Electric-field-control of resistance and magnetization switching in multiferroic \( \text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_{4}/0.7\text{Pb(Mg}_{2/3}\text{Nb}_{1/3}\text{)}\text{O}_{3}−0.3\text{PbTiO}_{3} \) epitaxial heterostructures

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Multiferroics, which exhibit simultaneous two or more ferroic orders, have been studied extensively for decades due to their potential applications.1 Strain-mediated multiferroic magnetoelectric (ME) composites,2 which combines ferroelectric (FE) and ferromagnetic (FM) phases, possess considerable room-temperature ME coupling and is more practical than single phase multiferroics, which usually show ME coupling at low temperature.3,4 FE/FM heterostructures provide an alternative route to obtain larger ME response. There have been tremendous studies on the magnetic and electric properties in perovskite oxides/FE heterostructures, e.g., \( \text{R}_{1-x}\text{A}_{x}\text{MnO}_{3} \) (\( \text{R=La,Pr,A=Ca, Sr, Ba} \)) / \((1-x)\text{Pb(Mg}_{2/3}\text{Nb}_{1/3}\text{)}\text{O}_{3}−x\text{PbTiO}_{3} \) (PMN-xPT).5,11 Eerenstein et al.11 have reported that the magnetization in perovskite \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3}/\text{BaTiO}_{3} \) heterostructure can be manipulated by electric-field-controlled strain due to the modification of magnetic anisotropy. Accordingly, electric-field-controlled electrical and magnetic properties in multiferroic spinel ferrite/FE heterostructures are also realized but quite limited and are not well understood. Only a few recent investigations on electric-field-controlled tunability of magnetization in spinel ferrite/FE epitaxial heterostructures were demonstrated in \( \text{CoFe}_{2}\text{O}_{4}/\text{PMN−xPT} \) (x=0.28, 0.3) (Refs. 13 and 14) and \( \text{NiFe}_{2}\text{O}_{4}/\text{PMN−xPT} \) (x=0.28).15 Studies on ME coupling and exploration of the spinel ferrite/FE heterostructures are also significant for the electric-field-controlled devices. In this letter, we will demonstrate that both electrical resistance and magnetization can be tuned by electric field via converse piezoelectric effect in spinel ferrite \( \text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_{4}/\text{PMN−xPT} \) (x=0.3, referred as ZFO/PMN−PT) epitaxial heterostructures.

The details about the sample preparation and structure characterization can be found in the online supporting materials. From reciprocal space mapping of the (206) peak of ZFO film [Fig. 1(a)], the in-plane lattice parameter is 0.831 nm, which is smaller than the 0.846 nm of the out-of-plane one, indicating that the film is expanded along c axis and constricted in the plane of the film. The lattice mismatch between the ZFO (cubic, bulk lattice constant \( \approx 0.841 \) nm) and the PMN−PT (rhombohedral, pseudocubic lattice constant \( \approx 0.804 \) nm) is about 4.6%, which leads to the in-plane compressive strain in the highly epitaxial ZFO film. However, the thermal expansion mismatch between the ZFO (thermal expansion coefficient \( \approx 20 \) ppm/K) and the PMN−PT (thermal expansion coefficient \( \approx 10 \) ppm/K) is so small (\( \approx 0.5\% \)) that its effect on the strain state of the ZFO film is neglected appropriately. Therefore, the initial in-plane compressive strain is stored in the ZFO film.

To study the strain state in the ZFO film, \textit{in situ} \( \theta−2\theta \) scans (not shown here) around (004) peak of the film under applied electric field was implemented. Figure 1(b) (square line) shows that the out-of-plane lattice parameter c, with a hysteresis, is increased by the bipolar electric field applied to the heterostructure, indicating that the in-plane compressive strain transferred effectively into the film via converse piezoelectric effect of PMN−PT. This similar behavior has been demonstrated by Levin et al.5 and Thiele et al.6

In order to study the strain controlled resistance, an electrical circuit7 with FE-field-effect-transistor configuration was constructed as shown in Fig. 2(a). Resistance between the source and the drain was measured by a voltmeter under a constant current when a switching electric field was applied to the PMN−PT plate through the gate and drain. Two resistors were used to protect the circuit. Figure 2(b) shows that the tunability of resistance \( [\Delta R/R=[R(E)−R(0)])/R(0)] \),
where $R(E)$ and $R(0)$ are the resistances of the ZFO film under electric field $E$ and zero field, respectively, about $-0.1\%$ for $\pm 1.0$ kV/cm at 296 K, which is on the same order as that of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$/PMN–0.3PT heterostructure (0.25%). We found that the resistance returns to its initial value at the same frequency when electric field is switched on and off. Moreover, resistance decreases whatever electric field is positive or negative. In order to understand this behavior, both the FE-field effect and converse piezoelectric effect of PMN–PT substrate should be considered. It is well known that the FE-field effect became weak in thin channel, which has higher density of carrier as the electric field would be screened within a few atomic layers from the interface. Characteristic screen length for our multiferroic ZFO/PMN–PT heterostructures is so short about 0.1 nm estimated at 296 K that the electric field will be screened at the interface and could not affect the film’s transport property (see the online supporting materials for details). Therefore, the resistance variation can be safely attributed to the strain effect. To further confirm this judgment, the tunability of resistance as functions of the in-plane strain and bipolar electric field was depicted in Fig. 2. When electric field of $\pm 8.7$ kV/cm is applied, the estimated in-plane compressive strain is about $-0.15\%$ with the tunability of resistance about $-0.9\%$. It is found that the tunability of resistance loop coincides well with the in-plane strain as a function of electric field in Fig. 1(b) (circular line), indicating that the in-plane compressive strain (see the online supporting materials for details) plays a major role in resistance variation. The hysteresis in Fig. 2(c) [Fig. 1(b)] is a general feature induced by complex FE domains rotation in relaxor FE near morphotropic boundary of the PMN–PT when it is applied high electric field. Our ZFO film has a charge transport behavior determined by the hopping of the $t_{2g}$ electrons between mixed-valent $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions with the similar activation energy as in the mixed-valent manganites, where transport was dominated by the hopping of $e_g$ electrons between mixed-valent $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions. The hopping amplitude between mixed-valent $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions will be significantly influenced if the bond length and angle of Fe-O-Fe are modulated by strain. Therefore, the in-plane compressive strain would give rise to an obvious decrease in the in-plane $B$-sited Fe-O bond length and the modulation of the bond angle in the ZFO film and thus an enhancement of hopping amplitude similar to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions in $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$/PMN–PT heterostructures, which is an open question and should be further studied in future. Consequently, we attribute the decrease in resistance under compressive strain to the enhancement of the hopping amplitude of spin-down $t_{2g}$ electrons between mixed-valent $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions. This result is further demonstrated by the tunability of resistance at 80 K (see Ref. 18 for details).
The electric-field-controlled magnetization of the heterostructure was also studied by using superconducting quantum interference device. The tunability of magnetization $\Delta M/M(0)=\Delta[M(E)-M(0)]/M(0)$ where $M(E)$ and $M(0)$ are the magnetization under E and zero electric field, respectively, is about 0.55% with the applied electric field 1 kV/cm as shown in Fig. 3(a). It is observed that the magnetization is enhanced by electric field and is modulated at the same frequency with the electric filed. The manipulation of magnetization by electric field can be explained by considering the inverse magnetostriictive effect. As the strain from PMN–PT substrate is effectively transferred into the ZFO film, the magnetic anisotropy of the ZFO film is modulated, and thus magnetization is tuned by electric field. To prove this picture, we turned to examine the relations between the tunability of magnetization $\Delta M/M$ and the electric-field-induced in-plane strain. Figure 3(b) plots $\Delta M/M$ as a function of the induced in-plane compressive strain estimated using the above results. Assuming $\varepsilon_{33}=K_3 E$ and $\Delta M/M(0)=\beta E$ (where $K_3$ and $\beta$ are two constants), we get $\varepsilon_{11}=-[K_3(1-\nu)/(2\nu)]E$ (Ref. 15) and $\Delta M/M(0)=\beta[-2\nu/[K_3(1-\nu)]]\varepsilon_{11}$, which accounts for the linear relationships between the tunability of magnetization and the in-plane compressive strain. When the electric field of 6.7 kV/cm is applied, the estimated in-plane compressive is about $-0.11\%$ with the tunability about 1.1%. The underlying physics of the enhancement of magnetization by electric field is a possible correlation between the in-plane compressive strain and the states of itinerant electrons of mixed-valent Fe$^{2+}$ and Fe$^{3+}$ ions on B-sited sublattice. In-plane compressive strain may help itinerant electrons delocalizing from the B-sited sublattice by weakening the spin canting of mixed-valent Fe$^{2+}$ and Fe$^{3+}$ ions on B-sited sublattice. Therefore, the hopping amplitude of itinerant electrons is enhanced and hence the FM double exchange interactions. This explanation agrees well with the decrease in the resistance by electric field as discussed above. Moreover, enhancement of magnetization under the in-plane compressive strain has been proved by density-function theory calculations in CoFe$_2$O$_4$/PMN–PT, and also demonstrated by x-ray absorption near edge structure in NiFe$_2$O$_4$/PMN–PT, where electrons hopped from Ni$^{2+}$ to Fe$^{3+}$ ions on B-sited sublattice.

In a conclusion, resistance and magnetization of the ZFO films can be modulated by the strain of substrate through converse piezoelectric effect, in which the strain effect dominates the tunabilities of resistance and magnetization over the FE-field effect at both low and high temperature. Tunabilities of resistance and magnetization are linearly correlated with the in-plane compressive strain which, in turn, is directionally proportional to the applied electric field. Enhancement of electron hopping between mixed-valent Fe$^{2+}$ and Fe$^{3+}$ ions under electric field-induced in-plane compressive strain was attributed to explain our observations.

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18See supplementary material at http://dx.doi.org/10.1063/1.3579994 for the structure characterization, field effect and tunability resistance at 80 K.