Electric-field tuning of magnetic anisotropy in the artificial multiferroic Fe$_3$O$_4$/PMN–PT heterostructure

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**ABSTRACT**

Modulation of the magnetic anisotropy by the electric field in epitaxial Fe$_3$O$_4$/PMN–PT multiferroic heterostructure is studied, which shows that the coercive field of Fe$_3$O$_4$ thin films can be decreased from 368 to 113 Oe by applying an electric field in PMN–PT [011] direction. Meanwhile, most shift of ferromagnetic resonance (FMR) field $H_r$ ($\Delta H_r$, [01$\bar{1}$]) can reach up to $-483$ Oe by applying an external electric field. The giant shift of $H_r$ from 251 to 9681 Oe is obtained as the sample rotated from $\theta = 90^\circ$ ($H//[01\bar{1}]$) to $\theta = 0^\circ$ ($H//[100]$) when the electric field was applied in Fe$_3$O$_4$/PMN–PT heterostructure.

**IMPACT STATEMENT**

A giant shift of ferromagnetic resonance field was obtained by simultaneously applying an external electric field and a rotating sample along axes both parallel and perpendicular to the magnetic field.

Multiferroic materials allow the realization of the magnetization change by an external electric field and vice versa. The magnetic structure variation driven by an electric input (electric field or current) has been proposed in broad and bright aspects regarding the potential applications in spintronics [1–3]. Compared with conventional electrical current, electric-field manipulation of magnetization has some significant advantages, including miniaturization, high efficiency, low energy consumption and multi-functionalization [4–6]. In addition, multiferroic materials have a promising prospect in next-generation devices, such as magnetic field sensors, microwave/radio frequency systems, radar and information storage devices [7–10]. However, the scarcity of single-phase multiferroic materials above room temperature (RT) has driven an intense research of artificial multiferroic heterostructures, which consist of ferromagnetic and piezoelectric phases [11]. So far, the magnetoelectric coupling has been observed in metal—and transition-metal-oxide-based multiferroic heterostructures. As we know that the magnetoelectric coupling involves the effect of charge, strain and exchange bias; so obviously the competition and coexistence of these factors show a dramatic difference in metal and oxide from the carrier density, dielectric constant and lattice-strain interaction point of view. Thus, a detailed picture of the magnetic structure change of the ferromagnetic layer by the electric field may supply the significant information to reveal the fundamental physics of magnetoelectric coupling in the artificial heterostructure as well as the magnetite [12–16].

Fe$_3$O$_4$ has been investigated to be a promising ingredient for several decades as it possesses a high Curie temperature (850 K) and extremely high (80%) spin polarization [17,18]. Magnetite offers exciting opportunities
in fundamental study and technological application, such as in electromagnetic wave absorption, data storage and photovoltaic devices among many others [19–21]. The magnetic anisotropy of Fe$_3$O$_4$ is highly expected as the in-plane anisotropy magnetoresistance (AMR), which can be reached at 10.7% at room temperature [22,23]. Generally, the AMR realization of an Fe$_3$O$_4$ single crystal thin film is based on the rigid strain effect of a non-ferroic substrate, which lacks tunability [24–26]. In order to in situ modulate the magnetic anisotropy of Fe$_3$O$_4$, a piezoelectric substrate 0.70Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.30PbTiO$_3$ (PMN–PT) with a high piezoelectric response is chosen to construct composite multiferroic heterostructure with Fe$_3$O$_4$ thin films. Moreover, the PMN–PT (011) single crystal is in favor of modulating magnetic anisotropy relative to the PMN–PT (001) single crystal ($d_{31} = d_{32}$), for its different lateral piezoelectric coefficients with $d_{31} = −1750 \text{ pC/N}$ (along [100] direction) and $d_{32} = 900 \text{ pC/N}$ (along [011] direction) [27–29]. In this multiferroic structure, the tunable Verway transition, resistance switching and even non-volatile state are exhibited by the electric field, besides a high AMR can be achieved below Verwey transition temperature [30–32]. Here we report a room temperature anisotropy of 30% in remanence ratio, strongly suggesting that the strain-engineered Fe$_3$O$_4$ could be a candidate for low energy consumption data storage. Meanwhile, the structural transition of Fe$_3$O$_4$ thin films can lead to a distinct change of the magnetization by the electric field. We have comprehensively studied the magnetic anisotropy of Fe$_3$O$_4$ variation by an electric field in the respective in- and out-of-plane orientation of magnetic field.

The Fe$_3$O$_4$/PMN–PT multiferroic heterostructures were prepared by pulsed laser deposition (PLD). The Fe$_3$O$_4$ thin films were deposited on a single crystal PMN–PT (011) substrate ($5 \times 4 \times 0.3 \text{ mm}^3$) using a KrF excimer laser with a frequency of 10 Hz and a pulsed laser energy of 2 J/cm$^2$. The substrate was kept at 350°C in an oxygen pressure of $2 \times 10^{-5}$ Torr, for 20 minutes in the course of deposition. The samples were cooled down naturally to room temperature under the same pressure.

The surface morphology of the magnetic film was performed by atomic force microscope (AFM, Asylum Research, MFP-3D) in contact mode. The cross-sectional morphology image of Fe$_3$O$_4$/PMN–PT heterostructure was characterized using a field emission scanning electron microscope (FESEM, JOEL, JSM-7800F). The structure of the Fe$_3$O$_4$/PMN–PT heterostructure was verified by standard $\theta$–$2\theta$ scan using X-ray diffraction (XRD, Rigaku, D/max-2500/PC) with Cu K$_\alpha$ radiation in the angular range of 20–80°. The ferroelectric hysteresis loop and strain-electric-field curve of the single-crystal PMN–PT were measured by a ferroelectric tester (Radiant Technology, Precision Premier II). Magnetic hysteresis loops were obtained via magnetic property measurement system (MPMS, Quantum Design, SQUID-VSM) and magneto-optical Kerr effect magnetometer (MOKE, Durham Magneto Optics Ltd, Nano MOKE$^{\text{TM}}$ 3). Ferromagnetic resonance spectra were measured by electron paramagnetic resonance (EPR, JEOL, JES-FA200) system with a TE$_{102}$ cavity in the X band.

Figure 1(a) shows the surface morphology of the Fe$_3$O$_4$ film and the cross-sectional SEM image of the Fe$_3$O$_4$/PMN–PT heterostructure. The average size of the crystall grain is about 100 nm. The Fe$_3$O$_4$ film exhibits a smooth and dense surface morphology, with a low root-mean-square surface roughness of 0.97 nm. The thickness of the Fe$_3$O$_4$ film is about 125 nm. Particularly, the Fe$_3$O$_4$/PMN–PT heterostructure shows a clear and tight interface structure. Figure 1(b) shows the XRD pattern of the Fe$_3$O$_4$/PMN–PT heterostructure. Only [011]-oriented diffraction peaks of Fe$_3$O$_4$ film and

![Figure 1. (a) The AFM image (an area of 2 × 2 $\mu\text{m}^2$) of an Fe$_3$O$_4$ film (Inset: Cross-sectional SEM image of Fe$_3$O$_4$/PMN–PT heterostructure). (b) XRD patterns under unpoled and poled states of Fe$_3$O$_4$/PMN–PT heterostructure and (inset) a close-up of XRD patterns around PMN–PT (022).](image-url)
PMN–PT substrate have been observed, showing highly epitaxial growth of the Fe₃O₄ film on the PMN–PT substrate. The out-of-plane lattice parameter of the Fe₃O₄ thin film is 8.424 Å, which is slightly larger than that of bulk Fe₃O₄ (a = 8.397 Å) [33] due to an in-plane compressive strain imposed by the PMN–PT substrate. In order to explore the Fe₃O₄/PMN–PT (011) heterostructure, we analyzed the crystal structure of the multiferroic heterostructure by applying an electric field of 6.7 kV/cm. The Fe₃O₄ thin film was used as the top electrode and silver slurry was used as the bottom electrode during the polarizing process. The out-of-plane lattice parameter changes 0.08% for Fe₃O₄ with the application of electric field. This result demonstrated the electric-field-induced strain can be successfully delivered from the PMN–PT substrate to the Fe₃O₄ film.

As shown in Figure 2(a), distinctly different in-plane hysteresis loops were observed along the PMN–PT [100] and [011] at room temperature. Along the easy axis (PMN–PT [011]), the coercive field reaches up to approximately 418 Oe and the remanence ratio was up to 59%. On the other hand, the coercive field drops to 350 Oe and the remanence ratio was only 22% along the hard axis (PMN–PT [100]). Figure 2(b) displays the obtained P–E hysteresis loop of the PMN–PT substrate at room temperature. It was observed that the saturation polarization was around 42 μC/cm², the coercive field was 4.2 kV/cm and the remnant polarization was 37 μC/cm². In addition, the out-of-plane strain-electric-field curve was also measured, as shown in Figure 2(b). The maximum strain was around 0.27%.

Figure 3 shows the Kerr hysteresis loops of Fe₃O₄/PMN–PT heterostructure at different electric fields. As shown in Figure 3(a), strain-induced magnetic anisotropy leads to a relatively small change, the remnant magnetization ratio decreases from 72% at 0 kV/cm to 65% at 6.7 kV/cm and the coercive field decreases from 466 Oe at 0 kV/cm to 447 Oe at 6.7 kV/cm when magnetic field along [011] direction of the PMN–PT substrate.

However, the Kerr hysteresis loops have stronger alteration when magnetic field is applied along PMN–PT [100], the remnant magnetization ratio decreases from 37% at 0 kV/cm to 7% at 6.7 kV/cm and the coercive field decreases from 368 Oe at 0 kV/cm to 113 Oe at 6.7 kV/cm (Figure 3(b)). Clearly, there are relatively significant differences in the changes of the remnant magnetization ratio and coercive field in Fe₃O₄ film along [011] and [100] when electric field parallels to [011] direction of PMN–PT substrate. According to the different lateral piezoresponse of PMN–PT (011) substrate (d₃₁ = -1750 pC/N along [100] and d₃₂ = 900 pC/N along [011], a compressive strain is applied in the [100] direction resulting in a strong change of the magnetic anisotropic energy of Fe₃O₄, which coincides with the MOKE measurement. In addition, the [100] direction is the hard axis in the as-growth Fe₃O₄ thin film; it is noted that the external electric field applied strengthens this scenario. The coercive field of Fe₃O₄ along the [011] shows a non-external electric-field sensitive behavior due to the small d₃₂, although a tensile strain exists.

Furthermore, electric-field tuning of magnetic anisotropy can be demonstrated by the electric-field-induced Kerr signal (remnant magnetization) change using the AC-mode MOKE technique without external magnetic field (as shown in Figure 3(c) and (d)). The result indicated that the butterfly-shaped Kerr loop corresponds to the piezostrain loop of PMN–PT single crystal (Figure 2(b)), demonstrating a converse ME effect by strain transformation across the Fe₃O₄/PMN–PT multiferroic composite interface. Meanwhile, the contrary tendency along the in-plane orthogonal [011] and [100] directions was also observed, manifesting that the magnetic anisotropy existed in the Fe₃O₄ thin film. The contrary tendency may be the result of opposite in-plane piezoelectric strain response of the PMN–PT substrate [34].

In addition, electric-field tuning magnetic anisotropy of the Fe₃O₄/PMN–PT heterostructure was quantitatively...
investigated by electric-field-induced ferromagnetic resonance shift. The in-plane biaxial stresses (compressive stress $\sigma_x$ along [100] ($d_{31}$) direction and tensile stress $\sigma_y$ along [011] ($d_{32}$) direction) induced effective magnetic anisotropy fields ($H_{\text{eff}}$) are

$$H_{\text{eff},[011]} = -\frac{3\lambda_s Y}{M_s(1 + v)}(d_{31} - d_{32})E, \quad (1)$$

$$H_{\text{eff},[100]} = \frac{3\lambda_s Y}{M_s(1 + v)}(d_{31} - d_{32})E, \quad (2)$$

$$H_{\text{eff},[011]} = \frac{3\lambda_s Y}{M_s(1 + v)}(d_{31} + d_{32})E, \quad (3)$$

where $\lambda_s$ is the saturate magnetostriction constant of the Fe$_3$O$_4$ film (20 ppm), $Y$ is Young’s modulus of magnetic film Fe$_3$O$_4$ ($2.3 \times 10^{11}$ dyne/cm$^2$) and $v$ is Poisson’s ratio (0.3) [35]. The $H_{\text{eff}}$ is equal to the change of ferromagnetic resonance field ($\Delta H_r$). The theoretical values of $H_{\text{eff}}$ can be calculated by applying the electric field of 6.7 kV/cm along the PMN–PT [011] direction from the equations. When the magnetic field was along PMN–PT [011], the $H_r$ shifts downwards from 734 Oe at 0 kV/cm to 251 Oe at 6.7 kV/cm (Figure 4(a)). The measured $\Delta H_{r,011}$ of $-483$ Oe is very close to the calculated result of $H_{\text{eff},011} = -487$ Oe (Equation (1)). On the other hand, as shown in Figure 4(b), when the magnetic field was along PMN–PT [100], the $H_r$ can be shifted from 1299 to 1713 Oe by applying an electric field of 6.7 kV/cm. The upward $\Delta H_{r,100}$ of 414 Oe is close to the theoretical value $H_{\text{eff},100} = 487$ Oe (Equation (2)). Therefore, a large tunable magnetic anisotropy from 251 Oe along PMN–PT [011] to 1713 Oe along PMN–PT [100] can be obtained under the electric field of 6.7 kV/cm by rotating the sample along an axis parallel to the magnetic field (Figure 4(c)).

As shown in Figure 4(d), the giant shift of $H_r$ from 1299 to 9905 Oe was measured when the sample rotated from $\theta = 90^\circ$ ($H//[011]$) to $\theta = 0^\circ$ ($H//[011]$). The angular dependence of the $H_r$ in Fe$_3$O$_4$/PMN–PT heterostructure has been changed when the electric field of 6.7 kV/cm was applied. While both the magnetic field and applied electric field were along the PMN–PT [011] direction, the shift of $H_r$ from 9905 Oe at 0 kV/cm to 9681 Oe at 6.7 kV/cm was observed. The measured descendent value $\Delta H_{r,011}$ of $-224$ Oe incline to the calculated result of $H_{\text{eff},011} = -156$ Oe (Equation (3)). As the sample was rotated to $\theta = 0^\circ$ ($H//[100]$), we obtained a larger tunable range from 734 to 9905 Oe without the electric field (Figure 4(e)). The tunable range has been changed under an external electric field of 6.7 kV/cm by rotating the sample along an axis perpendicular to the magnetic field, showing the shift from 251 Oe at $\theta = 90^\circ$ ($H//[011]$) to 9681 Oe at $\theta = 0^\circ$ ($H//[100]$).
In conclusion, we successfully observed the electric-field-induced switching of magnetic anisotropy in the Fe₃O₄/PMN–PT multiferroic heterostructure. The lattice parameter of the Fe₃O₄ film was changed due to the piezo strain/stress effect. We acquired a larger change in remanent ratio (30%) and coercive field (255 Oe) along [100] directions under the applying of the electric field. The shifts of $H_r$ reached to $-483$ and $414$ Oe along [01$\bar{1}$] and [100] directions of PMN–PT substrate respectively when the electric field of $6.7$ kV/cm was applied. The giant shift of $H_r$ from 251 to 9681 Oe by rotating the sample from $\theta = 90^\circ$ ($H// [01\bar{1}]$) to $\theta = 0^\circ$ ($H// [100]$) was obtained under the electric field of $6.7$ kV/cm. The tunable magnetic properties via external electric field provide more options for multifunctional multiferroic device applications.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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