Strain and Charge Co-Mediated Magnetoelectric Coupling in Thin Film Multiferroic Heterostructures

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Abstract

Recently, more and more researching has been focused on multiferroic materials and devices due to the demonstrated strong magnetoelectric coupling in new multiferroic materials, artificial multiferroic heterostructures and devices with unique functionalities and superior performance characteristics. This has resulted in opportunities for us to achieve compact, fast, energy efficient and voltage tunable spintronic devices. Traditionally, in magnetic materials based magnetic random access memories (MRAM) devices, magnetization is used to store the binary information. Since the high coercivity of the ferromagnetic media requires high magnetic fields for switching the magnetic states, so it needs large amount of energy.

A spin torque technique that is used in Modern MRAM information writing processes minimizes the large energy for generating a magnetic field by passing through a spin-polarized current directly to the magnets. However, this two methods still consumes a lot of energy because of the large current or current density requirement to toggle the magnetic bits. Many papers reports that spin is controlled by the electrical field which supplies new opportunities for power efficient voltage control of magnetization in spintronic devices for magnetoeletric random use for memories (MERAM) with ultra-low energy consumption. However, state of the art multiferroic materials still make it chatting to realize non-volatile 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. Compared with charge-mediated multiferroic, the strain-mediated multiferroic system needs much higher voltage than charge-mediated, because of the thickness of ferroelectric is different. In a strain-mediated multiferroic system, the substrate is bulk materials and in a charge-mediated multiferroic system, the substrate is a thin film on dielectric material.

In this work, we study the equivalence of direct and converse magnetoelectric effects. The resonant direct and converse magnetoelectric (ME) effects have been investigated experimentally. For a strain-mediated multiferroic system, we use PIN-PMN-PT, PMN-PT as the substrate. LFO, YIG, FeGaB are used as the magnetic thin film to study the tunability. This linear piezoelectric effect in converse magnetoelectric coupling would lead to “butter-fly” like magnetization vs. electric field curve which leads to a “volatile” behavior in magnetic memory system. In a charge-mediated system, we use NiFe/PLZT/Si to study the tunability. The frequency responses of direct and converse magnetoelectric effects were measured under the same electric and
magnetic bias conditions. In this study, VSM and FMR are studies in different situation. Furthermore, we studied the low temperature fabricated multiferroic heterostructure, to find out the best solution to get the thin film by spin spray. Different PH and temperature are used. VSM and FMR were employed to measure properties of thin film. XRD and SEM were used to analyse the composition and surface.
Chapter 1. Introduction to artificial multiferroic heterostructure and ferroelectricity

1.1 Multiferroic and magnetoelectric materials

Recently, more and more research has found on multiferroic materials because of its large potential for applications in novel electronic devices. 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 could be induced due to the strong coupling interaction between two ferroic orders. 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.

There are two different kinds of magnetoelectric coupling. One is called direct magnetoelectric coupling, the other is called 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. 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\textsuperscript{16-21}.

Figure 1.1 (a) Relationship between multiferroic and magnetolectric 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 magnetolectric 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 magnetolectric coupling coefficient may
be impractical to real device applications\textsuperscript{25,26}. On the other hand, the artificial multiferroic or magnetoelectric composites formed 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.

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

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

where P denotes the electric polarization, H denotes the magnetic field, M denotes the magnetization, E denotes the electric field. Other magnetoelectric mechanisms 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$^{19,27}$; ultra-thin magnetic thin film/dielectric thin film utilizing the charge-mediated magnetoelectric effect has been realized for voltage controlled magnetic tunnel junction.$^{28-30}$
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. Due to the converse piezoelectric effect from the ferroelectric phase, an external strain can be generated. That strain transfers 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). 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. Strain mediated magnetoelectric coupling can lead to a 90° 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. 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:

$$\Delta H_{\text{eff}} = \frac{3\lambda_S \cdot Y \cdot d_{\text{eff}} \cdot E}{\mu_0 M_S}$$  \hspace{1cm} (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 tuning 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\textsuperscript{35}. 
1.2.2. Charge-mediated magnetoelectric effect

The charge mediated magnetoelectric effect was first reported by Weisheit et al. describing that the magnetocrystalline anisotropy of ultra-thin iron-platinum and iron-palladium magnetic layer can be reversibly controlled by electric field in an electrolyte\textsuperscript{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\textsuperscript{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\textsuperscript{38-40}.

In previous research, researchers found the charge mediated ME coupling strength is highly dependent on magnetic film thickness. For example, 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\textsuperscript{41}. In Co\textsubscript{20}Fe\textsubscript{80}/MgO heterostructure, magnetic surface anisotropy change decreased rapidly as Co\textsubscript{20}Fe\textsubscript{80} film thicknesses were larger than 0.5nm.\textsuperscript{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 Ni0.81Fe0.19 (NiFe)/SrTiO3 (STO) magnetic/dielectric thin film heterostructures to quantitatively determine the thickness dependence of charge mediated magnetoelectric coupling\textsuperscript{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/m3 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/m3 and surface anisotropy of 6.7 \( \mu \text{J/m}^2 \). This investigation established a significant progress for magnetic/dielectric heterostructure’s application in novel interfacial charge mediated magnetoelectric devices\textsuperscript{29,43,44}. 
1.2.3. Exchange-bias mediated magnetolectric effect

The exchange bias-mediated magnetolectric effect, in most casea, involves a anti-ferromagnetic 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}. 

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1.2.4. Strain and charge co-mediated magnetoelectric coupling

Strain and charge co-mediated magnetoelectric coupling are expected in ultra-thin ferromagnetic/ferroelectric multiferroic heterostructures, which could lead to significantly enhanced magnetoelectric coupling. The quantification of the coexistence of strain and surface charge mediated magnetoelectric coupling was demonstrated by Nan’s work. From Nan’s work, ultra-thin Ni$_{0.79}$Fe$_{0.21}$ was deposited by PVD on PMN-PT(011) interface to get the strain and surface charge mediated magnetoelectric coupling. To study the only strain ME coupling, Ni$_{0.79}$Fe$_{0.21}$/Cu/ PMN-PT was used. The NiFe/PMN-PT heterostructure showed a very high voltage induced effective magnetic field change of 375 Oe (Fig 1.3(a)) enhanced by the surface charge on the PMN-PT interface. Without the enhancement of the charge-mediated magnetoelectric effect by inserting a Cu layer at the PMN-PT interface, the electric field modification of effective magnetic field was 202 Oe(Fig 1.3(b)).
Fig 1.3 (a) FMR fields of NiFe/Cu/PMN-PT(011) and (b) NiFe/PMN-PT(011) upon applying different electric fields with the bias magnetic field applied along the in-plane [0–11] direction. Insets show schematic of NiFe/PMN-PT heterostructure (up) with strain and surface charge at the interface and NiFe/Cu/PMN-PT heterostructure with only strain at the interface(d).\textsuperscript{113}
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 magneto-electric 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 $3.8 \times 10^{-8}$ Torr.
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 2.4

![Image of the LakeShore 7407 VSM](image)

**Figure 2.3 The LakeShore 7407 VSM.**

### 2.4 Introduction to Electron Paramagnetic Resonance (EPR)

EPR is a magnetic resonance technique very similar to NMR, Nuclear Magnetic
Resonance. However, instead of measuring the nuclear transitions in our sample, we are detecting the transitions of unpaired electrons in an applied magnetic field. Like a proton, the electron has spin, which gives it a magnetic property known as a magnetic moment. The magnetic moment makes the electron behave like a tiny bar magnet similar to one you might put on your refrigerator. When we supply an external magnetic field, the paramagnetic electrons can either orient in a direction parallel or antiparallel to the direction of the magnetic field. This creates two distinct energy levels for the unpaired electrons and allows us to measure them as they are driven between the two levels. Shown as Figure 2.5:

\[ hv = g \beta B_0 \]

*Figure 2.4 the schematic of measured theory, come from the user manual*

Initially, there will be more electrons in the lower energy level (i.e., parallel to the field) than in the upper level (antiparallel). We use a fixed frequency of microwave irradiation to excite some of the electrons in the lower energy level to the upper energy level. In order for the transition to occur we must also have the external magnetic field at a specific
strength, such that the energy level separation between the lower and upper states is exactly matched by our microwave frequency. In order to achieve this condition, we sweep the external magnet's field while exposing the sample to a fixed frequency of microwave irradiation. The condition where the magnetic field and the microwave frequency are "just right" to produce an EPR resonance (or absorption) is known as the resonance condition and is described by the equation shown in the above figure. Below is a diagram of a typical EPR spectrometer. We use a Bruker E580 spectrometer to measure electron spinning resonance, Figure 2.6 shown as below.

Figure 2.5 EPR measure system, come from the user manual
Chapter 3. Voltage Control of Magnetism in FeGaB/PIN-PMN-PT Heterostructures

3.1. Introduction

Multiferroic composites with combined ferromagnetic (FM) and ferroelectric (FE) phases have attracted extensive attention due to their strong magnetoelectric (ME) coupling at room temperature. Specifically in magnetic-piezoelectric heterostructures, an electric field $E$ applied to the piezoelectric layer produces a mechanical deformation that couples to the magnetic layer, and thus induces a change in the magnetization, ferromagnetic resonance field, ferromagnetic resonance frequency, or magnetic permeability. This converse ME coupling leads to effective E-field control of magnetism such as E-field tunable magnetic hysteresis loops, E-field tunable permeability, and E-field control of ferromagnetic resonance (FMR), which exhibits promising applications in tunable radio frequency (RF) microwave devices, multiple-state memories, spintronics, and magnetic field sensors.

Recently, giant E-field-induced FMR tunability has been demonstrated in multiferroic composites using relaxor-based lead magnesium niobate–lead titanate (PMN-PT) and lead zinc niobate–lead titanate (PZN-PT) single crystals with high piezoelectric coefficients. Unlike conventional devices where magnetic fields are used for FMR tuning, the E-field tuning process is fast, and power efficient as the biasing voltages applied on single crystals involve minimal currents. Therefore, these magnetic-piezoelectric heterostructures show great potential for the next-generation of compact, lightweight, and energy-efficient RF
microwave devices. However, the E-field tunable range has been limited by the electric coercive field. For example, the largest tunability is typically achieved between -2 and 6 kV/cm for multiferroic composites based on PMN-PT and PZN-PT due to low coercive field (~2 kV/cm).9-10 Under high electric field, the devices are susceptible to failure from corona breakdown induced by bias fields. Moreover, the low temperature stability of rhombohedral phase with TRT ~75–95 °C would lead to undesirable changes in performance with temperature.

To expand the operating conditions and enhance stability of piezo-crystal-based multiferroic composites, in this work, ternary single crystals lead indium niobate–lead magnesium niobate–lead titanate (PIN-PMN-PT) are used to fabricate novel FeGaB/PIN-PMN-PT heterostructures. Large E-field tuning of FMR is demonstrated in these heterostructures, comparable to that of the composites based on PMN-PT and PZN-PT. With higher coercive field and TRT >120 °C for PIN-PMN-PT,11-15 multiferroic FeGaB/PIN-PMN-PT heterostructures can be potential candidates for high-power tunable RF/microwave devices with wider temperature operational range.

3.2 Experiment

Multiferroic composites FeGaB/PIN-PMN-PT were prepared by co-sputtering of Fe80Ga20 and B targets onto (011)-poled PIN-PMN-PT substrates with a base pressure below 1 × 10−7 Torr at room temperature. The thickness of FeGaB film is determined to be 50 nm by fitting X-ray reflectivity (XRR). 5 nm Cu was then sputtered on top of FeGaB
as a capping layer. The ferroelectric property of PIN-PMN-PT was measured by the Radiant Ferroelectric characterization system. The strain vs E curve was measured using a photonic sensor by sweeping the sinusoidal electric field. The ferromagnetic resonance (FMR) spectra were measured using an X-band electron spin resonance (ESR) spectrometer in field sweeping mode with a microwave frequency of 9.5 GHz and a power of -20 dBm. In the FMR field angular dependence measurements, the samples were taped on the sample holder with a precise angle rotator. The magnetic hysteresis loops were measured using a vibrating sample magnetometer (VSM, Lakeshore 7400). During the VSM and FMR measurements, DC electric fields were applied through the thickness direction of PIN-PMN-PT, which was coated with Au on the back as an electrode.

3.3 Results and discussion

Figure 3.1(a) shows the polarization and piezoelectric strain of (011)-oriented PIN-PMN-PT single crystals as a function of electric field. At a maximum electric field of 10 kV/cm and a frequency of 10 Hz, we measured a remanent polarization (Pr) of ~25 µC/cm² for PIN-PMN-PT, comparable to that of PMN-PT and PZT-PT.8-10 (011)-oriented PIN-PMN-PT exhibits large in-plane piezoelectric coefficients of d31 = −2000 pC/N [100] and d32 = 1200 pC/N [01-1].13-15 The in-plane biaxial strain was ~0.25% along [01-1], as shown in Fig. 3.1(b). Given that the FeGaB film is very thin compared to the PIN-PMN-PT (011) substrate, it will experience the same strain states as the PIN-PMN-PT under electric field. Therefore, large E-field-induced in-plane biaxial strain is expected within the FeGaB overlayer, allowing E-field control of ferromagnetic resonance (FMR) by strain-
mediated ME coupling.
Fig. 3.1 Polarization and piezoelectric strain of (011) oriented PIN-PMN-PT as a function of electric field, where the electric coercive field was found at ±6.7 kV/cm

Figure 3.2(a) shows the in-plane magnetic hysteresis loops of the FeGaB/PIN-PMN-PT multiferroic heterostructures along the [01-1] direction of the PIN-PMN-PT single crystal at various electric fields. At zero E-field, well-defined magnetic hysteresis loop with a small coercive field of 15 Oe was observed. When applying electric fields through the thickness direction of the PIN-PMN-PT substrate, the magnetization of FeGaB turns out to be hard to saturate. Figure 3.2(b) demonstrates the magnetization ratio M/Ms as a function of E-field at a low magnetic bias field of 5 Oe. The butterfly shape curve was observed,
and magnetization ratio was varied from 65% to 25% with the change of E-field from -6.7 kV/cm to 11 kV/cm. This is consistent with the results in Fig. 3.2(a), implying a large E-field-induced negative effective magnetic field (Heff) along [01-1] direction.

(a)
Fig. 3.2 (a) Magnetic hysteresis loops of FeGaB/PIN-PMN-PT heterostructures measured at various electric field; (b) Magnetization ratio at a low magnetic bias field (i.e., 5 Oe) as a function of E-field.
Fig. 3.3(a) Ferromagnetic resonance (FMR) spectra of FeGaB/PIN-PMN-PT at various E-field with external magnetic fields along [100] direction of PIN-PMN-PT; (b) effective magnetic field as a function of E-field.
Fig. 3. 4(a) FMR spectra of FeGaB/PIN-PMN-PT at various E-field with external magnetic fields along [01-1] direction; (b) effective magnetic field as a function of E-field for [100] and [01-1] directions.
The field-sweep ferromagnetic resonance (FMR) spectra of the FeGaB/PIN-PMN-PT multiferroic composites under different electric fields are shown in Fig. 3.3(a). A microwave cavity operating at TE102 mode and X-band (9.5 GHz) was used to perform FMR measurements of the ferromagnetic/piezoelectric multiferroic. The external bias magnetic field was applied in the FeGaB film plane along the PIN-PMN-PT [100] (Fig. 3.3(a)) or [01–1] directions (Fig. 3.4(a)), with the microwave RF field in-plane and perpendicular to the DC bias field. Clearly, strong microwave ME interaction was observed in FeGaB/PIN-PMN-PT, which resulted in a high tunable FMR field range from 891 Oe to 1033 Oe when the electric fields across the PIN-PMN-PT thickness were changed from -6.7 kV/cm to 11 kV/cm. In FeGaB/PIN-PMN-PT heterostructures, the screening charges induced by ferroelectric polarization may exist at the interface of FeGaB and PIN-PMN-PT. However, for FeGaB with a thickness of 50 nm, the interfacial charge mediated ME coupling is negligible. Thus pure strain mediated magnetoelectric coupling was controlled by the electric field applied on the PIN-PMN-PT due to the piezoelectric effect. As expected, a butterfly-like curve of the FMR effective magnetic field (H_{eff}) as a function of electric field was observed, as shown in Fig. 3.3(b), having a maximum H_{eff} tunability of 142 Oe. The effective magnetic field as a function of E-field shares a similar shape with that of the piezoelectric strain of PIN-PMN-PT which has a sudden jump at the electric coercive field of > 6.7 kV/cm. The links between the H_{eff} -E and \sigma-E curves demonstrate the control of the effective magnetic field by E-field via strain mediated mechanism.

According to Kittel equation, the in-plane FMR frequency can be expressed as:
\[ f = \gamma \sqrt{(H + H_{\text{eff}})(H + H_{\text{eff}} + 4\pi M_S)} \]  \hspace{1cm} (3.1)

where \( \gamma \) is the gyromagnetic ratio (~2.8 MHz/Oe), \( H \) is the external magnetic field, and \( 4\pi M_S \) is the magnetization of FeGaB (1.5 T). The voltage-induced effective magnetic field \( H_{\text{eff}} \) is

\[ H_{\text{eff}} = \frac{3\lambda \sigma_E}{M_S} \]  \hspace{1cm} (3.2)

in which \( \lambda \) is the magnetostriction constant of FeGaB (~70 ppm), and \( \sigma_E \) is E-field-induced biaxial stress (compressive along [100] and tensile along [01-1]). It can be concluded from Equation 3.1 and 3.2 that the FMR frequency can be shifted upward or downward, depending on whether the external magnetic fields are in the direction of in-plane [100] or [01-1] of the (011)-cut PIN-PMN-PT. As shown in Fig. 3.3(a), increased FMR fields were observed when the external magnetic field was applied along [100] direction. When the external field was along [01-1], the FMR fields were reduced, as shown in Fig. 4.4(a). The total resonance field shift was 180 Oe when the external magnetic field was applied parallel to [100] and [01-1] directions (Fig. 3.4(b)). The large FMR field shift is comparable to that of the heterostructures based on PMN-PT and PZN-PT, indicating strong mechanical coupling at the interface between FeGaB and PIN-PMN-PT, and also constitutes a simple but effective approach for achieving larger FMR tunability.

From Figs. 3.3(b) and 3.4(b) we can see that operational E-field range is -6.7 to 11 kV/cm, almost double the range for PMN-PT and PZN-PT-based multiferroic composites. Meanwhile, the FMR linewidth of the FeGaB film, which is a critical parameter for
microwave magnetic materials, stays under 120±20Oe at different electric fields. The ratio between the total tunable magnetic field and the FMR linewidth is as high as 150%, indicating an excellent figure of merit for tunable microwave devices.

3.4. Conclusion

In summary, we have demonstrated large FMR tunability through E-field induced, strain mediated ME coupling in FeGaB/PIN-PMN-PT multiferroic composites. A large effective magnetic anisotropy field change of 180 Oe was obtained, comparable to that of the composites based on PMN-PT and PZN-PT. operational E-field range is -6.7 to 11 kV/cm, almost double the range for PMN-PT and PZN-PT-based multiferroic composites. With a high phase transition temperature TRT >120 °C for PIN-PMN-PT, FeGaB/PIN-PMN-PT heterostructures have great potential for high-power tunable RF/microwave device application with wider temperature operational range.
Chapter 4. E-tuning of FMR in ultrathin NiFe/PLZT heterostructures

4.1 Introduction

Strong magnetoelectric coupling has been recently demonstrated in different magnetic/ferroelectric and magnetic/dielectric thin film heterostructures, which enables power efficient voltage control of magnetism and magnetic manipulation of electric polarization, and has gained much interest in the recent decade. Magnetoelectric spintronics and tunable RF/microwave applications have been demonstrated, including voltage tunable resonators, magnetic field sensors, tunable inductors, and tunable filters. Strain-mediated magnetoelectric coupling has been investigated in both ferromagnetic (FM) thin film/ferroelectric (FE) slab heterostructures and in FM/FE thin film heterostructures. Thin film heterostructures have the advantage of requiring a relatively lower tuning voltages (<30 V) compared to magnetoelectric heterostructures with thick FE slabs which need high tuning voltages of up to 400–600 V. However, the strain mediated magnetoelectric coupling was significantly reduced in thin film heterostructures by substrate clamping effect.

Other magnetoelectric coupling mechanisms in thin film magnetoelectric heterostructures were reported, in which ME coupling was not limited by substrate clamping effect, such as interfacial spin-polarized charge-mediated magnetoelectric coupling in magnetic/ferroelectric or magnetic/dielectric thin film heterostructures, interfacial exchange coupling in magnetic/multiferroic thin film heterostructures.
Charge-mediated magnetoelectric coupling leads to a voltage controllable interface magnetic anisotropy at the magnetic/dielectric or magnetic/ferroelectric interface, which is directly related to the spin polarized charge at the interface. Surface charge induced magnetic surface anisotropy change in Fe/BaTiO$_3$ heterostructure was estimated through density-functional calculations; giant magnetoelectric coupling behavior was experimentally demonstrated in Fe/MgO heterostructures. Other magnetic/ferroelectric multiferroics heterostructure, such as, La$_{0.8}$Sr$_{0.2}$MnO$_3$/PbZr$_{0.2}$Ti$_{0.8}$O$_3$, was studied and large ME coupling coefficient of 0.8 x 10-3 Oe cm V-1 was obtained. Spin-polarized charge mediate ME coupling was also predicted in magnetic/dielectric heterostructure like, SrRuO$_3$/SrTiO$_3$, theoretically and was realized experimentally in Fe/MgO and CoFe/MgO heterostructures. Combined voltage controlled charge-mediated magnetoelectric coupling and strain-mediated magnetoelectric coupling were also reported in Ni/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) and Ni/BaTiO$_3$ (BTO) heterostructures. Further, pure interfacial charge effect was systematically investigated in very thin FM film (<1 nm) on dielectric layer (MgO). Large voltage tunable effective magnetic anisotropy change up to 20 kJ/m3 was achieved in Fe/MgO thin film heterostructures.

In the previous research, people found that 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 loop was significantly dependent on Fe film thickness, where the maximum magnetic surface anisotropy change was obtained at spin reorientation Fe thickness. In Co$_{20}$Fe$_{80}$/MgO heterostructure, magnetic surface
anisotropy change decreased rapidly as Co$_{20}$Fe$_{80}$ film thicknesses were larger than 0.5 nm. Nevertheless, the mechanism causing charge mediated ME coupling strength dependence on magnetic film thickness is still not clear. To obtain more understanding of the charge mediated ME coupling tunability, Zhou et al has reported the tunability of charge mediated ME coupling on Ni$_{0.81}$Fe$_{0.19}$(NiFe)/STO dielectric thin film. The FMR field shift is 65Oe. However, there is not polarization-electric field loop for STO thin film, that means there is no residual electric charge at zero voltage.

To optimize the charge mediated ME coupling tunability in real applications and study the Voltage Impulse Induced Bistable Magnetization Switching, we studied the voltage dependent ferromagnetic resonance (FMR) in Ni$_{0.81}$Fe$_{0.19}$ (NiFe)/ Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT)) magnetic/dielectric thin film heterostructures to quantitatively determine the thickness dependence of charge mediated magnetoelectric coupling. Voltage induced FMR field change was carried out through charge effect induced magnetic surface anisotropy change. Large voltage induced FMR field shift of 72 Oe and magnetic surface anisotropy change of 5.6 kJ/m$^3$ were obtained in NiFe/PLZT 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. This precise quantification and further understanding of the magnetoelectric coupling in magnetic/dielectric thin film heterostructures pave the way toward their applications in compact, fast, energy efficient in voltage tunable RF/microwave devices and spintronics.
4.2 Experiment

Multilayer dielectric/magnetic thin film heterostructures Ti (20 nm)/Pt (20 nm)/
Pb(Zr0.52Ti0.48)O3 (PZT, 350 nm)/Ni0.81Fe0.19 (01nm–2.8 nm)/Cu (3 nm) with different
NiFe layer thicknesses were deposited by magnetron sputtering system on Si(111) substrate
(0.5 mm). PLZT precursor solutions (0.5 M) with various Zr/Ti ratios (Zr/Ti=52/48) were
prepared by a modified 2-methoxyethanol synthesis route. In the solutions, 8 mol% lanthanum was added to enhance the relaxor behavior and insulating property. The starting chemicals were lead acetate trihydrate, lanthanum nitrate hexahydrate, zirconium propoxide, and titanium isopropoxide. Excess lead (20 mol%) was used to compensate for the lead loss during the high temperature crystallization. Detailed solution synthesis conditions can be found in our prior report. The PLZT films were grown by spin coating the solution on PtSi substrates at 3000 rpm for 30 s. Each layer was pyrolyzed at 450 °C for 10 min before being annealed at 650 °C for 5 min. An additional annealing at 650 °C for 5 min was applied after every three layers of coating. A final crystallization anneal was performed at 650 °C for 15 min. The thickness of the PLZT films with six layers of coating was ≈690 nm, resulting in a per-coating thickness of ≈115 nm. Platinum top electrodes with a diameter of 250 μm and a thickness of 100 nm were deposited on the prepared samples through a shadow mask by electron-beam evaporation. The NiFe Films of a 200um x 200um were sputtered onto the PZT films at room temperature. 3nm Cu was deposited on each NiFe layer as the capping layer. X-ray diffraction (XRD) system with Cu Kα radiation was used to measure the chemical
lattice structure of the NiFe/PLZT multiferroic structure. Atomic Force Microscope (AFM) was used to measured PLZT surface. The magnetic properties were characterized using Electron Paramagnetic Resonance (EPR) system at X-band (9.56GHz) and magneto-optocal Kerr effect (MOKE) magnetometer, respectively. Polarization vs applied voltage (P-V) loop of PLZT was taken by the radiance ferroelectric system. There was a small DC voltage was perpendicularly applied across the PLZT film between the upper NiFe film and bottom Pt electrodes. Fig 4.2(a) shows the measurement apparatus. All these measurements were measured at room temperature.

4.3 Results and Discussion

X-ray diffraction (XRD) patterns of the PLZT films are shown in Figure 4.1(a). All the diffraction patterns show only well-crystallized polycrystalline perovskite phases, together with Si substrate, and can be well indexed by a pseudocubic structure. No other phases were detected, suggesting that neither pyrochlore phases nor interfacial reactions affected the structure. Figure 3.1(a) shows the polarization and piezoelectric strain of PLZT thin film as a function of electric field. At a maximum electric field of 300 kV/cm and a frequency of 10 Hz, we measured a remanent polarization (Pr) of ~25 µC/cm2 for PLZT. The surface of
Fig 4.1 (a) X-ray diffraction pattern of the RF sputtered STO/Pt multilayer on Si substrate; (b) P-E hysteresis loops PLZT films; (c) AFM image of PLZT surface with calibrated roughness of 1.5nm.

PLZT thin film’s roughness of ~1.5nm was measured by AFM with 2 um x 2 um scan size on the top surface of one three layers (~ 350nm-thick) PLZT films. During the sputtering time in PVD chamber, we did etch by plasma to reduce the roughness of the surface. After etching, roughness of surface is ~1nm.

Figure 4.2(a) shows the schematic of FMR measurements of a NiFe (1.2 nm)/PLZT (50 nm) multiferroic heterostructure by applying voltage from -7 V to 7 V in an X-band (9.55 GHz) EPR system. The FMR field shift as a function of applied voltage can be obtained in the inset of Fig. 4.2(b). The total FMR field shift of NiFe (1.2 nm)/PLZT (350 nm) is 70 Oe, and the FMR field shift is linearly dependent on applied voltages, where the linear relations
between interfacial charge mediated magnetoelectric coupling strength and applied voltage are also observed in previously reports. From Zhou et al reports that an angle-independent isotropic FMR field shift around 60 Oe was observed, consistent with a surface charge induced out-of-plane magnetic surface anisotropy change. The total perpendicular magnetic energy of NiFe thin film can be expressed as \(27-31:\)

\[
E_{\text{perpendicular}} = -\frac{1}{2} \mu_0 M_s^2 d + K_{s,NiFe/Cu} + K_{s,NiFe/PLZT} + \Delta K_s(V) \quad 4.1
\]

Where \(E_{\text{perpendicular}}\), \(M_s\), \(\mu_0\), and \(d\) are perpendicular anisotropy energy, saturation magnetization, permeability of free space, and magnetic film thickness, respectively. Surface anisotropy between NiFe/Cu and NiFe/PLZT interface are \(K_{s,NiFe/Cu}\) and \(K_{s,NiFe/PLZT}\), respectively, and \(\Delta K_s(V)\) is the charge induced magnetic surface anisotropy change. Figure 4.2 (a) shows the FMR of NiFe with different thickness. That was demonstrated the perpendicular magnetic energy and corresponding FMR field increases monotonically as the NiFe thickness \(d\) decreases. The total energy of NiFe film can be expressed as

\[
E_{\text{total}} = -H^*M - 2\pi M_s^2 + (K_{s,NiFe/Cu} + K_{s,NiFe/PLZT} + \Delta K_s(V))/d. \quad 4.2
\]
Fig. 4.2. (a) Schematic of the sample used for a voltage-induced FMR field change. A schematic of multilayer structure of Cu/NiFe/PLZT/Pt/Si. The magnetic field was applied perpendicular to the film plane for FMR measurements; (b) voltage dependence of the in-plane field-sweep FMR spectra of the NiFe/PLZT multiferroic heterostructure measured at 9.5 GHz. The zero cross part was enlarged to demonstrate a clear ME coupling shift at bottom left inset.
To precisely calculate the voltage induced magnetic anisotropy change, we obtained the voltage induced FMR field shift as shown in Fig. 4.4(a)(c), where the FMR field formula can be described from total energy equation (2) as:

\[
f = \gamma \sqrt{(H_{\text{res}} + H_{\text{eff}})(H_{\text{res}} + H_{\text{eff}} + 4\pi M_s')}
\]

Where \( f \), \( H_{\text{res}} \), and \( H_{\text{eff}} \) are ferromagnetic resonance frequency, ferromagnetic resonance field, and effective anisotropy field, respectively, \( \gamma \) is gyromagnetic ratio (~2.8 MHz/Oe). \( 4\pi M_s' \) is effective saturation magnetization considering the surface anisotropy

\[
4\pi M_s' = 4\pi M_s - (K_{s,\text{NiFe/Cu}} + K_{s,\text{NiFe/PLZT}} + \Delta K_s(V))/d
\]

given a fixed resonance frequency of \( f_0 \approx 9.5 \text{ GHz} \), without applied voltage, at each thickness \( d \) and measured \( H_{\text{res}} \), we can calculate \( M_s \) through Eq. (4), where \( \Delta K_s = 0 \). Figure 4.4 demonstrates the magnetization ratio \( M/M_s \) as a function of E-field at a low magnetic bias field of 5 Oe. The polarization shape curve was observed, and magnetization ratio was varied from 65% to 25% with the change of E-field from -300 kV/cm to 300 kV/cm.
Figure 4.3 (a) FMR of NiFe with different thickness (b) the relative between the thickness of NiFe and effective field.
Figure 4.4 (a) FMR of NiFe with 1.5nm thickness by applying voltage from -15V to 15V; (b) Relative between PLZT polarization and magnetic field changes; (c) FMR of NiFe with 1.5nm thickness by applying voltage from -7V to 7V; (d) Relative between PLZT polarization and magnetic field changes.
4.4 Conclusion

In summary, we have demonstrated large FMR tunability through E-field induced, charge mediated ME coupling in NiFe/PLZT multiferroic composites. A large effective magnetic anisotropy field change of 70 Oe was obtained, comparable to that of the composites based on STO and MgO operational E-field range is -300 to 300 kV/cm. With a large tunability for PLZT, NiFe/PLZT heterostructures have great potential for high-power tunable RF/microwave device application with wider temperature operational range.
Chapter 5. Low temperature fabricated multiferroics heterostructure

5.1. Introduction

Soft magnetic material operated at high frequency range have attracted much attention in RF/microwave and telecommunication industries. Ferrite materials with high permeability and high resistivity at high frequency are one of most widely used material in RF/microwave applications. Especially, thin film ferrite material gives a better performance in microwave properties due to strong demagnetization factor related to its unique geometry. Several traditional fabrication method, such as, sputtering, pulse laser deposition (PLD), molecular beam epitaxy (MBE), exist for ferrites thin film deposition. Nevertheless, all these methods are costly and require high growth temperature (>600 °C), which limit the real application of these methods in industry. The spin spray method, however, can provide spinel ferrites thin films at low temperature(<100 °C) with low cost and high deposition rate, which is compatible with substrates like plastic, organic material, RFIC and MMIC, etc. Spin spray deposited ferrite thin films established excellent microwave properties at GHz frequency under self-bias condition, and increased Snoek limit by about 1 order of magnitude than their bulk counterpart. Spin spray deposited NiZn spinel ferrite thin film is great candidate for high frequency applications regarding its high permeability, resistivity and saturation magnetization and has been used in different GHz range microwave devices like, antennas and filters. In our experiment, we reports Ni$_{0.27}$Zn$_{0.1}$Fe$_{2.63}$O$_4$ thin films, around 0.7 μm thickness, deposited by spin spray method by varying growth condition, for instance, the pH value of precursor and oxidizer, the concentration of precursor, have high
permeability in GHz range, low magnetic loss and high self-bias FMR frequency.

5.2. Experiment

Ni$_{0.27}$Zn$_{0.1}$Fe$_{2.63}$O$_4$ thin films were manufactured by spin spray process on 0.2 mm thickness commercial glass substrates. A 1 L oxidation solution containing 2 mM NaNO$_2$ and 17.5 mM CH$_3$COONa varying pH value from 8 to 12 and 1 L precursor solution mixed of NiCl$_2$, ZnCl$_2$, FeCl$_2$ by varying pH value of 2 to 5 were sprayed at 90$^\circ$C temperature spinning heated plate simultaneously. The growth rate was approximately 40 nm/min, see detailed description of the spin spray deposition process. Microstructure and composition characterization of the NiZn ferrite films were studied by x-ray diffraction (XRD) with a Cu K$_\alpha$ source ($\lambda=1.541$ Å), scanning electron microscope (SEM) and atomic force microscope (AFM). The magnetization vs applied magnetic field loops were measured using a vibrating sample magnetometer (VSM), with an external magnetic field applied in the plane of thin film. The complex permeability spectrums of the films were taken using a broad band measurement technique using a coplanar waveguide network analyzer with a bandwidth from 0.5 to 5 GHz range.

5.3. Results and discussions

A typical spinel ferrite XRD pattern is given in Fig. 51(a), showing a pure polycrystalline phase of Ni$_{0.27}$Zn$_{0.1}$Fe$_{2.63}$O$_4$ thin film. The composition of NiZn ferrite film has large permeability compared with others. The growth condition here, of this NiZn ferrite film, is
pH of precursor 4.5, pH of oxidizer 9.8, 10 ML precursor concentration. Fig. 5.1(b) shows SEM images of NiZn ferrite of same growth condition; tightly packed atoms structure with grain size of ~70 nm is confirmed. The roughness of this NiZn ferrite film is around 50 nm with zero stress patterns (cracks) and growth defects present on the surface of the NiZn films. By varying the growth conditions, like pH value of precursor and oxidizer, precursor concentration, the grain size is changing, as given by Fig. 5.1(c). Red line gives the grain size, with error bar of ~10 nm, dependence of pH value of precursor (pH (P)), fixing the pH of oxidizer (pH (O)) as 9.6 and precursor concentration of 10 ML. Largest grain size of 110 nm was obtained at pH (P) = 2.2 and at pH (P) = 3.8, the smallest grain size is achieved as 68 nm. The blue line shows the grain size varying by pH (O) with fixed pH (P) = 4.6 and precursor concentration of 10 ML. The grain size is relatively large, 125nm at pH (O) = 6.2, 105 nm at pH (O)=11.6, however, small of 70 nm at pH (O)=9.6. At last, the precursor concentration(10 ML as 1, Y axis of precursor concentration, from 0.25 to 1.2, indicates the proportion compared to 10 ML, for instance, 1.2 means precursor concentration of 12 ML) have little influence to the grain size, as shown in Fig. 1(c). Figure 5.1(d) shows the atom force microscopy (AFM) image of NiZn ferrite thin film, same growth condition with SEM image sample.

The M-H loops of NiZn ferrite films made under varying growth conditions is examined by VSM, see Fig. 5.2. As demonstrated, the M-H loops of varying pH (P), pH (O) and precursor concentration is showed in Fig. 5.2(a), (b), (c). Coercivity field (H_c), Remanence Magnetization (M_r) and Magnetization at applied magnetic field of 100 Oe dependence of
growth conditions are listed in Fig. 5.2(d) (e) (f). By changing the pH (P) from 2.3 to 5.2, at fixed pH (O) of 9.6 and precursor concentration of 10 ML, the H\textsubscript{c} is decreasing from 20 Oe to 10 Oe as pH (P) increases from 2.3 to 4.6, and then increasing from 10 Oe to 35 Oe as pH (P) goes up to 6.3. The remanence magnetization (M\textsubscript{r}) dependence of pH (P) shows the similar trend compared to H\textsubscript{c}. The relative Mr drops from 0.25 to 0.13 and then increase to 0.6 as pH (P) increase from 2.3 to 6.2. The magnetization at 100 Oe gives similar behavior as pH (P) increasing, see Fig. 5.1(d). Fig. 1(e) demonstrated H\textsubscript{c}, M\textsubscript{r} and Magnetization at 100 Oe dependence of pH (O) and precursor concentration, Fig.5. 1(f) showed these static magnetic properties dependence of precursor concentration, respectively.
Figure 5.1(a) XRD pattern of NiZn ferrite thin film pH(P)=4.6, pH(O)=9.6, precursor concentration of 10ML; (b) SEM image of NiZn ferrite thin film, pH(P)=4.6, pH(O)=9.6, precursor concentration of 10ML; (c) Grain size of NiZn ferrite film dependence of growth conditions; (d) AFM image of NiZn ferrite thin film, pH(P)=4.6, pH(O)=9.6, precursor concentration of 10ML;
Figure 5.2 (a) $M-H$ loops of varying $pH(P)$ at fixed $pH(O)$ and precursor concentration; (b) $M-H$ loops of varying $pH(O)$ at fixed $pH(P)$ and precursor concentration; (c) $M-H$ loops of varying precursor concentration at fixed $pH(P)$ and $pH(O)$; (d) $H_c$, $M_r$, Magnetization at 100Oe dependence of $pH(P)$; (e) $H_c$, $M_r$, Magnetization at 100Oe dependence of $pH(O)$; (f) $H_c$, $M_r$, Magnetization at 100Oe dependence of precursor concentration;
The FMR spectrums of NiZn film prepared by varying growth condition was investigated on Fig. 5.3(a)(b)(c). The linewidth of FMR spectrum are listed in Fig. 5.3(d), varying with growth conditions. The minimum FMR linewidth of 160 Oe is obtained at pH (P) = 4.6 and pH (O)=9.6, which is important to RF/microwave application devices. Nevertheless, the FMR linewidth changed little with varying concentration. Fig. 5.4(a) represents the permeability spectra of NiZn ferrite film fabricated at pH (P) =4.6, pH (O)=9.6 and precursor concentration of 10ML. Large initial real permeability $\mu'_r>200$ was achieved at 0.5 GHz, $\mu'_r>80$ at 1 GHz(~80 times larger than bulk NiZn ferrite) and with low loss tan$\delta_m$ ($\mu''_r/\mu'_r<0.03$ at 3-5GHz range. In Fig. 5.4(b), the initial permeability at 0.5 GHz dependence of growth condition is studied, the NiZn ferrite film with maximum $\mu'_r$ is obtained at pH (P) =4.6, pH (O) =9.6, and precursor concentration of 10ML. The highest initial permeability is optimized by varying growth condition, and further the highest resistivity is also obtained at pH (P) =4.6, pH (O) =9.6, giving the good RF/microwave property in real devices. In our experiment, static magnetic properties, $H_c$, $M_r$, and dynamic magnetic properties, FMR linewidth, permeability, are changing as growth condition significantly. The reason may be by adjusting the pH value of growth solution, the grain size of NiZn films can be easily manipulated, therefore, tuning the static/dynamic magnetic properties. As shown in Fig. 5.1(c), the grain size $d$ is decreasing from $d>100$ nm to ~70 nm as pH (P) increasing from 2.3 to 4.6, pH (O) increasing from 6.2 to 9.6. After pH (P), pH (O) increased to 6.2, 11.5 correspondingly, the grain size $d$ increase to $d>100$ nm again. Grain size of NiZn films is independent with precursor concentration basically; see Fig. 5.1(c). The trends of grain size dependence of growth condition are similar to these magnetic/microwave property of NiZn.
film, for example, the initial permeability at 0.5 GHz is largest and FMR line width is 160 Oe at NiZn film grain size of ~70nm, prepared at pH(P)=4.6 and pH(O)=9.6. Therefore, the magnetic/microwave properties of NiZn films can be optimized by controlling the growth conditions.
Figure 5.3 (a) FMR spectrums of varying pH(P) at fixed pH(O) and precursor concentration; (b) FMR spectrums of varying pH(O) at fixed pH(P) and precursor concentration; (c) FMR spectrums of varying precursor concentration at fixed pH(P) and pH(O); (d) FMR linewidth dependence of pH(P), pH(O) and precursor concentration.
Figure 5.4 (a) Permeability spectrum of NiZn thin film with pH(P)=4.6, pH(O)=9.6 and precursor concentration of 10ML; (b) Permeability at 0.5 GHz of varying pH(P), pH(O) and precursor concentration; (c) Resistivity of NiZn films at varying pH(P), pH(O) and precursor concentration;
5.4 Conclusion

Controlling the growth condition of spin spray deposited NiZn ferrite thin film, the microstructure of NiZn thin film can be achieved; therefore, the magnetic/microwave properties of NiZn films can be optimized to fit the requirement of RF/microwave devices. The real permeability of >200 at 0.5 GHz and loss of <0.03 at 3-5 GHz with FMR linewidth of 160 Oe was realized. These properties are very useful for EMI suppression and also applicable to RF/microwave devices like antennas, inductors in the GHz range.
Chapter. 6 Conclusion and future work

6.1. Conclusion

In summary, we have demonstrated large FMR tunability through E-field induced, strain mediated ME coupling in FeGaB/PIN-PMN-PT multiferroic composites. A large effective magnetic anisotropy field change of 180 Oe was obtained, comparable to that of the composites based on PMN-PT and PZN-PT. Operational E-field range is -6.7 to 11 kV/cm, almost double the range for PMN-PT and PZN-PT-based multiferroic composites. With a high phase transition temperature TRT >120 °C for PIN-PMN-PT, FeGaB/PIN-PMN-PT heterostructures have great potential for high-power tunable RF/microwave device application with wider temperature operational range. Moreover, charge mediated ME coupling in NiFe/PLZT multiferroic composites. A large effective magnetic anisotropy field change of 70 Oe was obtained, comparable to that of the composites based on STO and MgO operational E-field range is -300 to 300 kV/cm. With a large tunability for PLZT, NiFe/PLZT heterostructures have great potential for high-power tunable RF/microwave device application with wider temperature operational range.

More work was performed with multiferroics heterostructure fabricated with low temperature controlling the growth condition of spin spray deposited NiZn ferrite thin film, the microstructure of NiZn thin film can be achieved; therefore, the magnetic/microwave properties of NiZn films can be optimized to fit the requirement of RF/microwave devices.
The real permeability of >200 at 0.5 GHz and loss of <0.03 at 3-5 GHz with FMR linewidth of 160 Oe was realized. These properties are very useful for EMI suppression and also applicable to RF/microwave devices like antennas, inductors in the GHz range.

6.2. Future Plan

6.2.1. 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. 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$_{0.8}$Sr$_{0.2}$MnO$_3$, on PZT produced a hysteretic-like M-E curve at 100 K due to a charge mediated magnetoelectric coupling; 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. 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. 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.

6.2.2. Power Efficient Tunable Inductors for RFIC

Strong magnetoelectric (ME) coupling has been demonstrated in magnetostrictive/piezoelectric magnetoelectric heterostructures, which has enabled different novel magnetoelectric devices, including magnetoelectric sensors, spintronics, voltage tunable microwave magnetoelectric devices, etc. Exciting progress has been made recently on power efficient tunable inductors, which have very high quality factor and inductance with large tunability of inductance based on magnetic control of electrical polarization in magnetic/piezoelectric magnetoelectric heterostructures. MEMS tunable inductors were reported\textsuperscript{104-112}. Tunable inductors are classified into two main groups:
discrete type and continuous type. Each of these groups is itself classified into other types based on tuning mechanism, actuation mechanism and so on. The discrete type tunable inductors are those whose inductance changes digitally employing series-parallel inductors concept, magnetic coupling coefficient concept, and CPW lines concept. The continuous type tunable inductors work based on continuously inductance changing and categorized into different types such as core properties changing concept, mutual inductance based inductors, store magnetic energy based inductors, and so on. Some properties of tunable inductors such as quality factor, tuning range, actuation voltage, etc. are investigated. Large tuning range are very difficult to reach. I propose that, by using magnetioelectric coupling, the tuning of inductor can be easily to control by applying electrical field.
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