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MAGNETIC THIN FILM CHARACTERIZATION

BY SPIN SPRAY PROCESS

A Thesis Presented

by

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Electronic Circuits, Semiconductor Devices and Microfabrication

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Abstract

An improvement on the fabrication of magnetic thin films is currently on a level of intense research as these films are of great interest in the device industry. Some of these thin films possess high permeability and ferromagnetic resonance (FMR) frequency in the GHz range which are suitable for electromagnetic use. Methods for fabricating these films include sputtering, pulse laser deposition (PLD), sol-gel, molecular beam epitaxy (MBE) and spin spray process.

Spin spray process is a ferrite plating process which involves the direct deposition of ferrite film from aqueous solution at temperature less than 100°C. An interest in the spin spray process is due to the fact that fabrication is done at low temperature (which enables the plating of non heat resistance materials) and no vacuum (which decreases the cost of production unlike the other conventional methods).

In this research, different types of magnetic thin films were fabricated using the spin spray process. A study into the processing conditions and substrate effect on the films was carried out. Also, characterization of these thin films and their implementations in the device industry was successfully carried out.
Acknowledgment

I would like to express my sincere gratitude and appreciation to my advisor Professor Nian X. Sun for his guidance, encouragement and total commitment throughout this research. I am grateful for the level of trust he demonstrate towards me. I would also like to thank Professor Vincent G. Harris and Professor Katherine S. Ziemer for agreeing to be on my thesis committee.

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Chapter 1

INTRODUCTION

1.1 Fabrication of Magnetic Thin Films

Various conventional techniques exist for the fabrication of thin films. These include pulse laser deposition PLD; a physical vapor deposition method which involves direct thin film deposition by the vaporization of a solid target with the use of high energy laser pulses in an ultra high vacuum chamber in the presence of a gas, sputter deposition; also a physical vapor deposition high vacuum process where ejected atoms or molecules from the surface of a solid target caused by plasma bombardment condenses to form thin film on the desired substrate, molecular beam epitaxy MBE; a slow growth process where the interaction of one or several atomic beams on the surface of a heated crystal in ultra high vacuum, leads to the epitaxial growth of films on the substrate, sol gel process; where annealing at high temperatures is required for film crystallization, etc. [1]-[5], [18], [19].

Since these conventional techniques involve the use of high temperature (above 500°C) and/or pressure, vacuum chambers or lasers for film growth and crystallization, they have a high cost of production and also can not be used on non heat resistant substrates like plastics and organic materials [1].

Spin spray processes however, is a low temperature (<100°C), no vacuum ferrite plating method that can produce thin films with properties comparable to bulk films. The basic principle of this ferrite plating method employs the oxidation of Fe^{2+} to Fe^{3+}. Spin spray process was invented in 1983 and has already been used to produce thin film spinel ferrites with amazing properties like high resistivity and permeability in the GHz range.
for wave absorbers, improve performance of patch antennas and inductors. Spin spray process can also be used for low temperature multiferroic composite materials on ferroelectric substrates with good magnetoelastic (ME) coupling. This is currently of interest in the spintronics industry [7].

1.2 Motivation

Currently, magnetic thin films are of great interest in the device industry as they can be used for electromagnetic means in enhancing the performance of microwave devices like patch antennas and inductors. Ways to improve the fabrication process of these thin films and also increase their practical applications is highly desired. Spin spray process as an alternative method is being investigated. It uses low temperature and no vacuum for film production and thus can increase the range of substrates and practical applications for these thin films. Also, its cost of production is a lot less than that of the other conventional method like PLD MBE etc. Therefore, there is a need to carefully investigate magnetic thin films produced by spin spray process and optimize process conditions involved in this ferrite plating method in order to produce high quality films with strong adhesion properties. This research deals with this need.
1.3 Objective

This study is an intense research on how to optimize the process conditions of magnetic thin film fabrication using spin spray process and thus produce strong adhesion films with good magnetic properties comparable to bulk films. The intention of this investigation is to develop magnetic thin films that will be used in microwave devices like patch antennas and inductors and also produce multiferroic composites materials on ferroelectric substrates with strong ME coupling which is of interest in the spintronics industry.

1.4 Thesis Outline

The thesis will be divided into six (6) chapters. Following Chapter 1, Chapter 2 contains a background research on spin spray process and materials that are currently being made. Chapter 3 outlines the experimental procedures for magnetic thin film fabrication using spin spray process. In Chapter 4 results, obtained including the magnetic hysteresis, SEM (scanning electron microscope) image, AFM (atomic force microscope) image, FMR and relative permeability results etc. will be discussed and analyzed. In Chapter 5, the implementation of these films will be reviewed. Finally, Chapter 6 concludes with a summary of achievements.
Chapter 2

BACKGROUND RESEARCH

2.1 Ferrite Plating Process

Ferrite plating was invented in 1983 by Masanori Abe and Yutaka Tamaura [9]. It is an electroless type of plating that involves the direct deposition of ferrite from an aqueous solution at low temperature, usually below 100°C, unto a substrate. Since it’s a low temperature process, metals as well as non-heat resistant materials like organic materials and plastics can be used as substrates [1], [8].

The principle of ferrite plating involves;

- Absorption of the Fe\(^{2+}\) and Mn\(^{n+}\) (Fe, Mn, Zn, Ni, Co etc) ions on the surface of the substrate brought about by the OH\(^-\) group on the substrate.

- Oxidation of some of the Fe\(^{2+}\) to Fe\(^{3+}\) ion by an oxidizing agent (e.g. NaNO\(_3\), O\(_2\) etc). The chemical equation for this reaction can be expressed as;

\[
Fe^{2+} \rightarrow Fe^{3+} + e^- \]

(2.1)

- Re-absorption of the Fe\(^{2+}\) and Mn\(^{n+}\) ions on the surface of the substrate with the layered pre-absorbed ions Fe\(^{2+}\) and Mn\(^{n+}\) and Fe\(^{3+}\) ion. This leads to the ferrite layer formation. This process is accompanied by the hydrolytic dissolution with the release of H\(^+\) and can be expressed by the equation;
\[ xFe^{2+} + yFe^{3+} + zM^{n+} + 4H_2O \rightarrow (Fe^{2+}, Fe^{3+}, M^{n+})_3O_4 + 8H^+ \] (2.2)

\[ x + y + z = 1 \]

\[ 2x + 3y + nz = 8 \]

This entire process is repeated and the ferrite thickness is increased since the OH\(^-\) group is still on the surface of the substrate [1], [8]. The schematic for the ferrite plating principle is shown below:

![Figure 2.1: Principle of Ferrite Plating [1]](image-url)
There are different types of ferrite plating, these include;

A. Reactor Ferrite Plating
B. Ultrasound Enhanced Ferrite Plating
C. Inner/Outer Wall Ferrite Plating
D. Thin-Liquid Film (laser enhanced) Ferrite Plating
E. Spin Spray Ferrite Plating

Ferrite plating process so far can only be used for the fabrication of crystalline spinel ferrites.

2.2 Spin Spray Process

The spin spray process consists of two solutions, reaction/precursor and oxidizing solution, simultaneously sprayed unto a spinning substrate on a heating table in the presence of nitrogen gas [1], [10]-[13].

The reaction solution is composed of FeCl₂ and MCl₂ (Where M is a metal ion like Zn, Co, Mn, Ni, etc) while the oxidizing solution is a mixture of a buffer (an acetate, e.g. CH₃COONa, CH₃COOK, CH₃COONH₄) and an oxidant (NaNO₃). Temperature range is between 70-90°C, and speed of rotation of the plates, between 120-200rpm for high quality films. A schematic layout for the spin spray process is shown below as well as a picture of an actual spin spray set up.
Figure 2.2: Schematics of Spin Spray Set up
Figure 2.3: Picture of a Spin Spray Apparatus
2.3 Magnetic Thin Films by Spin Spray Process

Several spinel ferrites have been fabricated using spin spray process. Some of these materials and their properties include;

2.3.1. Nickel Zinc (Ni-Zn) Ferrite Thin Films

Polycrystalline Ni-Zn ferrite thin films with various compositions have been studied and fabricated over the years. These fabricated films have been found to have well defined spinel structures. Coercivity as low as 15Oe and ferromagnetic resonance (FMR) frequency as high as 1.2GHz have been reported. Also, large saturation magnetization (Ms) greater than 400 emu/cc was observed [14]-[17]. Magnetic resonance was observed in the frequency spectra of initial permeability and thus gave the film a high potential as thin film electromagnetic noise absorber which is useful for integrated circuits and microwave devices working in the GHz range [20].

2.3.2. Nickel Zinc Cobalt (Ni-Zn-Co) Ferrite Thin Films

Magnetically isotropic Ni-Zn-Co ferrite thin films with low magnetic losses even at 900MHz have been fabricated. These films were reported to have high real permeability (µ’) greater than that of bulk films and low imaginary permeability (µ’’) with Tan[δ](.0.4) much lower than that for composite type magnetic sheets (Tan[δ] = µ’/ µ’’).[21], [22]. Some of these results can be seen in table 2.1 below.
Table 2.1: Chemical composition, thickness $t$, saturation magnetization $M_s$, anisotropy field $H_k$, real permeability $\mu'$, and natural resonance frequency for the films [21].

<table>
<thead>
<tr>
<th>Composition</th>
<th>$t$ (μm)</th>
<th>$M_s$ (emu/cc)</th>
<th>$H_k$ (Oe)</th>
<th>$\mu'$</th>
<th>$f_r$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 $\text{Ni}<em>{0.24}\text{Zn}</em>{0.47}\text{Fe}<em>{2.16}\text{Co}</em>{0.13}\text{O}_4$</td>
<td>1.1</td>
<td>340</td>
<td>85</td>
<td>20</td>
<td>650</td>
</tr>
<tr>
<td>#2 $\text{Ni}<em>{0.22}\text{Zn}</em>{0.53}\text{Fe}<em>{2.09}\text{Co}</em>{0.16}\text{O}_4$</td>
<td>1.5</td>
<td>320</td>
<td>160</td>
<td>20</td>
<td>900</td>
</tr>
<tr>
<td>#3 $\text{Ni}<em>{0.24}\text{Zn}</em>{0.43}\text{Fe}<em>{2.15}\text{Co}</em>{0.18}\text{O}_4$</td>
<td>1.0</td>
<td>360</td>
<td>135</td>
<td>10</td>
<td>1100</td>
</tr>
<tr>
<td>#4 $\text{Ni}<em>{0.23}\text{Zn}</em>{0.34}\text{Fe}<em>{2.20}\text{Co}</em>{0.23}\text{O}_4$</td>
<td>1.0</td>
<td>390</td>
<td>190</td>
<td>7</td>
<td>3300</td>
</tr>
<tr>
<td>#5 $\text{Ni}<em>{0.23}\text{Fe}</em>{2.50}\text{Co}_{0.27}\text{O}_4$</td>
<td>1.3</td>
<td>420</td>
<td>650</td>
<td>8</td>
<td>5400</td>
</tr>
</tbody>
</table>

Ni-Zn-Co ferrite thin films can be used as a shielding material against electromagnetic interference for RFID (900MHz or 2.45GHz).

### 2.3.3. **Manganese Zinc (Mn-Zn) Ferrite Thin Films**

The following properties for Mn-Zn ferrite thin films have been reported. Theses include;

I. High permeability in GHz range

II. Film resistivity, $\rho>10^4\,\Omega$ which increased as the amount of Fe content decreased

III. High surface resistance $R>108\,\Omega$/sq for film having Fe content $<2.6$

IV. Large $M_s$ (380-460 emu/cc)

V. Low coercivity (Hc=11-29 Oe)

VI. Very large transmission loss per thickness (as a microstrip), about 10 times larger that that of the commercialized composite sheets.
VII. Sufficiently low reflection coefficient $S11<-10\text{dB}$

VIII. FMR frequency of $300\text{MHz}$

Mn-Zn ferrite thin films can be used as noise suppressors for multilayered printed circuit boards [23].

### 2.4 Advancement in Spin Spray Process

In 2006, the “one liquid” spin spray process was put forward [24]. This process involved the use of only one aqueous solution which composed of dextran+$\text{FeCl}_2$+$\text{CH}_3\text{COOK}$ $+$NaNO$_2$. Dextran ($\text{C}_6\text{H}_{12}\text{O}_6)_n$, $n = 1100$-$1700$ was used to suppress iron hydroxides from precipitating in the solution. The set up for this process is as shown below;

![Figure 2. 4: Schematic of ‘one liquid’ Spin Spray set up [24]](image-url)
Single phased Fe$_3$O$_{4+\delta}$ thin film with spinel structure was successfully fabricated using the “one liquid” spin spray process. The following properties were reported:

- $M_s=403 \text{ emu/cc}$
- $H_c=53 \text{ Oe}$
- $F_r=0.9 \text{ GHz}$
- $\mu'=26 (@50\text{MHz})$
- Thickness, $t=1.6 \mu\text{m}$
- $S11<-10\text{dB}$
- Arithmetic mean roughness, $Ra=49 \text{ nm}$ in a 5x5 $\mu\text{m}^2$ range

So far, only Fe$_3$O$_{4+\delta}$ thin film have been fabricated using the “one liquid” spin spray method.
Chapter 3

EXPERIMENTAL PROCEDURE AND INSRUMENTATION

3.1 Experimental Procedure

Initial absorption of the ferrite ions (Fe$^{2+}$ and Mn$^{2+}$ (Fe, Mn, Zn, Ni, Co etc)) by the surface of the substrate is brought about by the presence of OH group on the surface. This means that the substrate has to undergo treatment before the spin spray process can be done. Substrates used for this experiment included glass, alumina, High-K materials, PZT, PMNPT etc. A schematic of the spin spray procedure is shown in Figure 3.1 below.

The substrates were thoroughly cleaned with acetone and alcohol in an ultra sonic and immersed into a seeding solution comprising of dil HCl + Fe$^{2+}$. The seeding solution is important for the deposition of OH group and the initial Fe$^{2+}$ ion on the surface of the substrate for easy absorption of the ferrite ions by the surface during film fabrication.

The oxidizing solution was a mixture of sodium nitrite (NaNO$_2$-oxidant) and sodium acetate (CH$_3$COONa-pH buffer) in the ratio of 2:140 while the precursor solution contained the Fe$^{2+}$ and Mn$^{2+}$ (Fe, Mn, Zn, Ni, Co etc) ions in the form of chlorides, that is, FeCl$_2$+MCl. The pH of the oxidizing solution was 7-11 and that of the precursor was 3-6.

The substrates were mounted on the spinning table as shown in Figure 3.1 below. Different spin spray conditions (pH of oxidizing and precursor solution, temperature and speed of the spin spray unit) were investigated.

After the fabrication process, the substrates (with the thin films) were washed with distilled water and dried.
Figure 3.1: Schematic of procedure involved in the spin spray process
3.1.1 Variation of Parameters

The properties of the magnetic thin film also depend on the condition of the spin spray system as well as the PH values and concentration of the precursor and oxidizing solutions. Experiments were conducted to optimize the process condition for the fabrication of these films. The results of these experiments are included in this thesis.

Parameters varied included;

- Temperature of the operating system
- PH of the oxidizing solution
- PH of the precursor solution
- Speed of rotation of the operating system

3.2 Instrumentation

After film fabrication, different measurements were done on the films to determine their properties. These measurements included;

3.2.1 Magnetic Hysteresis Measurement.

Magnetic hysteresis measurement was obtained with the use of a VSM (Vibrating Sample Magnetometer). The VSM employs an electromagnet which provides the magnetizing field (DC), a vibrator mechanism to vibrate the sample in the magnetic field, and detection coils which generate the signal voltage due to the changing flux emanating from the vibrating sample. The output measurement displays the magnetic moment M as a function of the field H [25].
3.2.2 FMR Measurements

The FMR linewidth and FMR frequency/permeability spectra were obtained using X-band and CPW (Coplanar Waveguide) respectively.

A. FMR Frequency/Permeability Spectra Measurement [26]

The permeability measurement was done with a CPW (Coplanar waveguide) permeater, the set up include a network analyzer with operating frequency from 500 MHz to 10 GHz, which was used to measure the S-parameters (S\(_{11}\) reflection and S\(_{21}\) transmission coefficients.) of the CPW with the ferrite film overlaying it.

Magnetic field was applied to saturate the film, and S\(_{11}^0\) and S\(_{21}^0\) were measured by the network analyzer. The desired magnetic field was applied to the film and S\(_{11}^1\) and S\(_{21}^1\) were obtained. S\(_{11}^0\) and S\(_{21}^0\) contain non-magnetic properties of the circuit while S\(_{11}^1\) and S\(_{21}^1\) contain both magnetic and non-magnetic properties of the film.

The relative permeability can be obtained with the formula below:

\[
\mu = \frac{Z_0 \frac{1 + s_{11}^1 - s_{21}^1}{1 - s_{11}^1} - \frac{1 + s_{11}^0 - s_{21}^0}{1 - s_{11}^0}}{iclt\mu_0\omega} \text{  ................................................3.0}
\]

Where:

Z\(_0\): characteristic impedance of the CPW

c: geometry factor – determined by measuring a standard sample with known \(\mu\) and identical sample geometry to the ferrite film. (thickness, length etc.)

l: length of the film
\( \mu_0 \): Permeability of vacuum

t: thickness of the film

\( \omega \): microwave angular frequency.

**B. FMR Linewidth Measurement**

The FMR Linewidth measurement was done using an Electron Paramagnetic Resonance (EPR) spectrometer at X band frequency (9-10GHz). Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR) and electron magnetic resonance (EMR), is the name given to the process of resonant absorption of microwave radiation by paramagnetic ions or molecules, with at least one unpaired electron spin, and in the presence of a static magnetic field [27].

**3.2.3 Image Results**

Image results were obtained using Atomic Force Microscope (AFM), which can image almost any type of surface and Scanning Electron Microscope (SEM) technique (which scans the films with a focus beam of electrons and produce secondary electrons that are detected and converted into images).

**3.2.4 Magnetostriction Measurements**

Magnetostriction measurements were obtained using a precision materials analyzer (a piezoelectric unit/ magnetostriction tester).
3.2.5 Composition Analysis

Composition analysis of the films was obtained using Energy Dispersive Spectroscopy (SEM-EDS) and the structure using X-Ray Diffractometer.

SEM-EDS provide a qualitative composition analysis. It involves the use of a stream of high-energy electrons to knock off specimen’s inner shell electrons. On contact, electrons from a higher energy level lose energy filling in the vacancies left (the energy conservation principle dictates photon creation). The released photon energy will be equal to the difference of the two exchanged energy levels. Since these energy levels are unique for an atom type, the released photon will be characteristic of the type of atom from which it was emitted. Therefore, from the released photon energy, the sample composition is determined. SEM-EDS analyses a spot size of about 1µm [28].

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter (ranging from fluids, to powders and crystals). A diffraction pattern records the X-ray intensity as a function of 2-theta angle, the diffraction angle in degrees (from the Bragg’s law). Once started, the goniometer moves through its range, stopping at each step for the allotted time. The X-ray counts at each step are saved to a file on the computer. Once finished, the data are smoothed with a weighted moving average and a diffractogram.

3.2.6 Thickness Measurement

Thickness measurements were done with the use of a profilometer.
RESULTS AND DISCUSSION

4.1. Magnetic Hysteresis

Well defined magnetic hysteresis loops were observed for the inplane (parallel direction) and outplane (perpendicular direction) of the magnetic thin films when an external field was applied to them. There was a huge difference in the inplane and outplane loops showing anisotropy magnetization in the film plane. Also, the coercivity of the inplane was smaller than that of the outplane, which implies that the uniaxial anisotropy was induced in the film plane with the easy axis parallel to the inplane direction. This can be seen in Fig. 4.1 for nickel cobalt ferrite (NCFO) and nickel zinc ferrite (NZFO). A summary of the coercivity, saturation magnetization and anisotropy field for some of our ferrite films is shown in table 4.1.

![Graph of Normalised Moment vs Field(Oe) for Inplane and Outplane](a)
Figure 4.1: Magnetic hysteresis loops of (a) NCFO on alumina and (b) NZFO on alumina

<table>
<thead>
<tr>
<th>Ferrite</th>
<th>Substrate</th>
<th>$4\pi M_s$ (Gauss)</th>
<th>Coercivity (Oe)</th>
<th>Anisotropy Field (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.25}$Co$</em>{0.13}$Fe$_{2.64}$O$_4$</td>
<td>Alumina</td>
<td>4700</td>
<td>165.31</td>
<td>540</td>
</tr>
<tr>
<td>Ni$<em>{0.27}$Zn$</em>{0.54}$Fe$_{1.45}$O$_4$</td>
<td>Alumina</td>
<td>4500</td>
<td>9.5</td>
<td>180</td>
</tr>
<tr>
<td>Co$<em>{0.79}$Fe$</em>{3.15}$O$_4$</td>
<td>Alumina</td>
<td>5600</td>
<td>357.32</td>
<td>1398.96</td>
</tr>
<tr>
<td>Ni$<em>{0.23}$Fe$</em>{2.77}$O$_4$</td>
<td>Alumina</td>
<td>3080</td>
<td>190</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of parameters from the magnetic hysteresis loops of some of our ferrites
4.2. FMR Measurement

The FMR Linewidth measurement was done using an Electron Paramagnetic Resonance (EPR) spectrometer at X band frequency (9-10GHz). Most of our ferrite thin films showed single phased FMR linewidth with the narrowest inplane linewidth being 170 (Oe), observed from ZnFO (on glass substrate) and 167 (Oe) outplane linewidth from NZFO (on glass substrate). Fig. 4.2 shows the graph of the FMR linewidth from ZnFO on glass substrate. Table 4.2 summarizes the FMR linewidth obtained for some of our ferrite films.
Figure 4.2: FMR linewidth measurement of ZnFO on glass (a) Inplane and (b) Outplane

<table>
<thead>
<tr>
<th>Ferrite/Glass</th>
<th>$\Delta H$ Inplane (Oe)</th>
<th>$\Delta H$ Outplane (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFO</td>
<td>170</td>
<td>310</td>
</tr>
<tr>
<td>MnFO</td>
<td>210</td>
<td>1000</td>
</tr>
<tr>
<td>NZFO</td>
<td>308</td>
<td>167</td>
</tr>
<tr>
<td>Fe3O4</td>
<td>470</td>
<td>540</td>
</tr>
</tbody>
</table>

Table 4.2: Measured FMR Linewidth data for some of our ferrites
4.3. Permeability Spectra

We could only obtain the permeability spectra for NZFO sample. This may be due to size of the FMR linewidth, which indicates that the spectra may be too broad.

Fig. 4.3(a) shows the permeability spectra of NZFO at 60 Oe. The FMR frequency at 60 Oe is GHz. The FMR frequency at 0 Oe can be with the formula

\[ F_{\text{FMR}} = \gamma \sqrt{(H_k + H_a) \cdot (4\pi M_s + H_k + H_a)} \]

Where
\[ \gamma \text{ is the gyromagnetic ratio } = 2.8 \text{MHz/Oe}, \]
\[ H_k \text{ = anisotropy field } = 180 \text{Oe}, \]
\[ H_a = \text{ applied field } = 0 \text{Oe} \]
\[ 4\pi M_s = \text{ saturation magnetization } = 4500 \text{ Oe} \]

Therefore, the FMR frequency is 2.56GHz for this particular sample.

Fig. 4.3 (b) is the permeability spectra of another NZFO sample at 200Oe.
\[ \gamma \text{ is the gyromagnetic ratio } = 2.8 \text{MHz/Oe}, \]
\[ H_k = \text{ anisotropy field } = 300 \text{Oe}, \]
\[ H_a = \text{ applied field } = 0 \text{Oe} \]
\[ 4\pi M_s = \text{ saturation magnetization } = 2500 \text{ Oe} \]

From equation 4.1, FMR frequency was calculated and found to be 2.57GHz at 0 Oe which is the same as for the sample above.
Figure 4.3: Permeability spectra of NZFO at (a) 60 Oe and (b) 200 Oe
4.4. AFM Results

The Atomic Force Microscope (AFM) images of the film surface showed uniform closely packed atomic structures with grain size of about 0.5 µm for NCFO on alumina substrate and 0.8 µm. These can be seen in Fig. 4.4 and Fig. 4.5 respectively.
Figure 4.4: Atomic Force Microscope (AFM) image of NCFO on alumina (a) top view, (b) angular view and (c) higher magnification of the angular view.
Figure 4. 5: Atomic Force Microscope (AFM) image of NZFO on alumina (a) top view, (b) angular view and (c) higher magnification of the angular view.
4.5. SEM Results

Scanning Electron Microscope (SEM) technique was used to obtain the surface image of our ferrite thin films. This is shown in Fig. 4.6 and 4.7 for NCFO and NZFO.

From Fig. 4.7 (b), stress pattern (crack) can be seen across the surface of the film + substrate. This may be due to the stress imposed on the PZT substrate during the fabrication of the thin film, that is, the sudden rise of temperature and rapid cooling effect.
Figure 4. 6: SEM Results of NCFO on alumina (a) top view and (b) higher magnification of top view
4.6. Magnetostriction Measurements

As seen from Fig. 4.8, the magnetostriction constant increased with the applied in-plane magnetic field. The maximum saturation magnetostriction constant observed was $-10$ ppm at 250Oe which is smaller than the saturation magnetostriction constant of pure NFO phase. This may be due to the limited magnetic field strength of our magnetostriction test system (250 Oe) or the fact that NFO was not saturated at 250Oe.
Crystallographic structures of these magnetic thin films were obtained by X-Ray Diffractometer (XRD). For most of the ferrite films, pure phases of the ferrites were clearly identified from the XRD spectrum although no preferential crystallographic orientation was observed. The XRD spectrum of NCFO is shown in Fig. 4.9 below.
4.8. Variation of Process Conditions

In order to obtain optimum fabrication conditions, we varied the process conditions one at a time. Below are the results that were observed.
Substrate Variation

Due to the structural difference on substrates, we observed that different substrates enabled same ferrites to have different properties. Keeping all other conditions constant, ferrite thin films were fabricated on different substrates, and their magnetic properties, measured. As seen in Fig. 4.10, CFO and NCFO both had different values of coercivity on glass, alumina, STO (strontium titanate) and PZT (lead zirconium titanate).

Figure 4.10: Plot to show coercivity changes observed in CFO and NCFO on different substrates.
➢ Precursor PH Variation

Keeping all other conditions constant, the PH value of the precursor solution was varied. We observed that PH lower than 5.0 produced ferrite films that were harder than for PH higher than 5.0 (except for 3.32 which was the same as 5.02) as seen from Fig. 4.11. Although no relationship was deduced between the hardness of the ferrite and the change of the PH value, we can conclude that the best PH for the precursor solution was 5.02 or 3.32.

(a)
Figure 4.11: Magnetic hysteresis loops of NZFO with varying precursor PH (a)

Inplane and (b) Outplane

➢ **Buffer PH Variation**

Keeping all other conditions constant, the PH value of the buffer solution was varied. We observed that apart from the film with a PH of 9.01, all other ferrites were not fully saturated 10KOe. This is shown in Fig. 4.12 below.
Figure 4.12: Magnetic hysteresis loops of NZFO with varying buffer PH (a) Inplane
and (b) Outplane
Temperature Variation

Keeping all other conditions constant, the fabrication temperature of the spin spray system was varied during film fabrication. We observed that the temperature parameter was one of the most important as it produced a huge variation in the magnetic hysteresis loop. From Fig. 4.12, it can be seen that for 70°C, the NZFO was hardest and 90°C was softest. Also, samples NS1, 4, 5 and 6 were not fully saturated at 10KOe.
Figure 4. 13: Magnetic hysteresis loops of NZFO with varying temperature (in °C)

(a) Inplane and (b) Outplane

Conclusively, we obtained optimum ferrite thin film fabrication by spin spray with process conditions as summarized below.

<table>
<thead>
<tr>
<th>PH of Precursor</th>
<th>PH of Buffer</th>
<th>Temperate (°C)</th>
<th>Speed of Rotation (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.02/3.32</td>
<td>9.0</td>
<td>90</td>
<td>140-150</td>
</tr>
</tbody>
</table>

Table 4. 3: Summary of optimum process condition for spin spray system
Chapter 5

IMPLEMENTATION

5.1. Miniaturized Bandpass Filter with Self-Biased Magnetic Films [31]

With the continuous growth of wireless communication technologies, design and manufacturing of miniaturized microwave components are among the most critical issues in communication systems. As a very important component in the RF front, bandpass filter with small size and high performance is growing vastly in most wireless communication systems. As a widely used type of microwave filter, the hairpin bandpass filter is known for its features like wideband, low loss and compact structure. However, at the low frequency of microwave band, the dimensions of a conventional hairpin bandpass filter are usually too large to satisfy the recent small size requirements. Conventional design theory and circuitry of microwave filters are meeting new and exciting challenges in realizing unprecedented demands and applications.

The combined high permeability and permittivity of magnetic film materials provide a great opportunity for achieving miniaturized microwave components, such as antennas and filters, etc. In order to be practically feasible in miniature microwave circuit applications, such as handheld wireless communication devices, it is important for the circuit substrates to be comprised of self-biased magnetic materials, in which no external bias field is applied. However, it has been challenging achieving self-biased magnetic materials for microwave circuit substrate applications in the GHz frequency range.
We introduce a novel miniaturized bandpass filter operating at 1.575 GHz with low insertion loss and simple planar geometry that makes it compatible with the existing microwave integrated circuit. Miniaturization is achieved by loading a commercially available substrate with self-biased magnetic films. One order Chebyshev hairpin bandpass filter was designed with the central working frequency is 1.575GHz. Self-biased magnetic film, which the relative permittivity is 13 and relative permeability is 10 with zero loss tangent, was adopted in the simulations.

### 5.1.1. Design of Bandpass Filter

Fig. 5.1 (a) and (b) show the layout of top view and side view of the hairpin bandpass filter. This bandpass filter consists of a U-shaped quarter-wave resonator and two quarter-wave resonators with tapped-line input and output. All these resonators and tapped-line are realized by patterned copper cladding on the top surface of the underlying dielectric substrate. The width of the quarter-wave resonator is 0.23mm and the length is 18.1mm as we adopted Rogers R3010 as the substrate in both simulations and fabrications, which has a relative permittivity of 10.2 and a thickness of 1.28mm. The width of the U-shaped quarter-wave resonator has the same value with the quarter-wave resonators to increase the coupling between the resonators. All the parameters are listed in the caption of Fig. 5.1. The proposed hairpin bandpass filter is designed and simulated with the help of High Frequency Structure Simulator (HFSS 10.0). The simulated results show that the central resonant frequency is 1.575GHz and the 3-dB bandwidth 335MHz.
Figure 5.1: Geometry of the hairpin bandpass filter. (a) Top view. \( W_1 = 1.18 \text{mm}, \ W_2 = 18.1 \text{mm}, \ S_1 = 4.1 \text{mm}, \ S_2 = 0.23 \text{mm}, \ S_3 = 0.07 \text{mm} \) and \( S_4 = 1.2 \text{mm} \). (b) Side view, \( H = 1.28 \text{mm} \).
We used the self-biased spinel NiCo-ferrite films fabricated by a low-cost spin-spray deposition process, a wet chemical process at a low-temperature of 90°C. NiCo-ferrite films with composition of $\text{Ni}_{0.23}\text{Co}_{0.13}\text{Fe}_{2.64}\text{O}_4$ can be deposited onto the substrate or the hairpin microstrip. The thickness of ferrite film is about 2 μm. The magnetic hysteresis loops were measured with vibrating sample magnetometer (VSM), as shown in Fig. 5.2 (a). And the XRD pattern is analyzed by copper Ka x-ray diffraction, which is shown in Fig. 5.2 (b). The in-plane resistivity of the film is $5.616 \times 10^3 \, \Omega \cdot \text{cm}$, and the coercivity is 165.31 Oe. The relative permittivity of the film is about 13 and the permeability is about 10. The loss tangent of the NiCo-ferrite film is estimated to be about 0.05 at 2 GHz.

For a uniformly magnetized sphere, the FMR frequency is linearly proportional to the net magnetic field $H_{\text{net}}$, with the gyromagnetic constant, $\gamma$ being close to 2.8 MHz/Oe. Large bias fields of the order of 1000 Oe are needed for the FMR frequency to reach GHz range, and allow device operation in that range.

The relative permeability of the magnetic sphere can be described by:

$$\mu_r = \frac{4\pi M_s}{H_{\text{net}}} + 1 \quad (5.1)$$

which is inversely proportional to the net magnetic field $H_{\text{net}}$. We can therefore readily reach the Snoek limit [21]:

$$f_{\text{FMR}} \cdot (\mu_r - 1) = \gamma \cdot 4\pi M_s \quad (5.2)$$

i.e. the product of the FMR frequency and the relative permeability is a constant that is determined by the saturation magnetization of the magnetic medium.
The permeability of the ferrite in the film plane is still \( \mu_r = \frac{4\pi M_s}{H_{net}} + 1 \) with \( H_{net} \) being the net in-plane field; while the FMR frequency is increased to be:

\[
f_{FMR} = \gamma \sqrt{H_{net} \cdot (4\pi M_s + H_{net})} = \gamma H_{net} \sqrt{\mu_r} \tag{5.3}
\]

The FMR frequency of magnetic films is therefore boosted to \( \sqrt{\mu_r} \) times of that of magnetic spheres, allowing self-biased FMR frequency as well as the operation frequency of magnetic films in the GHz range. Similarly, the product:

\[
\mu_r \cdot f_{FMR} = \gamma \cdot 4\pi M_s \cdot \sqrt{\mu_r} \tag{5.4}
\]

is also boosted to \( \sqrt{\mu_r} \) times of that of the magnetic spheres, indicating a significantly boosted Snoek Limit for magnetic films.

(a)
5.1.2. Bandpass Filters with Magnetic Films and Simulated Results

In order to obviate biasing of magnetic substrates by an external field, we propose using self-biased ferrites films with relative high in-plane anisotropy. This large anisotropy enables a low loss tangent of the ferrite films at GHz frequencies. Utilizing new spin spray technology we were able to coat these substrates with a 2um NiCo Ferrite. Once this had been completed we deposited a 2um copper layer with the use of our PVD (physical vapor deposition system). Photolithography was then used to develop this copper into our desired hairpin bandpass filter shape. The ferrite films used have a relative permittivity of 13 and relative permeability of 10 with zero loss tangent.
Three hairpin bandpass filters with ferrite films were designed as follows. Firstly, the ferrite film with the thickness of the 2um was covered over the hairpin microstrip. Secondly, the ferrite film was added under the hairpin microstrip bandpass filter. Finally, two lays of ferrite films were added in our simulation, one is under the hairpin microstrip and another is just over the hairpin microstrip.
Figure 5.3: (a) Bandpass filter with ferrite film above the microstrip. (b) Bandpass filter with ferrite film under the microstrip. (c) Bandpass filter with ferrite films both above and under the microstrip. The thickness of the film is $h=0.002\text{mm}$. (d) Simulated S-parameters against frequency for the four different cases.
In order to compare the results with the non-magnetic bandpass filter, the s-parameters of ferrite-loaded filters are plotted and analyzed next. The s-parameter curves in Fig. 5.3(d) are from simulations under the condition that all the geometrical dimensions of the filters are kept unchanged, and only the ferrite films are added at different layers. All the simulations, including the baseline non-magnetic bandpass filter, were carried out with Ansoft’s HFSS software.

From Fig. 5.3(d), we can see that the central resonant frequency of the non-magnetic BPF is about 1.575 GHz, and the -3dB bandwidth is 335 MHz. When a ferrite film was added above the microstrip, the resonant frequency shifted down to 1.50 GHz. This indicates a tuning range of 75 MHz relative to the non-magnetic filter, or equivalent to approximately 22% of the -3dB bandwidth. The bandwidth remained unchanged with addition of the ferrite film. When a ferrite film was added just under the microstrip, we observe that the resonant frequency is still equal to 1.505 GHz, indicating that the added ferrite film has the similar effect as the former one. When two ferrite films were added under and above the microstrip at the same time, this moved the resonant frequency further down to 1.45 GHz, a shift about 37% of the filter bandwidth relative to the non-magnetic filter. In summary, we note that the hairpin bandpass filter loaded with ferrite film can indeed miniaturize the geometrical dimensions effectively (as demonstrated by the shifting down of the resonance), while the bandwidth remains unaffected.
Figure 5.4: (a) Fabricated bandpass filter with/without ferrite films. (b) Measured S-parameters of bandpass filter with/without ferrite films.
The fabricated hairpin bandpass filter with/without NiCo-ferrite film are shown in Fig. 5.4 (a). We fabricated the bandpass filter with ferrite film above the hairpin microstrip line. The central frequency of the filter without ferrite film is about 1.552GHz, when the ferrite film is added above the microstrip, the resonant frequency shifts down to 1.475 GHz. This indicates a tuning range of 77 MHz, which is equivalent to approximately 22% of the bandwidth.

Conclusively, four hairpin bandpass filters with/without ferrite films were designed and analyzed for GPS application. The designed magnetic bandpass filters with self-biased ferrite films of thickness 2um could realize a tuning resonant frequency. When the film was added above, both under and above and under the hairpin microstrip, the central frequencies were 1.50GHz, 1.505GHz and 1.45GHz, respectively, which means a tuning range of 22 to 37% of the filter -3dB bandwidth. This result demonstrates that self-biased magnetic films lead to miniaturized bandpass filter without compromising the bandwidth and the insertion loss.
5.2. Loading Effects of Self-Biased Magnetic Films on Patch Antennas with Magneto-Dielectric Substrates [29]

With the continuous growth of wireless communication technologies, the requirement of smaller size RF (Radio Frequency) devices is becoming a critical issue in communication systems. Planar antennas, because of their ease of fabrication and integration, compactness, as well as the low-profile characteristics, are highly desired for the wireless communication systems. Besides the requirement of antenna miniaturization, other parameters such as antenna bandwidth, radiation efficiency, antenna gain, ground plane immunity, as well as omnidirectional performance at shallow elevation angles are also very important for modern wireless communication.

In most cases, antenna size can be greatly minimized by using a substrate with high relative permittivity. However, antennas with high-permittivity substrates result in decreased bandwidth and the excitation of surface waves, leading to lower radiation efficiency. Another problem is that it becomes difficult to impedance match antennas on high-permittivity substrates, because the input impedance is quite sensitive to feed point location on the patch, especially for circular polarization.

Achieving relative permeability larger than 1 ($\mu_r > 1$) in antenna substrates can lead to antenna miniaturization, enhanced bandwidth, tunable radiation frequency, polarization diversity and beam steering. Bulk ferrite materials, composites of ferrite particles in polymer matrix, metamaterials with embedded metallic circuits, etc. have been used as antenna substrates for achieving $\mu_r > 1$. For example, tunable circularly polarized radiation combined with a switchable radar cross section (RCS) has been obtained for a microstrip antenna by using biased ferrite substrate. Tunable resonant
frequency in patch antennas was obtained by applying external bias field to an yttrium iron garnet (YIG) film. It has also been reported that by applying a biasing magnetic field to the ferrite substrate of a patch antenna, two different radiation modes can be observed. It is possible to realize circular polarization in ferrite patch antennas by exciting radiation patterns of spatially cross linear polarizations.

However, all these magnetic antennas are based on magnetic materials or composites which are too lossy to be used at frequencies > 600 MHz, hence, large biasing magnetic fields are needed for these ferrites to operate at 600 MHz or higher frequencies. Metamaterials with embedded metallic circuits could be a good candidate for providing a high permeability in the application of antenna miniaturization. However they are still too lossy and hard to implement.

In order to be practically feasible in miniature antenna applications, such as handheld wireless communication devices, where battery power and space for electronics are at a premium, it is important for antenna substrates to be comprised of self-biased magnetic materials, in which no external bias field is applied. However, it has been challenging to achieve self-biased magnetic materials for antenna substrate applications at frequencies >600 MHz range due to the well known Snoek limit.

Magnetic thin films provide a unique opportunity for achieving self-biased magnetic patch antenna substrates with $\mu_r > 1$ at frequencies > 1 GHz due to the significantly extended Snoek limit. The strong demagnetization field for magnetic thin films, $H_{demag} = 4\pi M_s$, allows for a self-biased magnetization with high ferromagnetic resonance (FMR) frequencies up to several GHz, which are essential for microwave devices. Most recently, we have proposed to use novel magneto-electric composite
substrates for antennas with low-loss magnetic film materials and low-loss high permittivity dielectric materials. New designs for electronically tunable patch antennas with metallic magnetic films have been investigated. These showed a bandwidth increase of 50% over the non-magnetic antennas. In addition, a new self-biased NiCo-ferrite material have been developed and adopted in our recent research for antenna miniaturization. Self-biased annular ring antennas at 1.7 GHz with a wide range of tunable resonant frequency has been fabricated and characterized with self-biased NiCo-ferrite films, which shows great potential in the applications of antenna miniaturization for mobile handheld wireless communication devices.

Our reported results of patch antennas loaded on either side of the radiating element with single layer and multilayer self-biased NiCo-ferrite thin films essentially created a magneto-dielectric substrate/superstrate for practical applications. These magnetic patch antennas showed an enhanced bandwidth of >200% over the non-magnetic counterparts at 2.1 GHz, and a large resonant frequency tunability of about 38% ~ 272% of the -10dB (or VSWR=2) bandwidth. The antenna efficiency was increased from 41% for the non-magnetic antenna to 74% for ferrite film-loaded antennas. In addition, the omnidirectional radiation pattern was significantly enhanced with the -5dBi gain beamwidth increased from 140° to 173° and an enhanced antenna gain by >1dBi over the unloaded antenna. These magnetic antennas can be made conformably at a low cost near room temperature, making this approach very practical.
5.3. Spin-Spray Deposited Multiferroic Composite Ni$_{0.23}$Fe$_{2.77}$O$_4$/Pb(Zr,Ti)O$_3$ with Strong Interface Adhesion (an alternative route for novel integrated multiferroic materials and devices) [30]

Ni$_{0.23}$Fe$_{2.77}$O$_4$ (NFO)/ Pb(Zr,Ti)O$_3$ (PZT) multiferroic composites were synthesized by spin-spray deposition of NFO film onto PZT at 90°C. Strong interface adhesion between NFO and PZT was observed, which was verified by high resolution transmission electron microscopy indicating excellent wetting between the NFO and PZT, and by the strong magnetoelectric coupling in the NFO/PZT multiferroic composite showing an electric field induced remnant magnetization change of 10%. This strong interface adhesion and low-temperature spin-spray synthesis of multiferroic materials provides an alternative route for novel integrated multiferroic materials and devices.

Multiferroic composite materials with two constituent phases of ferro/ferrimagnetic phase and ferroelectric phase have drawn an increasing amount of interests due to their capability of efficient energy transfer between electric energy and magnetic energy and their potential applications in many multifunctional devices. Such materials can display a stress/strain mediated magnetoelectric (ME) effect, i.e. a dielectric polarization variation as a response to an applied magnetic field, or an induced magnetization by an external electric field, which enables many device applications. A strong adhesion at the interface between the two constituent phases, ferro/ferrimagnetic phase and the ferroelectric phase, is crucial in achieving the stress mediated magnetoelectric coupling.
Several synthesis methods have been developed for multiferroic composite materials with different levels of strength in interface bonding, such as glue bonding with different kind of glue and glue thickness, solid state sintering for bulk multiferroic composite materials; pulsed laser deposition, physical vapor deposition, and sol-gel process for thin film multiferroic materials. However, spin spray deposited ferrites provide great opportunities for low-temperature synthesized multiferroic composite materials on ferroelectric substrates. Since new chemical bonds are formed during spin-spray process, strong adhesion between the spin-spray deposited ferrite film and ferroelectric substrate can be expected, which is critical for magnetoelectric coupling. Typical ferroelectric materials such as PZT can be an excellent supplier of OH groups on its surface, thus facilitating the formation of ferrite film on its surface through spin-spray deposition. In addition, the good lattice match between the perovskite PZT (a=4.03Å) and spinel ferrites (a=8.33Å) may lead to excellent wetting between the ferrite phase and PZT, thus leading to strong interface bonding that is important for achieving strong magnetoelectric coupling.

We reported an alternative synthesis method for composite multiferroic materials, in which pure ferrite phase was spin-spray deposited onto PZT. Strong interface adhesion between the ferrite and PZT phase was observed, which was verified by examining the atomic arrangements at the interface by transmission electron microscopy and by the strong magnetoelectric coupling.

Multiferroic composite material NFO/PZT was obtained by spin-spray deposition of NFO ferrite on PZT substrates at 90°C. Commercially available PZT substrate with a thickness of 0.5 mm was used, which was treated in HCl acid solution containing Fe^{2+}...
before spin-spray process to form a seed layer for ferrite film. An aqueous solution with 1.15 mM Ni$^{2+}$ and 13.2 mM Fe$^{2+}$ and a pH value of 4.0 was used as ferrite precursor solution. At the same time an aqueous oxidization solution with 2 mM NaNO$_2$ and 140 mM CH$_3$COONa and a pH value of 8.0 was used. Through separate nozzles, these two solutions were sprayed at a flow rate of 40ml/min simultaneously onto a spinning hot PZT substrate at 90°C with rotation speed of 150 rpm. N$_2$ gas was blown into chamber to mitigate the oxidization effects from the oxygen in air. After thirty minutes plating, a uniform NFO film on PZT with strong adhesion and the thickness of 1μm was obtained with a growth rate of ~30nm/min.

Figure 5.5: X-ray diffraction pattern of spin-sprayed Ni ferrite film on PZT substrate.
NFO films were deposited using identical spin-spray processing onto three different substrates of glass, alumina, and PZT. Strongest adhesion was observed in the NFO/PZT multiferroic system through simple tape testing. Figure 5.10 shows the X-ray diffraction pattern of spin-sprayed NFO ferrite film on PZT substrate. Pure spinel NFO ferrite phase and perovskite PZT phase are clearly identified with no obvious preferential crystallographic orientations, thus a multiferroic composite of NFO/PZT is formed. The surface morphology of the NFO was examined by atomic force microscope (AFM). To investigate the initial growth process of NFO ferrite, AFM image of a thin NFO film on PZT was captured after five minutes spin-spray plating, i.e. a film thickness of 150 nm or so. Tightly-arranged crystallites of NFO ferrite with the grain size range of 50–100 nm can be observed on PZT substrate at such a thickness. After 30 minutes plating, a high density NFO ferrite film with a thickness of 1µm was obtained on PZT substrate. The roughness of film is around 10nm, or 1% of the ferrite film thickness.

We investigated the interface between NFO phase and ferroelectric PZT phase with high resolution transmission electron microscopy to better understand the origin of the strong adhesion between the NFO/PZT phases. A high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image (Z-contrast) at the NFO/PZT interface was shown in Fig. 5.11(a). A uniform ferrite film with a thickness of 1µm can be identified on the PZT phase, no voids were observed at the NFO/PZT interface. It is interesting to note that the NFO ferrite phase was growing into the small surface crack of the PZT phase with a crack width of ~100 nm (area I) as shown in Fig. 5.11(b), which was proved by the energy dispersive x-ray (EDX) results. This indicates that the excellent wetting between the NFO ferrite phase and the PZT phase during the spin-spray
deposition process, which leads to a tight interface and a strong adhesion between the two phases. A high resolution transmission electron microscope (HRTEM) image of the NFO/PZT interface was shown in Fig. 5.11(c), which shows a clearly tight interface between the ferrite NFO and ferroelectric PZT phase without obvious lattice matching, even though the lattice parameter of the spinel NFO and the perovskite PZT phases are well matched with the NFO lattice parameter being very close to two times of PZT.

Magnetic hysteresis loops of the spin-spray derived composite multiferroic materials NFO/PZT are presented in Fig. 5.12(a). Well-defined magnetic hysteresis loops were observed when external magnetic field is applied parallel and perpendicular to the film, showing an in-plane coercivity of 190 Oe and an out-plane coercivity of 260 Oe, respectively. The saturation magnetization of the NFO film is determined to be 245emu/cm$^3$. 
Figure 5. 6: A cross-sectional HAADF image of NFO/PZT (a) HRTEM of Ni ferrite growing in PZT crack (b), and HRTEM ferrite and PZT interface images (c)

Figure 5. 7: Typical magnetic hysteresis loops (a) and magnetostriction (b) of spin-sprayed Ni ferrite film on PZT.
The magnetic field dependent magnetostriction behavior of the NFO ferrite film on PZT substrate was measured on a customer-made magnetostriction tester, shown in Fig. 5.12 (b) with a maximum field of 250 Oe. The magnetostriction of the NFO ferrite film on PZT increases with the applied in-plane magnetic field, reaching -10 ppm at 250 Oe, which is smaller than the saturation magnetostriction constant of the pure NFO phase. This may be due to the limited magnetic field strength of our magnetostriction test system which can supply the highest magnetic field of 250 Oe. The NFO film is clearly not saturated at 250 Oe according to the hysteresis loops in Fig. 5.12(a).

The magnetoelectric effect between the ferrimagnetic NFO phase and the ferroelectric PZT phase was demonstrated by observing the electric field induced magnetic hysteresis loop change, as an external electric field of 1.3 MV/m was applied on PZT. Due to the inverse piezoelectric effect, the PZT substrate experiences an in-plane stress when an external electric field is applied through the thickness direction. This stress can be transferred to the NFO ferrite film, and induces magnetization change by the inverse magnetoelastic effect. In our experiment, the multiferroic NFO/PZT was mounted on the VSM holder and the in-plane M-H magnetic hysteresis curves were measured when applying external electric field of 0 MV/m and 1.3 MV/m across the thickness direction of PZT substrate as shown in Fig. 5.13. An obvious upward shift of M-H curve was observed at low external magnetic field. The remnant magnetization was increased by ~10% with applied electric field of 1.3 MV/m. In addition, we found both M-H curves reached the same saturation magnetization at high external magnetic field, indicating that magnetoelectric coupling disappeared at high magnetic field due to the diminished magnetostriction.
Figure 5.8: In-plane $M-H$ curves of spin-sprayed Ni ferrite film on PZT when applying 0 and 1.3 MV/m electric fields through the PZT substrate.

In summary, multiferroic material NFO/PZT was synthesized by spin spray deposition of NFO on PZT substrate at a low temperature, which displays strong adhesion between the two constituent phases at the NFO/PZT interface. The strong adhesion between the NFO phase and the PZT phase was confirmed by the excellent wetting between the NFO phase and the PZT phase, as well as a strong strain/stress mediated magnetoelectric coupling. The strong adhesion observed in the spin-spray deposited NFO/PZT multiferroic composite, as well as the low synthesis temperature provides a viable route to the synthesis of novel high quality multiferroic materials by spin-spray deposition.
Chapter 6

CONCLUSION

In this thesis, we presented the fabrication and characterization of magnetic thin films by spin spray process. The spin spray process is a low temperature (<100°C), no vacuum ferrite plating method that can produce thin films with properties comparable to bulk films. The basic principle of this ferrite plating method employs the oxidation of Fe$^{2+}$ to Fe$^{3+}$.

We discussed results of multiferroic composite materials on ferroelectric substrates with good magnetoelectric (ME) coupling. The strong adhesion observed in the spin-spray deposited NFO/PZT multiferroic composite, as well as the low synthesis temperature provides a viable route to the synthesis of novel high quality multiferroic materials by spin-spray deposition. This is currently of interest in the spintronics industry.

We also showed how self-biased magnetic thin films were successfully incorporation unto patch antennas, leading to significantly enhanced antenna performance at 2.1 GHz. The spin-spray deposited NiCo-ferrite films were not as lossy as bulk ferrites materials, because of the strong demagnetization field of magnetic thin films as well as the large in-plane anisotropy field of the magnetic films in the range of hundreds of Oe. These spin spray deposited self-biased ferrite films when incorporated into novel antenna designs, show great promise for mediating the adverse effects associated with the high permittivity substrates, thus leading to electrically small antennas with significantly improved antenna performance.
References:


