Non-volatile Switching of Magnetism in Multiferroic Heterostructures

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Abstract

Multiferroic materials and devices have attracted intensified interests due to the demonstrated strong magnetoelectric coupling in new multiferroic materials, artificial multiferroic heterostructures and devices with unique functionalities and superior performance characteristics. This offers great opportunities for achieving compact, fast, energy-efficient and voltage tunable spintronic devices. In traditional magnetic materials based magnetic random access memories (MRAM) devices, the binary information is stored as magnetization. The high coercivity of the ferromagnetic media requires large magnetic fields for switching the magnetic states thus consuming large amount of energy. In modern MRAM information writing process, spin-torque technique is utilized for minimizing the large energy for generating magnetic field by passing through a spin-polarized current directly to the magnets. However, both methods still need large current/current density to toggle the magnetic bits which consume large amount of energy. With the presence of multiferroic or magnetoelectric materials, spin is controlled by electric field which opens new opportunities for power-efficient voltage control of magnetization in spintronic devices leading to magnetoelectric random access memories (MERAM) with ultra-low energy consumption. However, state of the art multiferroic materials still have difficulty of realizing nonvolatile 180° magnetization reversal, which is desired in realizing MERAM.
In a strain-mediated multiferroic system, the typical modification of the magnetism of ferromagnetic phase as a function of bipolar electric field shows a “butterfly” like behavior. This is due to the linear piezoelectricity of ferroelectric phase which has a “butterfly” like piezostrain as a function of electric field curve resulting from ferroelectric domain wall switching. In this case, the magnetization state is volatile because of the vanishing of the piezostrain at zero electric field. However, the non-volatile switching of magnetization would be more promising for information storage or MERAM devices with lower energy consumption and the magnetic state can be further controlled by voltage impulse.

In this work, we first study the equivalent of direct and converse magnetoelectric effects. The resonant direct and converse magnetoelectric (ME) effects have been investigated experimentally and theoretically in FeGa/PZT/FeGa sandwich laminate composites. The frequency responses of direct and converse magnetoelectric effects were measured under the same electric and magnetic bias conditions. The resonant direct ME effect (DME) occurs at an antiresonance frequency, while resonant converse ME effect (CME) occurs at a resonance frequency. The antiresonance and resonance frequencies have close but different values under identical bias conditions. The magnitudes of resonant effective ME coefficients for direct and converse ME effects are also not equal. Based on different sets of constitutive equations of the materials for DME and CME, a new model was developed to describe the frequency
response of DME and CME in laminate composite, which was in good agreement with the experimental results. Inequivalence of resonant ME effects is ascribed to the different mechanical and electrical boundary conditions for DME and CME. On the other hand, similar bias E and H field dependence was observed for both DME and CME resonance frequencies and resonant coefficients, indicating consistency between DME and CME effects.

In the study of the frequency response of DME and CME, the linear piezoelectric effect is used. However, this linear piezoelectric effect in converse magnetoelastic coupling would lead to “butter-fly” like magnetization vs. electric field curve which leads to a “volatile” behavior in magnetic memory system. In the presented study, a unique ferroelastic switching pathway in ferroelectric substrates is utilized to produce two distinct, reversible and stable lattice strain states which leads to the establish of two stable magnetization states of the ferromagnetic thin film. In this process, instead of complete 180° ferromagnetic domain switching, 71°/109° ferroelastic domain wall switching is involved, where the electric polarization is switching between in-plane and out-of-plane direction. A voltage impulse induced reversible bistable magnetization switching in FeGaB/lead zirconate titanate (PZT) multiferroic heterostructures at room temperature is first demonstrated. Two reversible and stable voltage-impulse induced mechanical strain states were obtained in the PZT by applying an electric field impulse with its
amplitude smaller than the electric coercive field, which led to reversible voltage impulse induced bistable magnetization switching. Direct and converse magnetolectric effects are carefully quantified.
List of Figures

Figure 1.1 (a) Relationship between multiferroic and magnetoelectric materials. Illustrates the requirements to achieve both in a material (b) Schematic illustrating different types of coupling present in materials. Much attention has been given to materials where electric and magnetic order is coupled. These materials are known as magnetoelectric materials.10 ................................................................. 14

Figure 1.2 Electric field dependence of the in-plane field-sweep FMR spectra of the FeGaB/PZN-PT multiferroic heterostructure measured at ca. 9.6 GHz35 .............. 18

Figure 2.1 Schematic of Magnetron sputtering................................................................. 24

Figure 2.2 Radiant Precision LC ferroelectric test system.................................................. 26

Figure 2.3 The LakeShore 7407 VSM. ........................................................................... 27

Figure 2.4 Ultral-high frequency lock-in amplifier manufactured by Zurich Instrument. 28

Figure 3.1 (a) Schematic of the direct and converse magnetoelectric effect measurements. (b) Equivalent electric circuit of the direct and converse magnetoelectric effect..33

Figure 3.2 Bias magnetic field H dependence of (a) antiresonance frequency f_a ; (b) resonance frequency f_r ; (c) resonant $\alpha_d$ and (d) resonant $\alpha_c$ at fixed increasing bias voltage 0, 100, 200, 300, 400 V ................................................................. 41

Figure 3.3 Comparison of theoretical and experimental frequency response of effective DME and CME coefficients with $H_{bias} = 180 Oe$ and zero bias electric field.......43

Figure 3.4 Bias voltage dependence of: (a) $f_a$ ; (b) $f_r$ ; (c) resonant $\alpha_d$ and (d) resonant $\alpha_c$ at fixed bias magnetic field of 120 Oe. ................................................................. 44

Figure 3.5 Bias voltage dependence of: (a) $\alpha_d$ and (b) $\alpha_c$ at fixed bias magnetic field of 120 Oe and low frequency of 10 kHz................................................................. 46

Figure 4.1 Normalized Kerr rotation hysteresis curves (M-H) along they y direction under different electric fields (letters are the representatives of the labeled strain states in the inset). The inset shows in-plane strain difference ($\varepsilon_y-\varepsilon_x$) as a function of electric field. The drawings indicate the magnetization state: (c) permanent easy
plane, [(a) and (b)] temporary easy axis along x, and [(d) and (e)] permanent easy axis along x\(^72\).

Figure 4.2 (a) In-plane magnetic hysteresis loops of FeCoB/PMN-PT (011). Insets are schematic (upper left) and FMR spectra (bottom right). (b) Schematic of FMR measurement for (c-f). The sample is laid face down on an S-shape co-planar waveguide. Magnetic fields are applied in the [100] direction and electric fields are applied along the [011] direction. (c) Electric field dependence of the FMR frequency in field sweeping mode. (d) Electric field dependence of the FMR field in frequency sweeping mode. (e) FMR frequency responses under unipolar (red) and bipolar (blue) sweeping of electric fields at room temperature. (f) Voltage-impulse-induced non-volatile switching of FMR frequency\(^73\).

Figure 4.3 Schematics of domain structures and reciprocal space maps (RSMs) about (022) and (002) reflections of PMN-PT(011) under various applied electric fields and thus poling states. The first column (a,e,i) is for the unpoled state. The second column (b,f,j) is for the positive poling state with up to 90% of polarization pointing upward. The third column (c,g,k) is after applying an negative electric field of -1.5 kV cm\(^-1\) and then switching it off. The fourth column (d,h,l) is achieved by applying a positive electric field of 5 kV cm\(^-1\) and then switching it off\(^73\).

Figure 4.4 (a) to (d) show the electric-field tuned XRD-RSMs around the (113) reflection. (e) Configuration of the (113) crystal face (translucent blue plane) and the rhombohedral distortions as well as polarizations shown by the arrows, whose colors correspond to the colors of the ellipses in (a) to (d). (f) The 109° switching induced changes of in-plane distortions along the [110] direction as well as the corresponding lattice parameters and the in-plane projections of polarization vectors (broad arrows).

Figure 4.5 Hysteresis loops of E-field vs FMR frequency, measured under a bias magnetic field of 50 Oe, and E-field vs FMR field with working frequency of 12 GHz\(^17\).
Figure 4.6 E-field-impulse-induced dynamic memory-type of magnetization switching. ................................................................. 59

Figure 4.7 The polarization-electric field loop of the PZT ceramics and in-plane ε-E loops under application of E-field of 16kV/cm and 8kV/cm. .................................................. 62

Figure 4.8 Magnetic hysteresis loops of FeGaB/PZT heterostructure measured in length direction (Y direction) under application of E-field of -8kV/cm and 8kV/cm. The inset shows the schematic of FeGaB/PZT multiferroic heterostructure. .............. 64

Figure 4.9 Magnetization ratio versus E-field with a magnetic bias field (i.e., 3 Oe) under application of E-field of 16kV/cm and 8kV/cm................................................................. 66

Figure 4.10 Magnetic hysteresis loops of FeGaB/PZT heterostructure in state ‘1’; state ‘0’ which switched by voltage impulse; and holding a E-field of 8kV/cm 8kV/cm. Figure 4.10 inset shows the enlarged area................................................................. 67

Figure 4.11 Magnetization ratio of FeGaB/PZT heterostructure switched by voltage impulse measured in length direction with a magnetic bias field (i.e., 3 Oe) in time-domain measurement. ............................................................................................ 68
Contents

Abstract .................................................................................................................................................. 4

List of Figures ..................................................................................................................................... 8

Chapter 1: Introduction to artificial multiferroic heterostructure ............................................ 13

1.1. Multiferroic and magnetoelectric materials .............................................................................. 13

1.2. Electric field control of magnetism in magnetoelectric composite ....................................... 16

1.2.1. Strain-mediated magnetoelectric effect .............................................................................. 16

1.2.2. Charge-mediated magnetoelectric effect ........................................................................... 19

1.2.3. Exchange-bias mediated magnetoelectric effect ............................................................... 21

Chapter 2: Fabrication and characterization .................................................................................. 22

2.1. Metallic magnetic thin film fabrication: physical vapor deposition system (PVD) ........... 22

2.2. Ferroelectric characterization .................................................................................................... 25

2.3. Static magnetic property characterization: vibration sample magnetometer (VSM) ........... 26

2.4. Direct and converse magnetoelectric effect measurement .................................................... 28

Chapter 3: Quantification on the direct and converse magnetoelectric coupling ....................... 29

3.1. Introduction ............................................................................................................................... 29

3.2. Experiment .............................................................................................................................. 32
3.3. Theory ........................................................................................................... 33
3.4. Results and discussion ................................................................................. 39
3.5. Conclusion ..................................................................................................... 48

Chapter 4: Voltage Impulse Induced Bistable Magnetization Switching In Multiferroic Heterostructures ........................................................................................................ 49

4.1. Introduction .................................................................................................... 49
4.2. Experiment ..................................................................................................... 60
4.3. Results and discussion ................................................................................. 60
4.4. Conclusion ..................................................................................................... 69

Chapter 5: Conclusion and future plans ................................................................. 70

5.1. Conclusion of the present work ................................................................. 70
5.2. Future plans .................................................................................................. 71

5.2.1. Co-existence of strain and charge mediated magnetoelectric coupling for non-volatile control of magnetism ................................................................. 71

5.2.2. MEMS magnetoelectric sensor ............................................................... 72

References ........................................................................................................ 75
Chapter 1: *Introduction to artificial multiferroic heterostructure*

1.1. **Multiferroic and magnetoelectric materials**

Recently, multiferroic materials have drawn big interest because of its large potential for applications in novel electronic devices\(^1\)-\(^8\). Multiferroic materials are the group of at least two ferroic properties in one system, with the ferroic properties including ferroelectric, (anti-)ferromagnetism and ferroelastic. Strong magnetoelectric coupling can be induced due to the strong coupling interaction between two ferroic orders\(^9\). As shown in Figure 1.1 (a) multiferroic materials require two or all three of the properties ferroelectricity, ferromagnetism, and ferroelasticity occur in the same phase\(^10\).

By definition, magnetoelectric coupling can be specified into direct and converse magnetoelectric coupling. For the direct magnetoelectric coupling, there is an appearance of an electric polarization upon the application of a magnetic field. In this case, the magnetic field applied on the multiferroic material is capable of modifying the electric polarization of that material. Also, an electric potential or a voltage output can be induced by the applied alternating magnetic field which may lead to high resolution magnetic field sensor applications\(^11\)-\(^15\). Symmetrically, the converse magnetoelectric response is the existence of magnetization upon the application of electric field. This means the modification of magnetic property by an electric field which provides great opportunities in the voltage control of spintronics, reconfigurable electronics and tunable microwave devices with ultra-low energy consumption\(^16\)-\(^21\).
Figure 1.1 (a) Relationship between multiferroic and magnetoelectric materials. Illustrates the requirements to achieve both in a material (b) Schematic illustrating different types of coupling present in materials. Much attention has been given to materials where electric and magnetic order is coupled. These materials are known as magnetoelectric materials\textsuperscript{10}.

From the materials point of view, the multiferroic materials can be classified to single-phase and artificial composite multiferroics or magnetoelectrics. The multiferroic effect has been observed as an intrinsic effect in some natural material systems such as BiFeO\textsubscript{3} and some rare earth manganates\textsuperscript{6,22-24}. However, the single-phase multiferroic materials which have low Curie temperature or weak magnetoelectric coupling coefficient may be impractical to real device applications\textsuperscript{25,26}. On the other hand, the artificial multiferroic or magnetoelectric composites by combing ferroelectric and ferromagnetic phases show strong ME coupling with several orders of magnitude higher ME coupling coefficients compared to single phase multiferroics\textsuperscript{8}. The strong ME coupling realized in multiferroic materials enables effective energy conversion between
electric and magnetic fields, and has led to many different multiferroic devices from magnetic sensors, voltage tunable RF/microwave signal processing devices, spintronics, etc.

As shown in Figure 1.1 (b), the strain or elastic interaction between the ferroelectric/ferromagnetic interface leads to a large magnetoelectric coupling. The magnetoelectric coupling can be expressed as the cross product of the magnetoelastic coupling from ferromagnetic phase and the piezoelectric coupling from the ferroelectric phase as shown in equation 1.1.

\[ \alpha_{\text{Direct}} = \left( \frac{\partial P}{\partial H} \right)_{S,E} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \]

\[ \alpha_{\text{Converse}} = \mu_0 \left( \frac{\partial M}{\partial E} \right)_{T,H} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \quad (1.1) \]

Where P denotes the electric polarization, H denotes the magnetic field, M denotes the magnetization, E denotes the electric field. Other magnetoelectric mechanism including interfacial charge mediated magnetoelectric effect and exchange-mediated magnetoelectric coupling also show great capability in modifying the magnetism by electric field. In multiferroic composites, both ferromagnetic and ferroelectric phases can be selected separately to meet the devices design principles. For example, high quality microwave ferrite/ferroelectric heterostructures have been demonstrated for tunable RF/microwave devices\textsuperscript{19,27}; ultra-thin magnetic thin film/dielectric thin film utilizing the charge-mediated magnetoelectric effect has been realized for voltage controlled magnetic tunnel junction\textsuperscript{28-30}. 

15
1.2. Electric field control of magnetism in magnetoelectric composite

1.2.1. Strain-mediated magnetoelectric effect

Strain-mediated magnetoelectric coupling is one of the main approaches for the electric field control of magnetism\(^8\). Due to the converse piezoelectric effect from the ferroelectric phase, an external strain can be generated. That strain would transfer to the ferromagnetic phase through the interface, which finally modifies the magnetism of ferromagnetic phase due to the magnetoelastic coupling. Strain mediated magnetoelectric (ME) coupling in layered ferromagnetic/ferroelectric heterostructures provides great opportunities in realizing novel multiferroic devices such as magnetoelectric random access memories (MERAMs)\(^{31-33}\). Through phase field simulations, Hu and coworkers demonstrated a new approach towards voltage-controlled magnetic random access memory (MRAM) through strain mediated magnetoelectric coupling in magnetic tunneling junction on a ferroelectric layer heterostructure\(^{32}\). Strain mediated magnetoelectric coupling can lead to a 90\(^\circ\) rotation of the in-plane magnetization of the free layer in the magnetic tunneling junctions. Simulation results show that these voltage controlled MRAM devices have ultra-low writing energy (less than 0.16 fJ per bit), room temperature operation, high storage density, good thermal stability and fast writing speed. This mechanism has been achieved in the 1-3 type ferromagnetic BFO and ferroelectric CFO vertical heterostructure film\(^{34}\). The CFO nanopillars are embedded into the BFO film with an intimate lattice coupling between this two ferroic phases in nanoscale. The magnetoelectric coupling was
evidently proved by the MFM images, where the magnetic property of CFO was altered by the applied electric field on the BFO film.

Metallic magnetic films grown on ferroelectric substrates with large converse magnetoelectric coupling have also been widely reported. From the application point of view, the metallic magnetic thin films with low temperature fabrication process are promising for multiferroic devices. The voltage induced effective in-plane magnetic field, can be derived as follows:

\[
\Delta H_{\text{eff}} = 3\lambda_s \cdot Y \cdot d_{\text{eff}} \cdot E / \mu_0 M_s \quad (1.2)
\]

where \(\lambda_s\) is the saturation magnetostriction of the magnetic film, \(Y\) is the Young’s modulus of the magnetic film, \(M_s\) is the saturation magnetization of the magnetic material; \(d_{\text{eff}}\) is the effective piezoelectric coefficient of the piezoelectric beam, and \(E\) is the electric field applied on the piezoelectric substrates. In 2009, Jing et al. reported giant electric field tuning of magnetism in multiferroic FeGaB/Lead Zinc Niobate–Lead Titanate (PZN-PT) heterostructures. The new class of metallic magnetic film FeGaB shows a high saturation magnetostriction coefficient of 70 ppm and a narrow FMR linewidth of 16 Oe at X-band. The single crystal PZN-PT ferroelectric substrate exhibits large piezoelectricity with an anisotropic piezoelectric coefficients \(d_{31}= 3000\) pC/ N and \(d_{32}= 1100\) pC/ N. By combining these two materials together, giant voltage tunning of magnetic anisotropy was achieved as shown in Figure 1.2, where the ferromagnetic resonance of the FeGaB/PZN-PT heterostructure was characterized under various electric fields. The magnetic field bias was applied parallel to the in-plane direction of the FeGaB thin film. The ferromagnetic resonance field changed dramatically with the applied electric field. And a sudden shift of the resonance field from 898 Oe to 425 Oe was observed with the electric field sweeping
from 5.8 kV/cm to 6kV/cm. This was due to the phase transition from the rhombohedral to the tetragonal phase in the PZN-PT single crystal. The FeGaB/PZN-PT heterostructure exhibited a large mean ME coupling coefficient $\alpha=\Delta H/\Delta E=94$ Oe cm k/V, and a giant ME coupling coefficient of 2365 Oe cm k/V at the electric-field-induced phase transition region of the PZN-PT single crystal.

Figure 1.2 Electric field dependence of the in-plane field-sweep FMR spectra of the FeGaB/PZN-PT multiferroic heterostructure measured at ca. 9.6 GHz$^{35}$. 
1.2.2. Charge-mediated magnetoelectric effect

Charge mediated magnetoelectric effect was first reported by Weisheit et al. that the magnetocrystalline anisotropy of ultra-thin iron-platinum and iron-palladium magnetic layer can be reversibly controlled by electric field in an electrolyte\(^{37}\). The screening charge provided by liquid electrolyte modified the intrinsic magnetic properties. This direct way of voltage control of magnetism offers an opportunity for electric field induced resistance change in magnetic tunnel junctions, the core portion of MRAM devices. Maruyama et al\(^ {29} \) also reported the change of magnetic anisotropy in a Fe(001)/MgO(001) junction. By applying an electric field to dielectric MgO layer, the surface magnetic anisotropies in 3d ferromagnetic metal/noble metal interfaces were changed by the electron filling of 3d orbitals. From this origin, they showed a 40% change in the magnetic anisotropy by comparably small electric field which could lead to varies application in low power spintronic devices\(^ {38-40} \).

In previous research, people found the charge mediated ME coupling strength is highly dependent on magnetic film thickness. For instance, ME coupling strength of Fe/MgO heterostructure measured by Kerr hysteresis looper was significantly dependent on Fe film thickness, where the maximum magnetic surface anisotropy change was obtained at spin reorientation Fe thickness\(^ {41} \). In Co\(_{20}\)Fe\(_{80}\)/MgO heterostructure, magnetic surface anisotropy change decreased rapidly as Co\(_{20}\)Fe\(_{80}\) film thicknesses were larger than 0.5nm.\(^ {28} \) Nevertheless, the mechanism causes charge mediated ME coupling strength
dependence on magnetic film thickness is still not clear. To optimize the charge mediated ME coupling tunability in real applications, recently, Zhou and Nan et al. studied the voltage dependent ferromagnetic resonance (FMR) in Ni$_{0.81}$Fe$_{0.19}$ (NiFe)/SrTiO$_3$ (STO) magnetic/dielectric thin film heterostructures to quantitatively determine the thickness dependence of charge mediated magnetoelectric coupling$^{42}$. Voltage induced FMR field change was carried out through charge effect induced magnetic surface anisotropy change. Large voltage induced FMR field shift of 65 Oe and magnetic surface anisotropy change of 5.6 kJ/m$^3$ were obtained in NiFe/STO heterostructures. The voltage induced magnetic surface anisotropy showed a strong dependence on the thickness of the magnetic thin films, which was discussed based on the thin film growth model at the low thickness side, and on the charge screening effect at large thickness side. The thickness-dependent surface charge-mediated ME coupling has been studied in bi-layered NiFe/STO thin film heterostructures with varied thicknesses of the NiFe layer from 0.7 to 1.5 nm. High ME coupling induced FMR field shift of 65 Oe was obtained and measured by ESR system, corresponding to large voltage tunable effective magnetic anisotropy of 5.6 kJ/m$^3$ and surface anisotropy of 6.7 $\mu$J/m$^2$. This investigation established a significant progress for magnetic/dielectric heterostructure’s application in novel interfacial charge mediated magnetoelectric devices$^{29,43,44}$.
1.2.3. Exchange-bias mediated magnetoelectric effect

The exchange bias-mediated magnetoelectric effect, in most case, involved antiferromagnetic layer has been exploited for electric field control of magnet property in ferromagnetic film\textsuperscript{6,10}. The single phase multiferroic materials Cr\textsubscript{2}O\textsubscript{3} and YMnO\textsubscript{3} have first been studied for achieving the electric field control of exchange bias, however, which were observed in very low temperature\textsuperscript{25,45,46}. Then the room temperature multiferroic BFO which propose anti-ferromagnetic and ferroelectric properties attracted increasingly research interest. In the ferromagnetic (CoFe, CoFeB)/BFO heterostructure, the magnetization of the ferromagnetic can be modified by electric field induced ferroelectric polarization and the anti-ferromagnetic order of BFO layer through the ferroelectric-antiferromagnetic coupling\textsuperscript{24,47,48}. E-field control of magnetism, like magnetoresistance, magnetic anisotropy and magnetization, in a ferromagnetic layer exchange coupled to BFO layer has been most recently reported. Heron et al. discovered a nonvolatile, room temperature magnetization reversal determined by an electric field in a CoFe/BFO multiferroic heterostructure\textsuperscript{47}. 
Chapter 2: Fabrication and characterization

In this chapter, the fabrication and characterization of the multiferroic heterostructures are presented. The physical vapor deposition which is the main thin film deposition method in this work is introduced in detail. The characterization methods is categorized in ferroelectric polarization measurement, static magnetic property measurement, high frequency ferromagnetic resonance measurement and magnetoelectric coefficient measurement.

2.1. Metallic magnetic thin film fabrication: physical vapor deposition system (PVD)

PVD is a variety of vacuum deposition methods used to deposit thin films by the condensation of a vaporized form of the desired film material onto various work piece surfaces. The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapor deposition (CVD). PVD coatings are sometimes harder and more corrosion resistant than coatings applied by the electroplating process. Most coatings have high temperature and good impact strength, excellent abrasion resistance and are so durable that protective topcoats are almost never necessary.
Before the deposition, high vacuum below $1 \times 10^{-7}$ Torr is obtained as a base pressure for a “clear background” for high quality film deposition. Then noble gas such as Ar, with a controlled flow, is introduced into the main chamber to maintain a pressure in several or tens of mTorr as working pressure. After that, high voltage of hundred volts is applied to the target to generate a high electric field for ionizing the argon atoms and turning them into argon ions and electrons. When the energy of the surface atom is high enough, the sputtered atoms reach the substrate surface and become a dense film. In order to reach a higher sputtering rate, hard magnets are usually placed underneath the targets and the magnetic field generated confines the ions to the surface of the targets. Figure 2.1 shows the schematic of magnetron sputtering.
In our experiment, the magnetron sputtering system is manufactured by AJA International. It has six sputtering source with both DC and RF sputtering capability. The system can reach a base pressure as low as $1 \times 10^{-7}$ Torr.

*Figure 2.1 Schematic of Magnetron sputtering.*

![Figure 2.1 Schematic of Magnetron sputtering.](image-url)
2.2. Ferroelectric characterization

In order to measure the electric polarization of ferroelectric substrates, the Radient Precision LC ferroelectric test system is used. This is very important in our experiments since electric coercive field, remnant polarization and etc. of ferroelectric materials are critical parameters for reaching non-volatile switching of magnetism. Considering the thickness (~500um) and electric field (~10 kV/cm) needed in the experiments, up to 600 V is required. For that requirement, a high voltage interface and a high voltage amplifier with a gain of 1000 are also connected to the ferroelectric test system to generate large electric fields. Figure 2.2 shows the Radient Precision LC ferroelectric test system.
2.3. Static magnetic property characterization: vibration sample magnetometer (VSM)

In this experiments, the vibrating sample magnetometer (VSM) is used to measure the DC/low frequency magnetic properties of magnetic materials. A VSM system consists of a vibration stage, a pick-up coils and electromagnets. The sample is loaded on the vibration stage that vibrates at certain frequency, and then the pick-up coils are used to detect the change of the magnetic flux. Due to the Faraday’s law, the magnetization in
different bias magnetic field generated by the electromagnets can be obtained by the detected magnetic flux. Usually, in order to get a very small value of the magnetization, the induced voltage in the pick-up coils is measured by a lock-in amplifier whose modulation frequency is equal to the sample vibration frequency. With this configuration, the undesired noise is decreased and the sensitivity of a VSM system can be $1 \times 10^{-7}$ emu. We use a Lakeshore 7407 VSM system as shown in Figure 2.3.

*Figure 2.3 The LakeShore 7407 VSM.*
2.4. Direct and converse magnetoelectric effect measurement

In order to quantify the direct and converse magnetoelectric coupling coefficient, a magnetoelectric effect measurement system is setup. For DME effect measurement, a harmonic voltage from the lock-in amplifier (Zurich Instruments, UHF-DEV2031) shown in Figure 2.4 with frequency \( f = 1 - 100 \text{kHz} \) and magnitude \( U = 100 \text{mV} \) was applied to the coil and excited an AC magnetic field. The dc bias voltage was applied on the sample along thickness direction using high voltage amplifier. The generated ac voltage between the electrodes of PZT was measured by the lock-in amplifier with input impedance of 1 M\( \Omega \). For CME measurement, the same harmonic voltage signal and dc bias electric voltage were applied to the electrodes of PZT simultaneously using a bias tee (Picosecond Pulse Labs 5530B). The variation of magnetic induction results in a voltage in the coil, which was measured by the lock-in amplifier.

Figure 2.4 Ultral-high frequency lock-in amplifier manufactured by Zurich Instrument.
Chapter 3: *Quantification on the direct and converse magnetoelectric coupling*

3.1. Introduction

Strong magnetoelectric (ME) coupling can be achieved in multiferroic materials, which can be categorized as direct ME effect (DME, a change of polarization in an external magnetic field) and converse ME effect (CME, a change of magnetization in an external electric field)\(^{49-52}\). An ever increasing amount of interest has been devoted to investigations on DME and CME effects because of their fundamental science and potential applications in devices, such as sensors, transducers, and actuators. Compared to single phase multiferroic materials, multiferroic laminates composed of piezoelectric and magnetostrictive phases have shown much stronger ME effect due to product property. In order to further enhance the ME effect in multiferroic composites, a lot of efforts were devoted to selecting suitable highly magnetostrictive and/or piezoelectric components and to designing different structures of the composites, including 2-2, 3-0 and 2-2 connectivities. Besides, a sharp increase in the magnitude of ME coupling coefficient has been observed at the electromechanical resonance (EMR) for both DME and CME effects, which provides great opportunities for applications. However, the relationship between DME and CME, especially at the EMR, is controversial and confusing\(^ {53-56}\).
The first serious issue is about the resonance peak position of DME and CME. The results demonstrated that the resonance peak for DME and CME appears at the same EMR frequency; while other researchers reported that resonant DME and CME effect were observed at two very close but significantly different frequencies, i.e., antiresonance frequency \( f_a \) for DME and resonance frequency \( f_r \) for CME, respectively. Moreover, the origin of the discrepancy of antiresonance and resonance frequencies is not very clear. Cho et al. explained the difference between the two resonance frequencies by combining piezoelectric constitutive equations with resonance boundary conditions, believing that \( f_r \) is obtained when impedance \( z \) of piezoelectric phase is minimized while \( f_a \) is obtained when \( z \) is maximized\(^{57}\). On the theory side, Filippov et al. and Bichurin et al. derived the different resonance conditions for DME and CME effects using the same constitutive equations of the materials and equation of motion\(^{53,58}\).

Another issue is on the magnitude of peak value of resonant DME and CME coefficients. Usually, DME and CME coefficients are defined as \( \alpha_E = \partial E / \partial H \) and \( \alpha_B = \partial B / \partial E \), respectively, where \( E, H, B \) are electric field, magnetic field and magnetic induction, respectively. It is evident that these two coefficients are not equivalent according to unit dimension analysis. In order to compare the magnitude between these DME and CME, effective DME and CME coefficients defined as \( \alpha_d = dp / dH \) and \( \alpha_c = \mu_0 dm / dE \), respectively, were introduced, where \( p \) and \( m \) are effective electrical and
magnetic dipole moments of the entire system under equivalent conditions of electric and magnetic bias, respectively. Consequently, the equivalence between DME and CME effects in single phase, as well as in laminate composite at low frequency was verified theoretically and experimentally. It is of physical and technical interest to investigate if this equivalence still exists at the EMR.

In this work, we systematically measured the frequency response of DME and CME effect in FeGa/PZT/FeGa sandwich at the same bias conditions of different dc electric and magnetic fields. The experimental results confirm that antiresonance frequency for DME and resonance frequency for CME have close but different values, and the resonant DME and CME are not equivalent in magnitude, demonstrating the inequivalence of resonant DME and CME effects. At the same time, antiresonance frequency and resonance frequency, and resonant DME and CME coefficients show similar variation tendency with dc bias magnetic or electric fields, indicating the consistency between resonant DME and CME effects. In addition, based on analyzing the transfer relationship between stress and strain, as well as electric field and magnetic field, new expressions for frequency response of ME effects have been derived by adopting different sets of constitutive equations of the materials for DME and CME effect. The theoretical results are in good agreement with the experimental results.
3.2. Experiment

A schematic view of the measurement in this experiment is shown in Figure 3.1. The ME laminate composite consists of a thickness direction polarized 25mm×4mm×0.279 mm PZT slab whose faces are sandwiched between two polycrystalline 0.290 mm-thick layers of magnetostrictive Fe\textsubscript{82}Ga\textsubscript{18} (Galfenol, from ETREMA Products, Inc.). The much larger length than the width intensifies the dominating vibration mode along the length direction. An electromagnetic copper coil of 70 turns was wound around this structure to pick up variations in magnetic induction or apply an AC magnetic field. The dc bias magnetic field generated by an external coil was applied along the length direction.

For DME effect measurement, a harmonic voltage from the lock-in amplifier (Zurich Instruments, UHF-DEV2031) with frequency f=1-100kHz and magnitude U=100mV was applied to the coil and excited an AC magnetic field. The dc bias voltage was applied on the sample along thickness direction using high voltage amplifier. The generated ac voltage between the electrodes of PZT was measured by the lock-in amplifier with input impedance of 1 MΩ. For CME measurement, the same harmonic voltage signal and dc bias electric voltage were applied to the electrodes of PZT simultaneously using a bias tee (Picosecond Pulse Labs 5530B). The variation of magnetic induction results in a voltage in the coil, which was measured by the lock-in amplifier.
3.3. Theory

Consider a layered ME composite consisting of a piezoelectric plate sandwiched between two magnetostrictive plates with thickness $t$, width $w$ and length $L$, as shown in Figure 3.1(a). The piezoelectric phase is polarized along its thickness direction with electrodes on its top and bottom surfaces. It is assumed that the plate thickness and width are much smaller than its length, i.e., $t \ll L$, $w \ll L$. Since the plate is thin and narrow and the surfaces of the composite is free, the stress components of $T_2$ and $T_3$ may be ignored and only nonzero $T_1$ is taken into account.

Figure 3.1 (a) Schematic of the direct and converse magnetoelectric effect measurements.

(b) Equivalent electric circuit of the direct and converse magnetoelectric effect.
For the direct ME effect, the dc bias and ac magnetic field are applied along the length direction, as shown in Figure 3.1(b). The induced strain in the magnetostrictive component due to piezomagnetic effect is transferred to piezoelectric component by elastic coupling. Then the generated stress results in polarization and electric field between the two electrodes in the piezoelectric phase. During this process, strain and electric displacement are independent variables and stress and electric field are dependent variables, so the fourth set of constitutive equations should be adopted for the piezoelectric phase. Since the magnetic induction \( B \) in the magnetostrictive phase along length direction should satisfy the divergence-free condition, the third set of constitutive equations for the magnetostrictive phase is adopted. Thus the constitutive equations for the two phases can be written as following:

\[
\begin{align*}
\rho T_i &= \epsilon_{11}^p S_i - \rho h_{31} D_3 \quad (3.1) \\
E_3 &= -\rho h_{31} S_i + D_3 / \varepsilon_{33}^S \quad (3.2) \\
m S_i &= m_{s11}^B T_i + m_{g1} B_i \quad (3.3) \\
H_i &= -m_{g1} m T_i + B_i / \mu_{11}^T \quad (3.4)
\end{align*}
\]

where superscripts \( p \) and \( m \) denote piezoelectric and magnetostrictive phases, respectively; \( T_i \) is stress component; \( S_i \) is strain component; \( \epsilon_{11}^p \) is elastic coefficient under open-circuit condition; \( \rho h_{31} \) is piezoelectric coefficient defined as \( \rho h_{31} = \partial \rho T_i / \partial D_3 \); \( \varepsilon_{33}^S \) is permittivity under constant strain; \( E_3 \) and \( D_3 \) are electric field and electric displacement;
" s_{11}^m \) is compliance coefficients under open-circuit condition; \( H_i \) is magnetic field; \( g_{11}^m \) is piezomagnetic coefficients defined as \( g_{11}^m = \partial^n S_i / \partial B_i \); \( \mu_i^m \) is permeability under constant stress.

In the EMR region, the equation of motion for the medium has the following form:

\[
\bar{\rho} \frac{\partial^2 u_i}{\partial t^2} = v \frac{\partial^n T_{ij}}{\partial x_j} + (1 - v) \frac{\partial^{n+1} T_{ij}}{\partial x_j} \quad (3.5)
\]

where \( v \) is volume fraction of piezoelectric phase, \( \bar{\rho} \) is average density of the composite.

As the resistivity of the piezoelectric phase is much larger than that of the measurement circuit, the open-circuit condition is valid and thus \( D_3 = 0 \) is obtained. Expressing the stress components in terms of strain from Eq. (3.1) and (3.3) and substituting these expressions into Eq. (3.5), we can get the differential equation for \( u_x \), which has the general solution as

\[
u_x = A \cos k_i x + B \sin k_i x \quad (3.6)
\]

where \( k_i = \omega \sqrt{\frac{\mu_i^m}{s_{11}^m}} \left( \frac{v}{s_{11}^D} + \frac{1 - v}{s_{11}^B} \right)^{-1} \), \( \omega \) is the angular frequency, \( A \) and \( B \) are two integration constants, which can be determined from the stress-free boundary condition at both ends listed as following:

\[
(\nu^n T_1 + (1 - v)^m T_1 = 0 \text{ at } x = 0 \text{ or } x = L \quad (3.7)
\]
Substituting the displacement expression of Eq. (3.6) into Eq. (3.2) and averaging the electric field over the sample length, the effective DME coefficient is obtained as

$$\alpha_d = \frac{p_3}{H_3} = \frac{2v(1-v)\rho d_{31}^m d_{11} \mu_{\text{eff}}}{k_i L \mu_{11}^T (v s_{11}^m s_{11}^B + (1-v)\rho s_{11}^D)} \tan \frac{k_i L}{2}$$ (3.8)

where $\rho d_{31} = h_{31}^p s_{11}^D$, $m d_{11} = g_{11}^m \mu_{11}^T$, $V$ is volume of the composite, $\mu_{\text{eff}}$ is effective permeability that can be found from Eq. (4). Expressing $\rho T_1$ from Eq. (3.3), substituting it into Eq. (3.4) and then averaging over the sample length, the effective permeability can be obtained as

$$\mu_{\text{eff}} = \frac{k_i L (v s_{11}^m s_{11}^B + (1-v)\rho s_{11}^D) s_{11}^B \mu_{11}^T}{k_i L (v s_{11}^m s_{11}^B + (1-v)\rho s_{11}^D) s_{11}^B \mu_{11}^T + \mu_{11}^T s_{11}^B g_{11}^m g_{11}^m - 2 \tan \frac{k_i L}{2} \mu_{11}^T (1-v)\rho s_{11}^D}$$. (3.9)

According to Eq. (8), the resonance condition for DME effect is found as

$$f_a = \frac{2n+1}{2L} \sqrt{\frac{\rho}{\rho s_{11}^D} \left( \frac{v}{s_{11}^B} + \frac{1-v}{s_{11}^B} \right)}$$. (3.10)

where a sharp increase in the DME coefficient is observed at the antiresonance frequency $f_a$.

In the case of CME effect, the ac electric field is applied to the piezoelectric phase along the thickness direction and the dc bias magnetic field is applied the length direction of the magnetostrictive phase, as shown in Figure 3.1(c). Strain is generated in the
piezoelectric phase due to applied ac electric field by converse piezoelectric effect. The strain is transferred to magnetostrictive phase by elastic coupling, resulting in magnetization $M$ and magnetic induction $B$ by piezomagnetic effect, which is measured by means of the induced voltage in the coil wound in the composite. During this process, stress and electric field are independent variables, strain and electric displacement are dependent variables for piezoelectric phase, so the first set of constitutive equations are adopted. For the magnetostrictive phase stress and magnetic induction are dependent variables, the second kind of constitutive equations are used.

\[
^p S_1 = ^p s_{11}^E T_1 + ^p d_{31} E_3 \quad (3.11)
\]
\[
D_3 = ^p d_{31} T_1 + e_{33}^T E_3 \quad (3.12)
\]
\[
^m T_1 = ^m c_{11}^H S_1 - ^m e_{11} H_1 \quad (3.13)
\]
\[
B_1 = ^m e_{11} S_1 + ^S \mu_{11} H_1 \quad (3.14)
\]

where $^p s_{11}^E$ is compliance coefficient under short-circuit condition; $^p d_{31}$ is piezoelectric coefficient defined as $^p d_{31} = \partial D_s / \partial ^p T_1$; $e_{33}^T$ is permittivity under constant stress; $^m c_{11}^H$ is compliance coefficients under short-circuit condition; $^m e_{11}$ is piezomagnetic coefficients defined as $^m e_{11} = \partial H_1 / \partial ^m T_1$; $^S \mu_{11}$ is permeability under constant strain.
Applied $E_3$ in piezoelectric phase is a constant for CME. Since the input impedance of the lock-in is much larger than the coil resistivity, the open-circuit condition is valid and, hence, $H_i = 0$. Then with similar derivation as that for DME effect, the effective DME coefficient is obtain as

$$
\alpha_c = \frac{m}{E_3} = \frac{2v(1-v)\rho_{d_{31}}^m d_{11}^m}{k_2 L (v^m s_{11}^H + (1-v)\rho_{s_{11}}^E)} V \tan\left(\frac{k_2 L}{2}\right) \tag{3.15}
$$

where $d_{11}^m = e_{11}^m s_{11}^H$, $k_2 = \omega \sqrt{\rho \left(\frac{v}{\rho_{s_{11}}^E} + \frac{1-v}{\rho_{s_{11}}^H}\right)^{-1}}$. One can found that the resonance condition for CME effect is

$$
f_r = \frac{2n+1}{2L} \sqrt{\frac{1}{\rho_{s_{11}}^B} \left(\frac{v}{\rho_{s_{11}}^E} + \frac{1-v}{\rho_{s_{11}}^H}\right)} \tag{3.16}
$$

where a sharp increase occurs at the resonance frequency $f_r$.

Using Eq. (3.10) and (3.16), we can discuss the performance of DME and CME at low frequency and EMR. In the case of low frequency region, the difference between $\rho_{s_{11}}^B$ and $\rho_{s_{11}}^E$, $s_{11}^B$ and $s_{11}^H$ under different boundary conditions is negligible and $\tan\left(\frac{kL}{2}\right) \approx \frac{kL}{2}$ is satisfied, so Eq.(10) and (16) can be reduced to

$$
\alpha_c or \alpha_d = \frac{v(1-v)\rho_{d_{31}}^m d_{11}^m}{v^m s_{11}^H + (1-v)\rho_{s_{11}}^E} V \tag{3.17}
$$
Eq. (3.17) indicates that equivalence between DME and CME at low frequency can be expected and has been theoretically and experimentally proved.\textsuperscript{23,25} For the case at EMR, the difference between $p \sigma_{11}^D$ and $p \sigma_{11}^E$, $m \gamma_{11}^B$ and $m \gamma_{11}^H$ cannot be ignored, resulting in the prominent difference between $f_a$ and $f_r$. Moreover, the magnitude of resonant effective DME and CME coefficients cannot be exactly equivalent in spite of the same order, as can be seen from Eq. (3.8) and (3.15).

3.4. Results and discussion

First, we measured frequency dependence of DME and CME effect at increasing dc bias magnetic field and fixed dc bias voltage 0, 100, 200, 300, 400 V. Fig.2 shows the bias magnetic field dependence of $f_a$ and $f_r$, and corresponding resonant ME coefficients at fixed increasing bias voltage. As shown in Figure 3.2(a) and (b), at each same bias condition, there is distinct difference between $f_a$ and $f_r$. These two frequencies are very close but $f_a$ is a little larger than $f_r$, which is consistent with observations by other groups.\textsuperscript{13,24} In addition, it can be seen clearly from Figure 3.2(c) and (d) that resonant effective ME coefficients $\alpha_d$ and $\alpha_c$ are also not equal in magnitude, as predicted by Eq. (3.8) and (3.15). This observation is not consistent with the results for single phase or two-phase composites at low frequency. The measured $\alpha_d$ and $\alpha_c$ are calculated according to
\[
\alpha_d = \frac{p}{H_1} = \frac{u_{\text{out}}}{n I} \varepsilon V_p \quad (3.18)
\]

\[
\alpha_e = \frac{\mu m}{E} = \frac{u_{\text{out}}}{2\pi f N A u_m} V_m \quad (3.19)
\]

where \( u_{\text{out}} \) is induced output voltage in the piezoelectric phase or the search coil, \( t \) is the thickness of piezoelectric phase, \( n \) is the number of coil turns per meter, \( I \) is the current in the coil due to applied voltage, \( \varepsilon \) is permittivity of piezoelectric phase, \( f \) is applied ac electric field frequency, \( N \) is the number of coil turns, \( A \) is the cross section area of the coil, \( u_m \) is the input voltage onto the piezoelectric phase, \( V_p \) and \( V_m \) are the volume of piezoelectric phase and magnetostrictive phase. It should be pointed out that the electric field dependence of permittivity \( \varepsilon \) of piezoelectric phase has been taken into account in the calculation. As shown in the inst of Figure 3.2(c), the relative permittivity with bias voltage obtained by measuring capacitor versus voltage curve exhibits a butterfly characteristic, resulting from the ferroelectric property of PZT. Measured permittivity increases from 3800 to 4500 with increasing \( E \) field, then experiences an abrupt drop to 2954 around \( U_c \approx 150V \) and keeps the low value until \( U = 400V \). When the electric field is decreased back from this value, the permittivity continuously increases.
Figure 3.2 Bias magnetic field H dependence of (a) antiresonance frequency $f_a$; (b) resonance frequency $f_r$; (c) resonant $\alpha_d$ and (d) resonant $\alpha_c$ at fixed increasing bias voltage 0, 100, 200, 300, 400 V.

Now we apply our model to the experimental results. Figure 3.3 shows the comparison of calculated frequency response of $\alpha_d$ and $\alpha_c$ using Eq. (3.8) and (3.15) to the experimental results for FeGa/PZT/FeGa sandwich composite under optimum bias.
magnetic field $H_{\text{bias}} = 140\text{Oe}$ and zero bias electric field. The material parameters used for numerical calculation are listed as following: $^{p}\varepsilon_{11}^E = 1.61 \times 10^{-11} \text{m}^2 / \text{N}$, $^{p}d_{31} = -220 \times 10^{-12} \text{C} / \text{N}$, $^{p}\rho = 7800 \text{kg} / \text{m}^3$, $^{p}\varepsilon_{33} / \varepsilon_0 = 3800$, $^{m}\beta_{11}^H = 1.65 \times 10^{-11} \text{m}^2 / \text{N}$, $^{m}d_{11} = 10 \times 10^{-9} \text{m} / \text{A}$, $^{m}\rho = 7870 \text{kg} / \text{m}^3$, $\mu_{11} / \mu_0 = 70$, $l = 25 \text{mm}$. The circular frequency $\omega$ is represented by complex quantity $\omega(1 - i/Q)$ to take into account the energy loss, where $Q$ is quality factor, determined from the line-width the experimental curve. One observes good agreement between theory and data. The calculated antiresonance and resonance frequencies using are 58 and 56 kHz, respectively, consistent with the experimental results. The discrepancy between calculated and experimental resonance frequencies is mainly due to $\Delta E$ effect, namely, the shift of antiresonance and resonance frequencies with applied dc bias magnetic field, to be discussed in the following sections. The amplitude discrepancy for CME is attributed to the drawback of the experimental method, where the search coil is wound around the entire sample rather than magnetostrictive phase, resulting in lower measured value of magnetic induction than that actually induced in magnetostrictive phase. Even taking into account this factor, resonant DME and CME would not be expected to be equivalent in magnitude, as indicated in Eq. (3.8) and (3.15).
Figure 3.3 Comparison of theoretical and experimental frequency response of effective DME and CME coefficients with $H_{bias} = 180\text{Oe}$ and zero bias electric field.

It is well known that both DME and CME originate from the product of piezoelectric effect and magnetostrictive in laminate composites, so the magnitude of resonant ME is determined by piezoelectric coefficients of piezoelectric phase, piezomagnetic coefficients of magnetostrictive phase, interfacial mechanical coupling, the mechanical material parameters and the volume fraction of the constituent phase. As indicated in our theory, mechanical, electrical, and magnetic boundary conditions are different for DME
and CME due to opposite direction of energy conversion, which leads to the inequivalence of resonant DME and CME.

Figure 3.4 Bias voltage dependence of: (a) $f_a$; (b) $f_r$; (c) resonant $\alpha_d$ and (d) resonant $\alpha_c$ at fixed bias magnetic field of 120 Oe.

On the other hand, as can be seen from Figure 3.2 (a) and (b), $f_a$ and $f_r$ show similar variation tendency with bias magnetic field. With increasing bias magnetic field, both $f_a$
and $f_r$ decrease to a minimum value at around 180 Oe, then rise to a saturated value at bias magnetic field up to 400 Oe at each fixed bias voltage. It is interesting that resonant DME and CME exhibit a tendency with bias magnetic field in opposition to $f_a$ and $f_r$, as shown in Figure 3.3(c) and (d). The change of $f_a$ and $f_r$, as well as opposite change of resonant ME effects with increasing bias magnetic field can be explained in terms of motion of domain walls. That is, with bias magnetic field increasing to optimum value, deformation contribution from non-180° domain wall motion reaches maximum, leading to maximized compliance and magnetostrictive strain, and consequently lowest $f_a$ and $f_r$, and strongest resonant ME coefficients. Further increasing bias magnetic field the motion of non-180° domain-wall will be suppressed due to the interaction with applied magnetic field, resulting in a decrease in compliance and magnetostrictive strain. Accordingly $f_a$ and $f_r$ increase and resonant DME and CME decrease. The similar variation tendency of $f_a$ and $f_r$, as well as resonant ME effects indicates that bias magnetic field affects DME and CME at EMR in the same manner.
Figure 3.5 Bias voltage dependence of: (a) $\alpha_d$ and (b) $\alpha_c$ at fixed bias magnetic field of 120 Oe and low frequency of 10 kHz.
As indicated in Figure 3.2, bias electric field also has significant influence on resonant DME and CME. In order to further investigate the influence of bias voltage on resonance DME and CME, the frequency responses of DME and CME were measured with bias voltage variation loop at a fixed bias magnetic field 120 Oe. As shown in Figure 3.4(a) and (c), the bias voltage dependence of $f_a$ and $f_r$ shows similar standard “butterfly” curve, which is attributed to the widely observed butterfly curves of piezoelectric strain and electric field due to ferroelectric behavior of PZT. Figure 3.4(b) and (d) gives the corresponding resonant ME coefficients variation with bias voltage, which also exhibits similar butterfly variation tendency. It is worth noting that resonant ME effect also shows nearly opposite variation tendency with bias voltage to resonance frequency, similar with the case for bias magnetic field. In Figure 3.4(a) and (c), the lowest resonant frequencies occur at ~150V corresponding to the electric coercive field which is due to variation of the compliance coefficient of PZT with bias voltage; while in Figure 3.4(b) and (d) the maximum ME coefficients occur at ~50V which is possibly due to the combined effect of compliance coefficient, piezoelectric coefficient and permittivity of PZT with bias voltage, as indicated in Eq. (3.8) and (15). The dependence of DME and CME coefficients on bias voltage at EMR is consistent with that at low frequency of 10 kHz, as shown in Figure 3.5. The similar variation of $f_a$ and $f_r$, as well as resonant DME and CME coefficients indicate that the bias electric field affects DME and CME in the same manner.
3.5. Conclusion

For a laminated composite, we have measured the frequency response of DME and CME coefficients at the same bias magnetic and voltage conditions. The antiresonance frequency for DME and resonance frequency for CME, have very close but distinguishable values, showing similar variation tendency with bias magnetic and electric fields. The corresponding resonant DME and CME coefficients show similar variation tendency with bias magnetic field and voltage, but have inequivalent magnitude under the same bias magnetic and electric conditions, which is not consistent with the case at low frequency. A new theoretical model is developed to explain the inequivalence and consistency between resonant DME and CME, showing good agreement. This work is of significance for better understanding the relationship between DME and CME by demonstrating the inequivalence and consistency of resonant DME and CME effect in laminate composites.
Chapter 4: Voltage Impulse Induced Bistable Magnetization Switching In Multiferroic Heterostructures

4.1. Introduction

In strain-mediated multiferroic system, the typical modification of the magnetism of ferromagnetic phase as a function of bipolar electric field shows a “butterfly” like behavior\textsuperscript{16,60-68}. That is due to the the piezoelectricity of ferroelectric phase which has a “butterfly” like piezostrain as a function of electric field curve resulted from ferroelectric domain wall switching. In this case, the magnetization state is volatile because of the vanish of the piezostrain at zero electric field. However, the non-volatile switching of magnetization would be more promising for information storage or MERAM devices with lower energy consumption, and the magnetic state can be further controlled by voltage impulse\textsuperscript{17,32}.

Non-volatile switching of magnetism is experimentally demonstrated in ferromagnetic materials on different ferroelectric slab, such as (001) and (011) oriented PMN-PT single crystal, (011) oriented PZN-PT single crystal and PZT ceramic slab\textsuperscript{35,69,70}.
Wu et al. have first experimentally a revisable and permanent magnetic anisotropy reorientation in a muliferroic Ni/(011) oriented PMN-PT heterostructure. In this system, they achieved a 300 Oe anisotropy field change. The change is stable without applying electric field and is able to switch reversibly by an electric field below the electric coercive field.\(^{71}\)

![Normalized Kerr rotation hysteresis curves (M-H) along they y direction under different electric fields](image)

**Figure 4.1** Normalized Kerr rotation hysteresis curves (M-H) along they y direction under different electric fields (letters are the representatives of the labeled strain states in the inset). The inset shows in-plane strain difference \((\varepsilon_y - \varepsilon_x)\) as a function of electric field. The drawings indicate the magnetization state: (c) permanent easy plane, [(a) and (b)] temporary easy axis along \(x\), and [(d) and (e)] permanent easy axis along \(x\).\(^{72}\)
Figure 4.1 shows the Kerr rotation hysteresis loop of Ni/PMN-PT in application of different electric field which would lead to different piezo-strain state. The Figure 4.1 inset shows the relative strain difference as a function of electric field. By driving the electric field from A to C (A-B-C), due to the linear piezoelectric effect the PMN-PT is in the linear ferroelectric regime. In that case, from the M-H hysteresis loop, the remnant magnetization increases linearly. However, in the linear regime, the magnetic anisotropy change is unstable and the magnetic state would change back to its initial state after removing the applied electric field. When decreasing the electric field from 0 to coercive field (D), the non-180° polarization reorientation takes place in PMN-PT and induces a sudden increase of strain. This would cause the large change of the magnetic anisotropy. When removing the electric field (E), the strain remains and the magnetization is retained. Further increase the electric field from 0 to coercive field (B), another non-180° polarization reorientation occurs back to the initial poling direction. Thus the remnant strain is released, the magnetic state is switched back. However, the mechanism non-volatile switching of the magnetism using non-180° ferroelectric domain wall reorientation is unclear.

Most recently, Ming et al. used an unique ferroelastic switching pathway in (011) oriented PMN-PT (0.71Pb(Mg1/3Nb2/3)O3-0.29PbTiO3) single crystal that allows up to 90% of polarization to rotate from an out-of-plane to a purely in-plane direction (71° and 109° switching), thereby producing two distinct, stable and electrically
reversible lattice strain states. Domain distortion, polarization switching pathway and lattice strain in response to in situ vertical voltage in PMN-PT (011) are clearly presented using reciprocal space mapping (RSM) and piezoforce microscopy (PFM) measurements.

**Figure 4.2** (a) In-plane magnetic hysteresis loops of FeCoB/PMN-PT (011). Insets are schematic (upper left) and FMR spectra (bottom right). (b) Schematic of FMR measurement for (c-f). The sample is laid face down on an S-shape co-planar waveguide.
Magnetic fields are applied in the [100] direction and electric fields are applied along the [011] direction. (c) Electric field dependence of the FMR frequency in field sweeping mode. (d) Electric field dependence of the FMR field in frequency sweeping mode. (e) FMR frequency responses under unipolar (red) and bipolar (blue) sweeping of electric fields at room temperature. (f) Voltage-impulse-induced non-volatile switching of FMR frequency. As shown in Figure 4.2, the multilayer films with the structure of Au(5 nm)/Fe$_{60}$Co$_{20}$B$_{20}$ (50 nm)/Ti(5 nm) were deposited on (011) oriented single crystalline PMN-PT substrates and the multiferroic heterostructure was characterized by electric field dependence of ferromagnetic resonance field using coplanar-waveguide (CPW) FMR test unit. Figure 4.2 (e) shows the resonance frequency in response to in situ electric fields applied normally to the sample. A "Butter-fly" curve (blue) is observed as cycling triangle electric fields. By applying a positive electric field on a negatively poled FeCoB/PMN-PT (011), a giant frequency jump takes place near the coercive field of 1.5 kV cm$^{-1}$. In this process, the polarization undergoes 71° and 109° ferroelastic switching from the out-of-plane to the in-plane direction associated with a lattice strain induced by the domain distortion. Therefore, the hysteresis loop of the FMR frequency as a function of the electric field is observed (Fig. 4.2(e) ). Similar to magnetic memory, two stable and reversible frequency remnant states A and B would facilitate the realization of non-volatile frequency switching by reversing the applied electric field at the coercive field.
The voltage impulse induced magnetization switching was also realized shown in Figure 4.2 (f). As a PMN-PT (011) is subjected to an impulse of -6 kV cm\(^{-1}\), the remnant strain in poling state A is retained and results in the maximum FMR frequency of 9.9 GHz. Upon applying an impulse field of 1.5 kV cm\(^{-1}\), the resonance frequency is reduced to 7.6 GHz, indicating that the strain state is switched to remnant state B.

*Figure 4.3 Schematics of domain structures and reciprocal space maps (RSMs) about (022) and (002) reflections of PMN-PT(011) under various applied electric fields and thus poling states. The first column (a,e,i) is for the unpoled state. The second column (b,f,j) is for the positive poling state with up to 90% of polarization pointing upward. The*
third column (c,g,k) is after applying an negative electric field of -1.5 kV cm\(^{-1}\) and then switching it off. The fourth column (d,h,l) is achieved by applying a positive electric field of 5 kV cm\(^{-1}\) and then switching it off\(^{23}\).

High resolution x-ray diffraction (HRXRD) measurements were used to understand the polarization switching pathway and lattice strain in response to in situ electric fields. Figure 4.2 shows the electric field dependence of the reciprocal space maps (RSMs) in the vicinity of the (022) and (002) reflections of the bare PMN-PT (011) substrates. For the unpoled state of PMN-PT (011) (the first column in Fig. 4.2), a single broad spot is observed in both (022) and (002) reflections ((Fig. 2(e) and 2(i)). Analysis on RSM patterns suggests that two possible domain structures r3 and r4 are dominant in the unpoled state, and most of the polarization lies in the plane. As the sample is vertically poled with a strong positive voltage, the RSM in Fig. 2(f) shows an addition high intensity (022) reflection spot with a lower Q022 value, corresponding to the r1/r2 domain structures. Meanwhile, the intensity of the spot corresponding to r3/r4 reduces dramatically. This indicates that 71° and 109° ferroelastic polarization switching from the in-plane direction to the out-of-plane direction takes place and results in a large out-of-plane lattice strain. After a small negative electric field of -1.5 kV cm\(^{-1}\) is applied and removed, the domain distortion returns to r3/r4 and polarization is suppressed from the out-plane direction to the in-plane direction (Fig. 4.2(g)). As a large positive electric field of 5 kV cm\(^{-1}\) is applied and then switched off, the domain structure is switched again and
back to r1/r2 (Fig. 4.2(h)). Therefore, a stable and reversible ferroelastic domain switching pathway is confirmed, which enables polarization rotation between the in-plane direction and the out-of-plane direction.

In (001) oriented PMN-PT, different non-volatile switching behavior was observed. Zhang et al. reported a large and nonvolatile bipolar-electric-field-controlled magnetization switching at room temperature in a CoFeB/ (001) oriented PMN-PT multiferroic heterostructure, which exhibited an electric-field-controlled loop like magnetization behavior.

![Figure 4.4](image)

*Figure 4.4* (a) to (d) show the electric-field tuned XRD-RSMs around the (113) reflection. (e) Configuration of the (113) crystal face (translucent blue plane) and the rhombohedral distortions as well as polarizations shown by the arrows, whose colors correspond to the colors of the ellipses in (a) to (d). (f) The 109° switching induced changes of in-plane
distortions along the [110] direction as well as the corresponding lattice parameters and the in-plane projections of polarization vectors (broad arrows).

Figure 4.4 (a)-(d) shows the XRD-RSM of the (113) peak under electric fields of -8kV/cm, -0V/cm, +8kV/cm and +0kV/cm. The reflections are unchanged by removing the electric field; while the positive and negative poled cases displayed remarkable difference which is the origin of the non-volatile and reversible electrically control of magnetism. By analyzing the RSM data, the negatively and positively poled PMN-PT showed a change of the percentage of \( r_2/r_4 \) from 4\% to 30\%. Because the change between \( r_1^+ / r_3^+ \) and \( r_2^- / r_4^- \) corresponds to the 109\° switching, percentage of the 109\° switching is about 26\% and the 71/180\° switching have the percentage of 74\%. This nonvolatile electric field control of magnetization in CoFeB/PMN-PT was believed to be related to the combined action of 109\° ferroelastic domain switching and the absence of magnetocrystalline anisotropy in the CoFeB film.

Besides ferroelastic switching, the phase transition of (011) oriented PZN-PT was also utilized for non-volatile switching of magnetism\(^\text{17}\). The rhombohedral-to-orthorhombic phase transition happened under sufficient poling condition. The orthorhombic phase can also be reverted back when the electric field is removed. Liu et al. reported a bistable magnetization switching in a FeGaB/PZN-PT multiferroic heterostructure.
Figure 4.5 Hysteresis loops of E-field vs FMR frequency, measured under a bias magnetic field of 50 Oe, and E-field vs FMR field with working frequency of 12 GHz.

Figure 4.5 shows loop like FMR frequency under a bias magnetic field of 50 Oe and FMR field at 12GHz as a function of electric field. At low electric field, the linear relation between the FMR field/ FMR frequency and electric field indicates a linear piezoelectric effect in the rhombohedral phase of PZN-PT. By increasing the electric field to a critical threshold of 5.8 kV/cm, the phase transition of PZN-PT takes place from rhombohedral to orthorhombic with a large lattice change which may lead to a giant magnetoelctric coupling. This induced a dramatic and sudden change of the FMR field and FMR frequency. At high field, FMR field and frequency saturate with little strain variation. When the electric field decreased from 8kV/cm, the orthorhombic phase and
strain state kept unchanged until the electric field was lower than another critical field of 3 kV/cm. This also induced a large change of the magnetism.

Figure 4.6 E-field-impulse-induced dynamic memory-type of magnetization switching.

Figure 4.6 shows the dynamic voltage-impulse-induced nonvolatile memory-type magnetization switching in FeGaB/PZN-PT heterostructure. In order to induce a phase transition in PZN-PT, an electric field bias of 5 kV/cm is maintained. When an electric field impulse of 3 kV/cm is applied, the magnetization of FeGaB increased and remains at a high magnetization ration of 95%. The magnetization can be switched back to low magnetization ratio of 35% by applying an electric field impulse of 7 kV/cm.
4.2. Experiment

Multiferroic heterostructures of FeGaB/PZT were prepared by magnetron-sputtering. 15 nm thick Permalloy (Ni$_{80}$Fe$_{20}$) film and 100nm thick FeGaB film were sequentially deposited onto PZT ceramic slab [10 mm(L)*2 mm(W)*0.25 mm(T)] which was pre-poled along its thickness direction, followed by 5 nm Cu for passivation. The Ni$_{80}$Fe$_{20}$ thin film was used as a seed layer to increase the magnetic softness and improve adhesion of the FeGaB thin film. The FeGaB film has a composition of Fe$_{75}$Ga$_{10}$B$_{15}$ and the deposition condition of the FeGaB film was reported elsewhere. Magnetic properties of FeGaB thin film were measured by Vibrating-Sample Magnetometer. Piezoelectric strain of PZT slab was measured by a photonic sensor.

4.3. Results and discussion

Figure 4.7 presents the electric polarization $P$ as a function of the electric field $E$ applied along the thickness direction of the PZT slab, indicating a remnant polarization of 32 $\mu$C/cm$^2$ and an electric coercive field $E_c$ of about 8 kV/cm. The curves of in-plane strain $\varepsilon$ of the PZT slab measured by cycling sinusoidal electric field $E$ with amplitude of 8 kV/cm and 16 kV/cm are also shown in Fig. 1. When $E > E_c$ (i.e., at 16 kV/cm), the whole butterfly curve was observed due to the complete ferroelectric domains switching.
On the other hand, only ferroelectric domain wall motion was induced when $E < E_c$ (i.e., at 8 kV/cm), which resulted in a strain $\varepsilon$-$E$ hysteresis loop with a large remnant strain. This $\varepsilon$-$E$ hysteresis loop generated two different strain states at $E=0$ depending on the $E$-field history at $E < E_c$, leading to bistable magnetization states in the FeGaB film through converse magnetoelectric coupling in the FeGaB/PZT heterostructures. Figure 4.8 demonstrates the magnetic hysteresis loops under positive and negative $E$-field of ±8 kV/cm measured along the length direction of the FeGaB/PZT heterostructure, respectively. The remnant magnetization ratio shows a large change from 70% to 54% when the $E$-field was varied from -8 kV/cm to 8 kV/cm; moreover, the magnetic coercive field was also found to be reduced from 15 Oe to 6 Oe, respectively.
The polarization-electric field loop of the PZT ceramics and in-plane $\varepsilon$-$E$ loops under application of $E$-field of 16kV/cm and 8kV/cm.

The $\varepsilon$-$E$ hysteretic loop with large remnant strain enables two stable strain states under zero $E$-field. More specifically, a positive $E$-field on the PZT led to a contraction in the length direction of the PZT slab through the inverse-piezoelectric effect, which resulted in a compressive strain in FeGaB thin film that led to a reduced uniaxial anisotropy along the length direction of the PZT. While a negative $E$ field would results in a tensile strain along the length of the PZT slab, and an enhanced uniaxial anisotropy of the FeGaB film along the length direction of the heterostructure. The schematic of the heterostructure was presented in Figure 4.8 inset to better understand the concept of the
bistable magnetization switching. The strain in the width direction (X direction) was very small compared to the length direction (Y direction) since the length of the PZT slab is 5 times larger than its width ($\sigma_Y \gg \sigma_X$). In that case, the total free energy that consists of the Zeeman energy, shape anisotropy, and magnetoelastic energy can be expressed as

\[
F_{\text{free}} = -\vec{H} \cdot \vec{M}_s + 2\pi M_s^2 \cos^2 \theta - \frac{3}{2} \lambda(\sigma_Y - \sigma_X) \sin^2 \theta \sin^2 \phi, \tag{4.1}
\]

where \( \theta, \phi \) are the angles defined in Figure 4.8 insert, \( \lambda \) is the in-plane magnetostriction coefficient of PZT ceramic. A compressive strain would be produced ($\sigma_y < 0$) when a positive E-field (i.e., at 8 kV/cm) was applied on the PZT slab the magnetic easy axis would be forced to rotate toward the x direction by minimizing the free energy. A large energy barrier was formed due to the remnant strain difference leading to the bistable magnetization states.
Figure 4.8 Magnetic hysteresis loops of FeGaB/PZT heterostructure measured in length direction (Y direction) under application of E-field of -8kV/cm and 8kV/cm. The inset shows the schematic of FeGaB/PZT multiferroic heterostructure.

Figure 4.9 demonstrates the magnetization ratio M/Ms as a function of E-field with the amplitude varied within -8~8kV/cm and -16~16 kV/cm. The applied E-field was generated by the sinusoidal voltage with a frequency of 0.04 Hz, and the magnetization was measured under a bias field of 3 Oe. The M-E curve was observed with the butterfly shape when E-field was larger than Ec (i.e. at 16 kV/cm); while a loop–like M-E curve was observed when the amplitude of E-field was 8kV/cm, close to Ec. In the loop-like M-E curve, the magnetization ratio was varied.
from 71% to 56% with the change of E-field from -8 kV/cm to 8 kV/cm, leading to bistable magnetization that was consistent with the magnetic hysteresis loop in Figure 4.8.

The electric field leads to a large hysteresis of in the $\varepsilon \sim E$ loop and bistable magnetization states at $E < E_c$. In comparison, further increasing E-field to 16kV/cm would completely switch the FE domain leading to the relaxation of strain in the interface and a mono state of magnetization. We can define the two magnetization states defined by different signs of E-field as ‘1’ and ‘0’ in order to understand the magnetization control process by continuous E-field. As mentioned above, a positive E-field would induce a reduced effective magnetic anisotropy along the length direction; this magnetic state is defined as ‘0’, which could be maintained when the E-field is decreased to zero. By further decreasing the applied E-field the magnetization started to increase and was stabilized at -8 kV/cm which forms another magnetic state defined as ‘1’. State ‘1’ remained unchanged when the E-field was increased from -8 kV/cm to zero as well. The whole process can be traced by following the arrow in Fig 4.9.
Voltage impulse control of magnetization would lead to further reduced energy consumption compared to continuous voltage or electric field. The voltage impulse induced magnetization control in the FeGaB/PZT multiferroic heterostructures was also measured, and the stability of the two magnetic states was tested in open circuit rather than close-loop at a fixed voltage. Figure 4.10 shows the magnetic hysteresis loops presenting this process. Firstly, magnetic state ’1’ was manipulated by increasing E-field from -8 kV/cm to zero. Then an 8 kV/cm voltage impulse with duration of about 100 ms was applied on the multiferroic heterostructure. The duration of the voltage impulse in our experiment is controlled by a relay and limited by the...
comparatively large scale of our samples. Magnetic hysteresis loop of state ‘0’ was maintained after open circuit for 30 min, which was basically the same as another magnetic hysteresis loop measured by holding the E-field at 8 kV/cm. The slight change of the magnetization can be clearly seen in enlarged area (Figure 4.10 inset). In other words, the nonvolatile reversible control of bistable magnetization can be achieved by using voltage impulses.

Figure 4.10 Magnetic hysteresis loops of FeGaB/PZT heterostructure in state ‘1’; state ‘0’ which switched by voltage impulse; and holding a E-field of 8kV/cm. Figure 4.10 inset shows the enlarged area.

In order to simulate the real memory write process, the impulse induced bistable magnetization switching was measured continuously. Figure 4.11 represents magnetization ratio
under the same bias field (i.e., 3 Oe) together with the applied voltage impulse in time-domain measurement. A positive impulse remarkably decreases the magnetization ratio from 70% to 55% which means a switch from state ‘1’ to state ‘0’. Similarly, a negative impulse then alters the state from ‘0’ to ‘1’. The two distinct states keep stable in open circuit, which is consistent with Fig. 4 and demonstrates that nonvolatile voltage impulse control of magnetization can be realized in magnetoelectric multiferroic heterostructures.

![Graph showing magnetization ratio of FeGaB/PZT heterostructure switched by voltage impulse measured in length direction with a magnetic bias field (i.e., 3 Oe) in time-domain measurement.]

**Figure 4.11** Magnetization ratio of FeGaB/PZT heterostructure switched by voltage impulse measured in length direction with a magnetic bias field (i.e., 3 Oe) in time-domain measurement.
4.4. Conclusion

In summary, we have demonstrated voltage-impulse controlled nonvolatile, reversible bistable magnetization switching in FeGaB/PZT heterostructures. Two distinct strain and magnetization states were induced by positive and negative sign of E-fields close to coercivity $E_c$, which remained stable in open circuit. The reversible and nonvolatile change of magnetization is due to the strain-induced ME coupling between FM and FE layers and the large remnant strain states in $\varepsilon$-E loop. Our results show the feasibility of strain-mediated magnetoelectric multiferroic heterostructures for application in voltage impulse writable MRAMs\(^7\).
Chapter 5: Conclusion and future plans

5.1. Conclusion from the presented work

In this work, a unique ferroelastic switching pathway in ferroelectric substrates was utilized to produce two distinct, reversible and stable lattice strain states which leads to the establish of two stable magnetization states of the ferromagnetic thin film. Voltage impulse induced reversible bistable magnetization switching in FeGaB/lead zirconate titanate (PZT) multiferroic heterostructures at room temperature was first demonstrated. Two reversible and stable voltage-impulse induced mechanical strain states were obtained in the PZT by applying an electric field impulse with its amplitude smaller than the electric coercive field, which led to reversible voltage impulse induced bistable magnetization switching.

Moreover for a laminated composite, we have measured the frequency response of DME and CME coefficients at the same bias magnetic and voltage conditions. The antiresonance frequency for DME and resonance frequency for CME, have very close but distinguishable values, showing similar variation tendency with bias magnetic and electric fields. The corresponding resonant DME and CME coefficients show similar variation tendency with bias magnetic field and voltage, but have inequivalent magnitude under the same bias magnetic and electric conditions, which is not consistent with the
case at low frequency. A new theoretical model was developed to explain the inequivalence and consistency between resonant DME and CME, showing good agreement. This work is of significance for better understanding the relationship between DME and CME by demonstrating the inequivalence and consistency of resonant DME and CME effect in laminate composites\textsuperscript{59}.

5.2. Future plans

5.2.1. Co-existence of strain and charge mediated magnetoelectric coupling for non-volatile control of magnetism

Strong magnetoelectric coupling has been demonstrated in magnetic/dielectric or magnetic/ferroelectric thin film heterostructures through a voltage controllable magnetic surface anisotropy mediated by spin polarized charge\textsuperscript{28,37-39,74-76}. Combined strain-mediated and charge-mediated magnetoelectric coupling is expected in ultra-thin magnetic film/ferroelectric slabs, which has the potential for achieving even stronger magnetoelectric coupling. For example, a multiferroic heterostructure with a magnetic semiconductor, 4nm La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}, on PZT produced a hysteretic-like M-E curve at 100 K due to a charge mediated magnetoelectric coupling\textsuperscript{74,77}; while a characteristic strain-mediated piezoelectric “butterfly” like M-E curve was observed in a heterostructure with
50 nm La$_{0.7}$Sr$_{0.3}$MnO$_3$ on PMN-PT$^{78}$. Shu et al. reported a thickness-dependent M-E behavior in Ni/BTO multiferroic heterostructures through the voltage controlled magneto-optical Kerr signal, where the charge-mediated magnetic surface anisotropy increasingly dominates over the magnetoelastic anisotropy when decreasing the thickness of Ni thin film down to 5 nm$^{41}$. It is however difficult to separate the strain mediated magnetic coupling from the charge mediated magnetic coupling in such ultra-thin magnetic films on ferroelectric substrates. This is due to the weak magnetic signal that results from the ultra-thin film; and there has been no report of the precise measurements of the strain and charge co-mediated magnetoelectric coupling.

By distinguishing the strain and surface charge magnetoelectric effect strength, the hysteretic loop like M-E curve, in which the voltage controlled switch of the magnetization corresponds to the switch of the ferroelectric polarization may be obtained. The co-existence of strain and charge mediated magnetoelectric coupling in ultra-thin magnetic/ferroelectric heterostructures could lead to non-volatile magnetoelectric devices with significantly enhanced magnetoelectric coupling.

5.2.2. MEMS magnetoelectric sensor

Strong magnetoelectric (ME) coupling has been demonstrated in magnetostrictive/piezoelectric magnetoelectric heterostructures$^{1,8,10,79-81}$, which has
enabled different novel magnetoelectric devices, including magnetoelectric sensors\textsuperscript{82-85}, spintronics\textsuperscript{32,70,86,87}, voltage tunable microwave magnetoelectric devices\textsuperscript{88-90}, etc. Exciting progress has been made recently on magnetoelectric sensors, which are highly sensitive magnetometers based on magnetic control of electrical polarization in magnetic/piezoelectric magnetoelectric heterostructures\textsuperscript{11,82,83,85}. In particular, these magnetoelectric sensors show over 1~2 orders of magnitude enhanced magnetoelectric coefficients and sensitivity when the AC excitation magnetic field frequency matches the electromechanical resonance of the laminates. A high magnetoelectric coefficient of 737 V/cm Oe at the electromechanical resonance frequency of 753 Hz was demonstrated using FeCoSiB/AlN thin film magnetoelectric heterostructures at a bias magnetic field of 6 Oe\textsuperscript{14}. An optimum DC bias magnetic field is required for magnetoelectric sensors to reach maximum magnetoelectric coupling coefficient and sensitivity, which results in additional source of noise and makes it hard for integration. Exchange bias has been most recently introduced in IrMn/FeCoSiB/AlN heterostructures to achieve magnetoelectric sensors with strong magnetoelectric coupling coefficient at zero bias magnetic field, which made possible self-biased thin film magnetoelectric sensors at the cost of a reduced magnetoelectric coupling coefficient compared to FeCoSiB/AlN bilayer\textsuperscript{14,91}.

It has been an open challenge in sensing weak DC and low frequencies AC magnetic fields. The DC magnetic field dependence of magnetoelectric coupling can be used for DC magnetic field sensing\textsuperscript{13}. However, an AC magnetic field is needed for driving the
magnetoelectric sensors at certain frequency for sensing DC magnetic field\textsuperscript{13}. The large power consumption for generating AC magnetic fields and comparatively low sensitivity make it challenging in sensing DC magnetic fields for magnetoelectric sensors. Moreover, a significant amount of recent research effort has also been devoted to increasing the sensitivity for $<$10 Hz AC fields due to the large $1/f$ noise\textsuperscript{92,93} in magnetoelectric sensors by lowering the electromechanical resonance frequency of magnetoelectric devices\textsuperscript{94,95} or reducing the equivalent magnetic noise at low frequency\textsuperscript{96}. However, further reducing the electromechanical resonance frequency of magnetoelectric sensors will lead to excessively large sensor sizes that would be impractical for real applications.

I proposed that, by miniaturized the magnetoelectric sensors size, the resonance frequency of the sensor may reach to hundreds of megahertz or even gigahertz. The high frequency resonance field and high quality factor of the sensor will decrease the $1/f$ noise and make the sensor only sensitive to the external magnetic field.
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