voltage impulse control of magnetization modulation in the ferrite film, thereby further reducing energy consumption. Thus, this method has potential applications in many RF/microwave devices. If the ferrite film with a higher magnetostriction constant was chosen or an external H-field on the z-direction was applied when the ferrite film was produced (resulting in an easier magnetization modulation from the in-plane to the out-of-plane direction), then a more significant non-volatile modulation effect would be achieved.

4. Conclusion

In summary, we have demonstrated the continuous non-volatile voltage control of magnetization modulation in ferrite/PZT heterostructures. The non-volatility resulted from reversible and stable voltage-impulse-induced residual strain states in the PZT substrate. The non-volatile biaxial residual strain, via the strain-mediated magnetoelectric coupling between the PZT substrate and the ferrite layer, caused the non-volatile magnetization modulation. This phenomenon finally led to the non-volatile modulation in FMR and M-H characteristics. The results of this work presented potential applications in non-volatile tunable and low energy consumption RF/microwave devices.

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