SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF NOVEL RF FERRITES BY LOW-TEMPERATURE SPIN-SPRAY DEPOSITION

A Dissertation Presented

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Abstract

High frequency operation of magnetic materials has received much attention in the microwave and telecommunication industries. Ferrite materials are one of the most widely used materials due to their high permeability and resistivity at high frequency range. In thin film form, they provide a unique opportunity for microwave device application in GHz range due to their significantly extended Snoek limit. In this research, novel RF ferrites by the direct deposition spin-spray process were synthesized and characterized.

Spin-spray deposition process unlike the other conventional techniques, is a low cost (no vacuum required), low temperature process (<100°C) which is compatible with a wide range of substrates like organic materials, plastics, RFIC and MMIC etc.

Properties of these spin-spray synthesized ferrites required for RF/microwave applications were examined. Strong interface adhesion in Ni_{0.23}Fe_{2.77}O_4/PZT (lead zirconium titanate) and magnetoelectric (ME) coupling leading to record-high electrostatic field induced ferromagnetic magnetic resonance (FMR) field change of 860 Oe, microwave ME coefficient of 108 Oe cm/kV and FMR microwave tunability of 1450 Oe were achieved in Fe_3O_4/PZN-PT multiferroic heterostructure. These properties will enable low temperature fabrication of electrostatic tunable microwave devices. Nickel zinc (NiZn) ferrite films with high permeability
that exceeded the Snoek limit for bulk NiZn-ferrite films and those previously reported for spin-spray deposited ferrites, and with low magnetic losses in the GHz range were also developed.

Thicker ferrite film loading, which could lead to an even greater performance enhancement in RF/microwave devices, have been difficult to achieve due to their degraded RF performance. Ferrite/non-magnetic multilayers serve as a good solution to this problem. Spin-spray deposited two-period ferrite/non-magnetic multilayer films with significant enhancement in RF/microwave magnetic properties over their single layer counterparts were fabricated and extensively characterized.

Furthermore, novel RF devices (antennas) with improved performance such as miniaturization, bandwidth enhancement, directivity and gain improvement were developed using these ferrites.

Lastly, a study into spin-spray processing condition effects on semiconductor zinc oxide (ZnO) microstructures was successfully carried out. Though the spin-spray process was initially developed for ferrite making, it is currently been explored as a growth technique for ZnO micro/nanostructures.
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Chapter 1: Introduction to Ferrites

Magnets have become an important part of human endeavor, and are found in many industries such as automobile (e.g. starter motors, anti-lock braking systems, controls for windows, seats etc), telecommunication (e.g. speakers, switches, core components for many microwave passive components including miniaturized strip antennas, etc), data processing, electronics (including microwave), and Instrumentation [1].

Ferrites are ferrimagnetic materials with iron(iii)oxide as their principle component, that have been considered as highly important electronic materials for more than half a century [2]. The crystal structure of a ferrite can be regarded as an interlocking network of positively-charged metal ions (Fe$$^{	ext{+++}}$$, M$$^{2+}$$) and negatively-charged divalent oxygen ions (O$$^{	ext{-}}$$) [3], which utilizes the transition element Fe as in Fe$_2$O$_3$ to exhibit magnetism similar to ferromagnetic materials below the Curie temperature, $T_c$, but become paramagnetic above $T_c$ as in the case of ferromagnetic materials [1].

High resistivity and low RF loss ferrites have found an abundance of application in passive microwave components such as isolators, circulators, phase shifters, and miniature antennas operating in a wide range of frequencies (1–100 GHz) and as magnetic recording media owing to their novel physical properties [4].
1.1 Crystal Structures of Ferrites

Based on their crystalline structure, ferrites can be categorized into 3 crystal groups; spinel, magnetoplumbite (hexagonal structure) and garnet ferrites.

1.1.1. Spinel Ferrites

Spinel ferrites are closely-packed cubic possessing the structure of the mineral spinel MgAl$_2$O$_4$, and with the general formula of MFe$_2$O$_4$, where M is a divalent metal ion with an ionic radius of ~ 0.6 to 1Å such as Fe, Ni, Mn, Mg, Zn, Co etc, or a combination of ions with an average valency of two, and the Fe ions are of the trivalent type Fe$^{3+}$. The trivalent Fe$^{3+}$ can be partially or completely replaced by another trivalent ion such as Al or Cr, thus producing mixed crystals of aluminates and chromites which are also ferrimagnetic at room temperature if the non-magnetic ions are in small concentrations [5].

The smallest unit cell of the spinel lattice as shown in Fig 1.1a has a cubic symmetry with eight molecules of MFe$_2$O$_4$, with the relatively large oxygen ions forming a face-centered cubic structure. Between the oxygen ions layers, exist interstices that may accommodate the metal ions. The ‘A’ sites are surrounded by 4 nearest neighboring oxygen ions forming a tetrahedron with their connecting centers as seen in Fig 1.1b. Thus, ‘A’ sites are called tetrahedral sites. The ‘B’ sites are surrounded by 6 nearest neighboring oxygen ions forming an octahedron, and are thus called octahedral sites as seen in Fig 1.1c. In a unit cell of 32 oxygen ions, there
are 64 tetrahedral and 32 octahedral sites, of which only 8 and 16 respectively are occupied by metal ions.

Fig 1.1: a) Spinel unit cell structure, b) tetrahedral interstice or ‘A’ sites, and c) octahedral interstice or ‘B’ sites [1].
Spinel ferrites are the most widely used ferrites due to their high permeability and ease of magnetic property manipulation (e.g. saturation magnetization, magnetic anisotropy etc). They find practical application in EMI suppression, RF devices (e.g. in antenna miniaturization, inductors).

1.1.2. Magnetoplumbite (Hexagonal Structure)

Ferrites

Magnetoplumbite ferrites are hexagonal crystal-structured ferrites similar to that of the mineral magnetoplumbite (PbFe$_{7.5}$Mn$_{3.5}$Al$_{0.5}$Ti$_{0.5}$O$_{19}$), and with chemical composition MeO.6Fe$_2$O$_3$, where Me is a divalent ion (e.g. Ba, Pb, Sr etc). Barium hexaferrite is the most common type of hexaferrite of which different types (M, W, Y, Z, U and X) are derived by its combination with the spinal ferrite structure as shown in Fig 1.2.

![Chemical composition diagram showing how hexaferrite structures are derived from the spinel MeOFe$_2$O$_3$ structure](image1)

Fig 1.2: Chemical composition diagram showing how hexaferrite structures are derived from the spinel MeOFe$_2$O$_3$ structure [1].
Like the spinel ferrites, the oxygen ions in hexaferrites are closely packed. They also contain the Me divalent ion which can replace these oxygen ions in the lattice since they are of the same ionic radii. The hexagonal ferrite structure of the M-type barium hexaferrite (BaO.6Fe₂O₃ or BaFe₁₂O₁₉) is shown in Fig 1.3. Its structure is constructed from 4 building blocks S and S⁺ blocks (which are spinels with oxygen layers and six Fe³⁺ ions), R and R⁺ blocks (which are hexagonal consisting of three oxygen layers with one oxygen ion replaced with a Ba²⁺) and contain ten layers of oxygen atoms along the c axis. The asterix (*) indicates that the corresponding sub-unit is rotated 180° around the hexagonal axis. In total, the unit cell contains a total of 38 O²⁻ ions, 2 Ba²⁺ ions, and 24 Fe³⁺ ions. Fe³⁺ ions in octahedral (12 k, 2a), and hexahedral (2b) sites (16 total per unit cell) have their spins up, while the Fe³⁺ ions in octahedral (4f₁) and tetrahedral (4f₂) sites (8 total per unit cell) have their spins down, which results in a net total of 8 spins up, and therefore, a total moment of 8 x 5 \( \mu_B = 40 \mu_B \) per unit cell that contains two Ba²⁺ ions. The R and S sub-units shown have chemical formulae R = (Ba²⁺ Fe₆³⁺ O₁₁²⁻)²⁻ and S = (Fe₆³⁺ O₈²⁻)²⁺ [1].

Hexaferrites are used in microwave device applications that require low eddy current losses.
Fig 1.3: The schematic structure of the hexaferrite BaFe$_{12}$O$_{19}$. The arrows on Fe ions represent the direction of spin polarization. 2a, 12k, and 4f$_2$ are octahedral, 4f$_1$ are tetrahedral, and 2b are hexahedral (trigonal bipyramidal) sites [1].
1.1.3. Garnet Ferrites

These are ferrites that crystallize in the dodecahedral or 12-sided structure related to the ideal mineral garnet Mn$_3$Al$_2$Si$_3$O$_{12}$, thus, the general formula for garnet ferrites is M$_3$Fe$_5$O$_{12}$ or 3M$_2$O$_3$.5Fe$_2$O$_3$, where M is a trivalent metal ion, usually rare earth. Yttrium garnet (YIG) is considered the most important magnetic garnet. Yttrium, even though not a rare earth metal, behaves like one and so is included in the designation “rare earth” garnet [3].

There are three different types of sites present in the garnet structure. These are the tetrahedral (a) sites, the octahedral (b) sites and the 12-sided distorted polyhedral or dodecahedral (c) sites. In a unit cell containing 8 formula units, there are 24 tetrahedral, 16 octahedral and 16 dodecahedral sites. There are actually 8 units of M$_3$Fe$_5$O$_{12}$ or 4 units of 3M$_2$O$_3$.5Fe$_2$O$_3$ in the unit cell of a garnet ferrite. The crystal structure of the garnet is quite complicated and thus difficult to adequately show a two-dimensional representation of all the ions (160) in the unit cell [1]. An octant of the garnet structure that illustrates the cation positions is shown in Fig 1.4 for simplicity.
Fig 1.4: Schematic of an “octant” of a garnet crystal structure (lattice constant “a”) showing only cation positions. RE represents rare earth [1].
The moments of the Fe ions in the tetrahedral \((a)\) sites are antiferromagnetically coupled to those on the octahedral \((b)\) sites by superexchange mechanism while the rare earth ions, which have magnetic moments, in the dodecahedral site \((c)\) are antiferromagnetically coupled to the net moment of the Fe ions [5]. The coupling between the ions in the \((c)\) site and the resultant Fe ions is much weaker than that between the Fe ions in the \((a)\) and \((b)\) sites. As a result, the magnetization of the rare earth ions drops very quickly with increasing temperature, approximately as \(1/T\).

A more detailed crystal structure of an octant of the garnet ferrite showing the octahedral, tetrahedral and dodecahedral symmetry is shown in Fig 1.5 below.
Fig 1.5: An “octant” of a garnet crystal structure (lattice constant “a”) showing a trivalent ion of iron on a site surrounded by six oxygen ions in octahedral symmetry, a divalent ion of iron on a site surrounded by four oxygen ions in tetrahedral symmetry, and a rare-earth ion surrounded by 8 oxygen ions which form an 8-cornered 12-sided polyhedron. RE represents rare earth [1].

Garnets most especially YIG are mostly used for microwave applications.
This dissertation focuses on the most widely used form of ferrites, spinel ferrites, due to their high permeability and ease of magnetic property manipulation (e.g. saturation magnetization, magnetic anisotropy etc). They find practical applications in EMI suppression and RF device as previous mentioned, which makes them of great interest in the microwave/RF device industry.

1.2 Synthesis of Spinel Ferrite Thin Films

Here, more focus is given to the synthesis of spinel ferrite thin films as opposed to bulk films owing to the fact that the operating frequency of bulk ferrite materials is limited to < 500 MHz under self-bias condition as a result of the excessive magnetic loss tangent associated with the Snoek limit. A method to increase the thickness of these thin films without having to suffer from much magnetic property degradation will be discussed in chapter 4 of this dissertation.

Various conventional techniques exist for the synthesis of spinel ferrite 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 [6]. These conventional techniques involve the use of high temperature (above 500°C) and/or pressure, vacuum chambers or lasers for film growth and crystallization, have a high cost of production and also cannot be used on non-heat resistant substrates like plastics and organic materials [7].

Spin-spray deposition process, unlike the other conventional processes is a direct deposition low temperature (<100°C), no vacuum ferrite plating method with high deposition rate (40~100 nm/minute), that is compatible with substrates like plastics, organic materials, RFIC and MMIC, etc [8]-[10]. 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 magnetoelectric (ME) coupling. This is currently of interest in the spintronics industry [11].

Spin-spray deposition process was invented in 1983 by Masanori Abe and Yutaka Tamaura [8]. 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, onto 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 [7], [12].

The principle of spin-spray process involves:

- Absorption of the Fe$^{2+}$ and M$^{n+}$ (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$_2$, O$_2$ etc). The chemical equation for this reaction can be expressed as:

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

(1.1)

- Re-absorption of the Fe$^{2+}$ and M$^{n+}$ ions on the surface of the substrate with the layered pre-absorbed ions Fe$^{2+}$ and M$^{n+}$ 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;
This entire process is repeated and the ferrite thickness is increased since the OH\(^-\) group is still on the surface of the substrate [7], [12]. The schematic for the spin-spray plating principle is shown in Fig 1.6 below;

Fig 1.6: Principle of spin-spray process [6], [7].

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 [7], [13], [14].
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 (NaNO₂). 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 in Fig 1.7 below.

![Diagram of spin-spray set up](image)

**Fig 1.7: Schematics of spin-spray set up.**
1.2.2. Ferrite Thin Films By Spin-spray Process

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

a) 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 15 Oe, and ferromagnetic resonance (FMR) frequency as high as 1.2 GHz have already been reported. Also, large saturation magnetization ($M_s$) greater than 400 emu/cc was observed [15]-[18]. 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 [19].

b) 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 ($\mu'$) greater than that of bulk films and low imaginary permeability ($\mu''$) with $\tan\delta$ (0.4) much lower than that for
composite type magnetic sheets ($\tan[\delta] = \mu'/\mu''$) [20], [21]. Some of these results can be seen in table 1.1 below.

Table 1.1: Chemical composition, thickness $t$, saturation magnetization $M_s$, anisotropy field $H_k$, real permeability $\mu'$, and natural resonance frequency for the films [20].

<table>
<thead>
<tr>
<th>Composition</th>
<th>$t$ ((\mu m))</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 $\text{Ni}<em>{0.23} \text{Fe}</em>{2.20} \text{Co}_{0.27} \text{O}_4$</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 (900 MHz or 2.45 GHz).

c) Manganese Zinc (Mn-Zn) Ferrite Thin Films

The following properties for Mn-Zn ferrite thin films have been reported. These 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 Ms (380-460 emu/cc)
V. Low coercivity (Hci =11-29 Oe)
VI. Very large transmission loss per thickness (as a microstrip), about 10 times larger than that of the commercialized composite sheets.
VII. Sufficiently low reflection coefficient S11<-10 dB
VIII. FMR frequency of 300 MHz

Mn-Zn ferrite thin films can be used as noise suppressors for multilayered printed circuit boards [22].

1.3 Motivation

Currently, magnetic films are of great interest in the RF device industry as they can be used for electromagnetic means in enhancing the performance of microwave devices like antennas and inductors. Methods to develop these ferrite films and also increase their practical applications are 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 synthesize and characterize these RF ferrites for device application.
1.4 Objective

The main objective of this dissertation is to successfully develop RF ferrites by the low temperature spin-spray process for novel RF device applications. These ferrite films will enable major improvements and advancements in microwave devices including miniaturization, gain enhancements etc, and provide great opportunity for tunable microwave devices. Also, ferrite/non-magnetic multilayers, a good approach to thicker ferrite film loading, will also be extensively studied. These ferrite films will be applied to novel RF devices like antennas and their properties will be extensively characterized.

Though the spin-spray process was original designed for ferrite plating, it is currently being researched as a good candidate for semiconductor zinc oxide (ZnO) fabrication due to the fact that it requires no seed layer for film growth, has a continuous supply of fresh solution; which preserves the high concentrate of solute, and has a high deposition rate, making it suitable for thick film growth. This therefore, necessitates a need to carefully investigate the optimum process conditions and their effects on the ZnO micro/nanostructures by the spin-spray technique. This research deals with this need. In addition, aluminum doped ZnO thin films are studied.
1.5 Dissertation Outline

This dissertation is categorized into seven (7) chapters highlighting the different aspects of this work. Following the introductory chapter, Chapter 2 contains detailed experimental/fabrication and characterization procedures for the ferrite films. In Chapter 3, the properties of these spin-spray ferrites needed for RF/microwave applications will be discussed and analyzed. Chapter 4 presents spin-spray deposited ferrite/non-magnetic multilayers with improved RF properties over their single layer counterparts, suitable for thicker ferrite film loading in microwave devices, and Chapter 5 deals with the implementation of these ferrite films in novel RF devices. Chapter 6 examines the processing condition effect of the spin-spray technique on ZnO microstructure growth; including Al doped ZnO thin films. Finally, Chapter 7 concludes with a summary of achievements and future recommendations.
References


Chapter 2: Spin-spray Ferrites-

Experimentation and Instrumentation

This chapter deals with the experimental procedures involved with the spin-spray process and a description on the different measurements that were carried out on these films to determine their properties.

2.1 Experimentation

Initial absorption of the ferrite ions (Fe$^{2+}$ and Mn$^{n+}$ (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. 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 have already been conducted to optimize the process condition for the fabrication of these films [1], and so, only the optimized parameters will be described in the section.

The substrates were thoroughly cleaned in acetone and alcohol in an ultra sonic for 10mins respectively to remove all impurities from the surface. They were place in a seed-layer bath consisting of dil. HCl and Fe$^{2+}$ in order to introduce the OH$^{-}$ group and the initial Fe$^{2+}$ ion onto the surface of the substrate for easy absorption of the ferrite ions by the surface during film fabrication.
The oxidizing solution consisted of a mixture of an oxidant, sodium nitrite (NaNO₂), and a pH buffer, sodium acetate (CH₃COONa) in the ratio 2:140 (except otherwise stated) in deionized water, resulting in a pH of 7-12. The precursor/reaction solution is a combination of Fe²⁺ and Mn⁺ (Fe, Mn, Zn, Ni, Co etc or a combination of these ions) ions usually in chloride form in deionized water. The resultant pH was 3-6.

The substrates were mounted on the spinning table with a speed of rotation of 120-200rpm. Fabrication was done in the presence of nitrogen gas. The growth rate of the films was ~30-40 nm/min.

After the fabrication process, the substrates (with the thin films) were thoroughly washed with deionized water and dried. A schematic of the procedures involved is shown in Fig 2.1.
Fig 2.1: Schematic of the spin-spray procedure.
2.2 Instrumentation

The different measurements carried out on the fabricated ferrites include;

2.2.1. Thickness Measurement

Thickness measurements were done using a Veeco Dektak 3 stylus profilometer.

2.2.2. 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 \( H \) [1], [2].

Magnetic hysteresis measurements were carried out with the dc magnetizing field applied inplane (parallel and perpendicular) and out of plane to the film axis as shown in Fig 2.2.
2.2.3. Composition and Structural Analysis

The structural analysis 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).

Composition analysis of the films was obtained using Energy Dispersive Spectroscopy (SEM-EDS) and the structure using X-Ray Diffractometer with a Cu Kα source (λ=1.541 Å).

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 [1], [3].

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.

2.2.4. Magnetostriction Measurement

Magnetostriction measurements were obtained using a precision materials analyzer (a piezoelectric unit/ magnetostriction tester) [1].
2.2.5. Ferromagnetic Resonance (FMR) Measurements

- **FMR Frequency/Permeability Spectra Measurement**

The complex permeability spectra of the films were measured using a broad band custom-made permeameter consisting of a coplanar waveguide connected to a network analyzer with a bandwidth of 0.045-10 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 as shown in Fig 2.3.
Fig 2. 3: Schematic of the set-up for the FMR/permeability spectra measurement.
Magnetic field was applied to saturate the film, and \( S_{011} \) and \( S_{021} \) were measured by the network analyzer. The desired magnetic field was applied to the film and \( S_{111} \) and \( S_{121} \) were obtained. \( S_{011} \) and \( S_{021} \) contain non-magnetic properties of the circuit while \( S_{111} \) and \( S_{121} \) contain both magnetic and non-magnetic properties of the film.

The relative permeability can be obtained with the formula [4] below:

\[
\mu = \frac{Z_0 \left( \frac{1 + s_{11} - s_{21}}{1 - s_{11}} - \frac{1 + s_{01} - s_{02}}{1 - s_{01}} \right)}{iclt\mu_0\omega} \tag{2.1}
\]

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.
Permeability calibration was done using a Co-Zr-Ta film with a known magnetization, in-plane anisotropy field and initial permeability.

- **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 [5].
Reference


Chapter 3: Characterization/Properties of 
Spin-spray Ferrites

3.1 Spin-spray Multiferroic Materials

Multiferroic materials have gained a lot of interest due to their capability of efficient energy transfer between electric and magnetic energy which makes for potential applications in multifunctional devices [1]-[10]. These materials have two or more constituent phases of ferri/ferromagnetic phase and ferroelectric phase that can cross interact with each other to create a magnetoelectric (ME) coupling/effect. ME effect is defined as a dielectric polarization variation as a response to an applied magnetic field, or an induced magnetization by an external electric field, which may arise directly between the phases, or indirectly via strain/stress. This direct interaction between ferri/ferromagnetism and ferroelectricity enables E-field control of magnetism which is of great fundamental and technical importance in magnetic and spintronics device applications or M-field control of polarization.

Multiferroic materials can be categorized into two; single phase multiferroic materials (which have co-existing ferroic properties in the same material) and composite multiferroic (which have individual ferroic characteristics existing solely within the separate phases in the material).
A schematic diagram showing the overlap required to achieve multiferroic materials is shown in Fig 3.1.

![Schematic Diagram](image)

**Fig 3.1:** A schematic diagram showing the overlap required to achieve multiferroic properties in a single material [11].

Despite a much effort by a wide number of researchers, the search for a single phase multiferroic material showing strong coupling at room temperatures has proved to be a difficult one due to the weak coupling of order parameters present in these materials. Thus, recent research has been directed towards composite multiferroic materials.

In composite multiferroic systems, operation is by coupling of the magnetic and electric properties of two materials, generally a ferri/ferromagnetic material and a ferroelectric material via strain or stress.
An in-plane magnetic field (H) induces strain in the magnetic component due to the magnetostrictive effect, which is mechanically transferred to the ferroelectric component inducing a dielectric polarization through the piezoelectric effect as shown in Fig 3.2 (a). This type of ME effect is known as direct ME effect. Conversely, an out-of-plane electric field (E) induces strain in the ferroelectric component due to the inverse piezoelectric effect, which is mechanically transferred to the magnetic component, inducing a change in magnetization as depicted in Fig 3.2 (b). This is known as converse ME effect. Thus the ME effect is the cross interaction in the two phases and is product of the magnetostrictive effect in the magnetic phase and the electrostrictive effect in the electric phase [11], [12].
Fig 3.2: Schematic illustration of strain-mediated magnetoelectric (ME) effect in a composite system consisting of a magnetic layer (blue) and ferroelectric layer (purple). (a) Direct ME effect (b) Converse ME effect [12].
Based on their structure, composite multiferroic materials can be categorized into three groups. These are horizontal heterostructures (alternating ferri/ferromagnetic and ferroelectric layers), vertical nanostructures (nanopillars embedded in another phase) and nanoparticle embedded films (magnetic particles embedded in a ferroelectric film). Fig 3.3 (a), (b) and (c) shows the structural diagrams of the different types of composite multiferroic materials respectively. Of these three types, the horizontal heterostructures are most widely investigated because of their ease of fabrication and great potential for device applications [11].

Fig 3.3: Schematics of the different types of composites multiferroic materials (a) horizontal heterostructures, (b) vertical nanostructures, and (c) nano-particle embedded films.
It is important to note that in order for a strong ME effect to be realized, a strong interface adhesion between the two phases of the multiferroic composite material is vital.

Spin spray deposited ferrites provide great opportunities for low-temperature synthesized horizontal 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, which can lead to magnetoelectric coupling can be expected. Therefore, it is possible to synthesis horizontal composite multiferroic materials by spin-spraying ferrite film on ferroelectric materials. Only a few studies on composite multiferroic materials derived by spin-spray process have been reported.

In this work, we fabricated horizontal heterostructures comprising of ferrimagnetic thin films on ferroelectric substrates by the spin-spray process of which strong interface adhesion, static and microwave ME interactions and magnetic tunability were demonstrated.

3.1.1. Strong Interface Adhesion

Typical ferroelectric materials such as Pb(Zr\textsubscript{x},Ti\textsubscript{1-x})O\textsubscript{3} (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=4.03A) and spinel ferrites (a=8.33A) 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. Furthermore, PZT is a ceramic perovskite material that is widely used in all sorts of engineering applications such as ultrasound transducers, ceramic capacitors and actuators [13]. Being ferroelectric, PZT has spontaneous electric polarization (electric dipole) which provides an extremely large dielectric constant and piezoelectric coefficient practically at the morphotrophic phase boundary (MPB) near $x = 0.52$. These properties make PZT-based compounds one of the most prominent and useful electroceramics [14].

In this work, nickel ferrite $\text{Ni}_{0.23}\text{Fe}_{2.77}\text{O}_4$ (NFO) was fabricated on commercially available 0.5 mm PZT substrate to form horizontal heterostructure multiferroic composite with strong interface adhesion between the NFO film and PZT substrate which is essential for ME interactions and magnetic tunability.

An aqueous solution comprising of 1.15 mM Ni$^{2+}$ and 13.2 mM Fe$^{2+}$ and a pH value of 4.0 was used as the precursor solution, while the oxidization solution consisted of 2 mM NaNO$_2$ and 140 mM CH$_3$COONa and a pH value of 8.0. A detailed description of the spin spray deposition process is discussed in the previous chapter. The thickness of the NFO film was 1 µm.

Fig 3.4 shows the X-ray diffraction pattern of the NFO ferrite film on PZT substrate. Pure spinel polycrystalline NFO phase with no obvious preferential orientation was observed.
When the magnetization in a magnetic material changes with the direction of the applied external magnetic field, it is said to exhibit magnetic anisotropy. Magnetic anisotropy was demonstrated in the NFO/PZT composite with external magnetic field applied parallel and perpendicular to the NFO/PZT as seen in Fig 3.5, showing an in-plane coercivity of 190 Oe, an out-plane coercivity of 260 Oe and a saturation magnetization of 245 emu/cm³.
Fig 3.5: Magnetic hysteresis loops of NFO/PZT multiferroic composite [15].

To investigate the initial growth process of NFO ferrite, the AFM image (Fig 3.6(a)) of the NFO film on PZT substrate was captured after five minutes spin-spray plating, i.e. with a film thickness of ~150 nm. Tightly-arranged crystallites of NFO ferrite with the grain size range of 50 to 100 nm were observed. After 30 minutes plating, a high density NFO ferrite film with a thickness of 1µm was obtained on the PZT substrate, which displays a mean grain size of ~300nm, as shown in Fig 3.6(b). The roughness of film is ~ 10nm, or 1% of the ferrite film thickness.
The strong interface adhesion in the NFO/PZT composite was further investigated by high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The Z-contrast image at the NFO/PZT interface is shown in Fig 3.7(a). A uniform ferrite film with a thickness of 1µm can be identified on the PZT phase with no visible voids at the NFO/PZT interface. It is interesting to note that the NFO ferrite phase grew into the small surface crack of the PZT phase with a crack width of ~100 nm (area I) as shown in Fig 3.7(b). This indicates that there is indeed 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 as seen in Fig 3.7(c), clearly shows a 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.

Fig 3.7: (a) A cross-section high-angle annular dark field (HAADF) image of NFO/PZT, (b) high resolution transmission microscope image (HRTEM) of Ni ferrite growing in PZT crack, and (c) HRTEM ferrite and PZT interface image [15].

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.
3.1.2. Magnetoelectric (ME) Coupling and Magnetic Tunability

Tuning of magnetization has become of immense essential and technological significance. Typically, magnetization tuning in various microwave magnetic devices involves the use of bulky external electromagnets for magnetic field generation. This however, puts significant drawbacks on the device application due to the fact that these electromagnets are slow, noisy and consume a lot of energy.

The main interest in multiferroic materials is their potential ability to enable electric and magnetic field control of the piezoelectric or magnetic phase, which if realized, would lead to a wide variation of magnetic devices that are high-speed, compact and energy efficient. Multiferroic materials operate through the magnetoelectric (ME) coupling of the magnetic and electric properties via strain. This means that impressing an electric field induced strain or stress on the piezoelectric phase leads to a stress on the magnetic phase and applying a magnetic field induced strain or stress on the piezoelectric phase induces an electric displacement through magnetoelectric (ME) coupling.

Applying a magnetic field strain or stress on a ferri/ferromagnetic material not only induces material deformation but also produces magnetic anisotropy. This signifies that in a multiferroic material, an electric field could produce a change in the magnetic anisotropy which can facilitate a magnetization rotation. This change in magnetic anisotropy can be
quantitatively ascertained by ferromagnetic resonance (FMR) measurement since the FMR field can be driven by applying electric fields.

In this work, we demonstrate the static and microwave ME interactions as well as the magnetic tunability of spin-spray derived ferrite/ferroelectric multiferroic heterostructures. This was done through electrostatic field induced FMR field changes at room temperature, with the application of external bias magnetic fields in the magnetic film plane along [100] or [01-1] direction for single crystal PMN-PT (lead magnesium niobate-lead titanate) or PZN-PT (lead zinc niobate-lead titanate) respectively with microwave RF field being in-plane and perpendicular to the DC bias field as shown in Fig 3.8.

Fig 3.8: Schematic of magnetoelectric (ME) measurement (Adapted from ref [14]).
Various multiferroic heterostructures were synthesized by spin-spray process. These include thin films of thicknesses ~1µm of iron (III) oxide, Fe₃O₄, on ferroelectric polycrystal PZT, (011) cut single crystal PMN-PT and (011) cut single crystal PZN-PT substrates, nickel zinc ferrite, Ni₀.₂₆Zn₀.₄Fe₂.₆₃O₄ (NZFO), on (011) cut single crystal PMN-PT substrate and zinc ferrite, Zn₀.₁Fe₂.₉O₄ (ZFO), on (011) cut single crystal PMN-PT substrate. The dimensions of the substrates were 15×7×0.5 mm (L×W×H) for the PZT substrate, 10×5×0.5 mm (L×W×H) for the (011) cut single crystal PMN-PT and PZN-PT substrates. The substrates were coated with electrodes on both sides and were polarized under a poling field of 6 kV cm⁻¹ across the thickness direction before deposition of the ferrite films. A detailed description of the spin-spray process is discussed in chapter 2 of this dissertation.

The static ME coupling measurements were performed by vibrating sample magnetometer (VSM). The samples were mounted on the VSM holder and the in-plane hysteresis loops were measured under various electric fields which were applied across the thickness of the ferroelectric substrates coated with Cu as electrodes. Microwave ME interaction were investigated by microwave cavity operated at X-band (9.5 GHz). The static electric field was applied across the sample thickness direction. Both the external bias magnetic field and microwave magnetic field were applied orthogonal and in-plane of the films. The ferroelectric property of the
substrates was measured by a Radiant RT-6000 ferroelectric testing station.

Pure spinel ferrite phase were clearly identified with no obvious preferential crystallographic orientations in all the samples. The XRD patterns for the ZFO/PMN-PT, Fe₃O₄ on PZT and PMN-PT are shown in Fig 3.9 (a) and (b) below.
Fig 3.9: X-ray diffraction patterns of multiferroic (a) Zn$_{0.1}$Fe$_{2.9}$O$_4$ on PMN-PT, and (b) Fe$_3$O$_4$ on PMN-PT and PZT substrates [15].
Well defined magnetic hysteresis loops were observed in all the samples when an external magnetic field was applied parallel (inplane) and perpendicular (out of plane) to the plane of the film as typically shown in Fig 3.10 below. The magnetostriction constant of the Fe$_3$O$_4$ film on PZT substrate which was measured with a custom-made magnetostriction tester, demonstrated a saturation magnetostriction of 30ppm as shown in Fig 3.10 insert.

Fig 3.10: Magnetic hysteresis loops and magnetostriction curve (inset) of the Fe$_3$O$_4$ ferrite film on PZT substrate.
A summary of the magnetic properties of the films are shown in table 3.1 below.

Table 3.1: Summary of film (ferrite) structures and magnetic properties (saturation magnetization, $M_s$, coercivity, $H_c$, and FMR linewidth $\Delta H$ at X-band (9.6 GHz)).

<table>
<thead>
<tr>
<th>Film Structure</th>
<th>Substrate</th>
<th>$4\pi M_s$ (Gauss)</th>
<th>$H_c$(Inplane) (Oe)</th>
<th>$H_c$(Outplane) (Oe)</th>
<th>$\Delta H$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.26}$Zn$</em>{0.1}$Fe$_{2.63}$O$_4$</td>
<td>PMN-PT</td>
<td>4500</td>
<td>70</td>
<td>85</td>
<td>350</td>
</tr>
<tr>
<td>Zn$<em>{0.1}$Fe$</em>{2.9}$O$_4$</td>
<td>PMN-PT</td>
<td>5100</td>
<td>36</td>
<td>68</td>
<td>270</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>PMN-PT</td>
<td>5100</td>
<td>100</td>
<td>114</td>
<td>480</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>PZT</td>
<td>5100</td>
<td>90</td>
<td>110</td>
<td>590</td>
</tr>
</tbody>
</table>

Static ME coupling of the multiferroic heterostructures was studied by electrostatically induced changes in magnetic hysteresis loops. This was achieved by applying an electric field across the thickness of the substrates. Imposing a strain on a magnetic material by a mechanical stress alters the magnetization and changes the shape of hysteresis loops; therefore, through electric field induced stress/strain by piezoelectric effect, magnetization manipulation can be realized. As shown in Fig 3.11 and Fig 3.12, the in-plane magnetization process of the ZFO/PMN-PT, Fe$_3$O$_4$ on PZT and PMN-PT multiferroic composite
displayed an electric field dependence of the magnetic hysteresis loops. This was also the case for the rest multiferroic composites.

Fig 3.11: Magnetic hysteresis loops and remanence changes while external magnetic fields are along (a) the compressive stress direction [1 0 0] (d31) of ZFO/PMN–PT and (b) the tensile stress direction [0 1−1] (d32) of ZMFO/PMN–PT [14].
Fig 3.12: Magnetic hysteresis loops and remanence changes with external magnetic fields along the compressive stress direction (d31=d32<0) of Fe₃O₄/PZT (a), compressive stress direction [01-1] (d31) of Fe₃O₄/PMN-PT (b), and tensile stress direction [100] (d32) of Fe₃O₄/PMN-PT (c) [14].
In addition, the (011) cut PMN-PT single-crystal slab has large anisotropic in-plane piezoelectric coefficients of $d_{31}$ and $d_{32}$, which could generate in-plane compressive stress along [100] ($d_{31}$) and tensile stress along [01-1] ($d_{32}$) while applying electric field parallel to [011] ($d_{33}$) direction. The ZFO ferrite on PMN-PT displayed a remarkably different magnetization process when it was magnetized along the two in-plane orthogonal directions [01-1] and [100] of the PMN-PT slab, which was reflected by the opposite trend of electric field dependence of the magnetic hysteresis loops and remanence vs. electric field “butterfly” curves, as shown in Fig 3.11. The remanence was minimized to ~44% at an electric field of 8kV/cm and maximized to ~62% at 0 kV/cm when the external magnetic field was applied along the PMN-PT [100] ($d_{31}$) direction. However, when the external magnetic field was applied parallel to the PMN-PT [01-1] ($d_{32}$) direction, the remanence was maximized to be about 59% at an electric field of +8 kV/cm and minimized to be 49% at 0 kV/cm. The Fe$_3$O$_4$ ferrite on PMN-PT also displayed a remarkably different magnetization process when it was magnetized along the two in-plane orthogonal directions [01-1] and [100] of the PMN-PT slab as demonstrated in the “butterfly” curves shown in Fig 3.12 (b) and (c). The remanence was minimized to ~45% at an electric field of +2 kV cm$^{-1}$ and maximized to ~66% at -8 kV cm$^{-1}$ when the external magnetic field was applied along the PMN-PT [01-1] ($d_{32}$) direction. However, when the external magnetic field was applied parallel to the PMN-PT [100] ($d_{31}$)
direction, the remanence was maximized to about 70% at an electric field of +2 kV cm\(^{-1}\) and minimized to 40% at -8 kV cm\(^{-1}\). It is notable that the anisotropic in-plane electric field induced remanence change from 40% to 70% for the Fe\(_3\)O\(_4\)/PMN-PT is much larger than the in-plane isotropic remanence change for the Fe\(_3\)O\(_4\)/PZT.

The magnetoelectric interactions and magnetic tunability at microwave frequencies for the spin-spray derived multiferroic heterostructures were demonstrated by an electrostatic field induced in-plane magnetic anisotropy field \(H_{\text{eff}}\) which resulted in a ferromagnetic resonance field shift at X-band (9.5 GHz). Depending upon whether the \(H_{\text{eff}}\) is parallel or perpendicular to the applied external magnetic field, the FMR field could be tuned up or down by electric field. The in-plane FMR frequency can be expressed by the well known Kittel equation:

\[
f = \gamma \sqrt{(H_r + H_k + H_{\text{eff}})(H_r + H_k + H_{\text{eff}} + 4\pi M_s)} \tag{3.1}
\]

where \(g\) is the gyromagnetic ratio, \(H_r\) is the FMR field, \(H_k\) is the in-plane anisotropy field, and \(4\pi M_s\) is the magnetization. \(H_{\text{eff}}\) is the orthogonal in-plane compressive and tensile stress corporately induced internal effective magnetic field which could be positive or negative, and can be expressed as

\[
H_{\text{eff}} = \frac{3\lambda_S \sigma}{M_s} \tag{3.2}
\]
where $\sigma$ is compressive or tensile stress generated by electric field $E$ and $\lambda_s$ is the saturate magnetostriction constant. A microwave cavity operating at TE$_{102}$ mode at X-band (9.5 GHz) was used to perform FMR measurements of the ferrite/ferroelectric multiferroic composites. The external bias magnetic field was applied in the ferrite film plane along the [100] or [01-1] direction of the single crystal PMN-PT and PZN-PT substrates, respectively, with microwave RF field being in-plane and perpendicular to the DC bias field. As shown in Fig 3.13 (a), a giant microwave ME interaction was observed in the Fe$_3$O$_4$/PMN-PT, which resulted in a record-high tunable FMR field range from 1185 Oe to 1786 Oe, or $\delta H_r$=600 Oe, when the electric fields across the PMN-PT thickness were changed from 3 kV cm$^{-1}$ to -6 kV cm$^{-1}$ and when the external magnetic field was applied along the [100] ($d_{31}$) direction of PMN-PT. This corresponded to a high microwave ME coupling coefficient of 67 Oe cm kV$^{-1}$. An even greater electrostatically tunable FMR field range of 860 Oe, with a linewidth of 330-380 Oe was demonstrated in Fe$_3$O$_4$/PZN-PT heterostructure as shown in Fig 3.13(b), when the external magnetic fields were applied along the in-plane [100] direction ($d_{31}$=-3000 pC/N) and the external electric fields were applied across the thickness of PZN-PT substrate starting from 0 kV/cm to 8 kV/cm. This corresponded to a record-high ME coupling coefficient of 108 Oe cm /kV. Compared to the Fe$_3$O$_4$/PZN-PT, the FMR linewidth was reduced from $\Delta H$=480-620 Oe in Fe$_3$O$_4$/PMN-PT to $\Delta H$=330-380 Oe in Fe$_3$O$_4$/PZN-PT, which lead to a
significantly enhanced ratio of tunable FMR field over FMR linewidth of 2.5. In the ZFO/PMN-PT multiferroic heterostructure, a large upward shift of the ferromagnetic resonance field $\delta H_r = 140$ Oe was observed, corresponding to a magnetoelectric coefficient of 23 Oe cm/kV when external magnetic fields were applied along the PMN-PT [100] ($d_{31}$) (compressive) direction, and electric fields were applied across the PMN-PT thickness from 0 kV/cm to 6 kV/cm. This upward shift of the ferromagnetic resonance field can be explained by an electric field induced compressive stress which resulted in a negative anisotropy filed ($\lambda_a \sigma < 0$). In contrast, a downward shift of the ferromagnetic resonance field $\delta H_r = -100$ Oe was observed when external magnetic fields were applied along PMN-PT [01-1] ($d_{32}$) (tensile) direction, corresponding microwave ME coefficient of 18 Oe cm/kV. Both of them had FMR linewidth of 270 Oe at zero electric field, which were suitable for microwave application.
Fig 3.13: FMR absorption spectra of the multiferroic composites under different electric fields.
Static electric field induced FMR field shifts were also investigated in the Fe$_3$O$_4$/PZT and NZFO/PMN-PT heterostructures as shown in Fig 3.13 (e) and (f), in which FMR field tunable range of 80 Oe and 50Oe were observed with FMR linewidths of 500 Oe and 350 Oe respectively. These strong microwave ME interactions, which resulted in large FMR field tunability at microwave frequencies, could lead to novel ME devices.

The FMR field of the Fe$_3$O$_4$/PZT and Fe$_3$O$_4$/PMN-PT multiferroic composites exhibited the characteristic “butterfly” shape in their FMR field vs. electric field curves as shown in Fig 3.14, which coincided with the ferroelectric hysteresis loops of the PZT and PMN-PT respectively. This once again confirmed that the change of FMR field of the Fe$_3$O$_4$ film was resulted from the electric-field induced stress in piezoelectric and ferrite film.

Fig 3.14: “Butterfly” curves of resonance fields vs. electric fields and ferroelectric hysteresis loops of multiferroic composite Fe$_3$O$_4$/PZT (a) and Fe$_3$O$_4$/PMN-PT (b) [14].
It can be concluded from equation (3.1) that the FMR frequency in the Fe$_3$O$_4$/PMN-PT and Fe$_3$O$_4$/PZN-PT can be shifted upward or downward, depending on whether the applied magnetic field is parallel or perpendicular to the effective magnetic field induced by the electric field across the (011) cut PMN-PT or PZN-PT, which is a natural result of the anisotropic piezoelectric coefficient of the (011) cut PMN-PT and PZN-PT. Considering the anisotropic in-plane piezoelectric coefficients of the (011) cut PMN-PT and PZN-PT, which can generate orthogonal tensile and compressive stresses under an electric field, a new concept is introduced that FMR frequency could be tuned up or down and achieve a larger tunable range by applying the external magnetic field parallel to [100] (d$_{31}$) or [01-1] (d$_{32}$) direction of the (011) cut PMN-PT and PZN-PT. This concept was demonstrated in the Fe$_3$O$_4$/PZN-PT and Fe$_3$O$_4$/PMN-PT multiferroic composites as shown in Fig 3.14 and 3.15 respectively.
Fig 3.15: Ferromagnetic resonance absorption spectra shifts while the external magnetic field along tensional (a) and compressive (b) directions of PZN-PT. c) The cooperation of magnetic orientation and electric field generated resonance field change shift is up to 1450 Oe [14].
Fig 3.16: Ferromagnetic resonance absorption spectra shifts while the external magnetic field along tensional (a) and compressive (b) directions of PMN-PT. c) The cooperation of magnetic orientation and electric field generated resonance field change shift is up to 1000 Oe [14].
As shown in Fig 3.15 and 3.16, an external magnetic field applied along the [01-1] direction led to a reduced FMR field of 750 Oe (Fig 3.15 (a)) and 1200 Oe (Fig 3.16(a)) in the Fe$_3$O$_4$/PZN-PT and Fe$_3$O$_4$/PMN-PT multiferroic composites respectively. When the external field was parallel to the [100] direction, the FMR fields were shifted up to 2200 Oe (Fig 3.15 (b) and 3.16(b)). Each of them had the same resonance field of 1680 Oe at zero electric field due to the in-plane isotropic magnetic property of the Fe$_3$O$_4$ film. The total resonance field shift was $H_r=1450$ Oe when the external magnetic field was applied to be parallel to [100] and [01-1] direction (Fig 3.15(c)) for the Fe$_3$O$_4$/PZN-PT multiferroic composite and $H_r=1000$ Oe (Fig 3.15(c)) for the Fe$_3$O$_4$/PMN-PT multiferroic composite. This constitutes a simple but effective approach for achieving twice the tunable FMR frequency range, leading to new opportunities of electrostatically tunable magnetic device design with large effective magnetic field tunability.

### 3.2 High Permeability in GHz Range

High frequency operation of soft magnetic materials have recently received much attention in the microwave and telecommunications industries [16], [17]. Ferrite materials are one of the most widely used materials due to their high permeability and high resistivity at high frequency range, more so in thin film form which provides a unique opportunity for microwave device application in GHz range due to the
strong demagnetization factor associated with such geometry. Various conventional techniques like sputtering, molecular beam epitaxy, pulsed laser deposition, etc exists for the fabrication of thin films. However, unlike the other processes, the spin spray deposition process is a low temperature (<100°C), high deposition rate (40~100 nm/minute), direct deposition process that is compatible with substrates like plastics, organic materials, RFIC and MMIC, etc [18]-[20]. Spin spray deposited thin ferrite films exhibit an enhanced Snoek limit by about one order of magnitude over their bulk counterparts, excellent microwave magnetic properties at GHz frequencies under self-bias condition [17], [20], [21], and have been used in different microwave devices such as antennas and filters operating in the GHz range [22]-[24]. Spin spray deposited NiZn-ferrite which is a great candidate for high frequency applications due to its high permeability, resistivity and saturation magnetization [25], [26], only show an application frequency < 300 MHz [20], [21].

The present work reports on spin-spray deposited Ni_{0.27}Zn_{x}Fe_{2.73-x}O_{4} (with x = 0.03-0.1) thin films with high real permeability $\mu'_r$ in the GHz range. The ferrite films were fabricated onto glass substrates in the presence of an external magnetic field of 360 Oe. These films exhibit high permeabilities that exceeded the Snoek limit for bulk NiZn-ferrite films and those previously reported for spin spray deposited ferrites. The NiZn-ferrite film with x=0.06 is low in magnetic losses, having $\tan\delta_m (\mu''/\mu'_r) \sim 0.027$ from 1 to 1.5 GHz, and a high ferromagnetic resonance (FMR)
frequency of 2.7 GHz, while the x=0.1 film exhibited a high $\mu_r'$ of ~50 and $\mu_r'' > 50$ at 1 GHz. These properties are ideal for microwave applications such as antennas, inductors and electromagnetic interference (EMI) suppression in the GHz range.

$\text{Ni}_{0.27}\text{Zn}_x\text{Fe}_{2.73-x}\text{O}_4$ (with $x = 0.03$, 0.06 and 0.1) films of ~0.7 $\mu$m thicknesses were fabricated at 90$^\circ$C using the spin spray process on to commercially available 0.1 mm thick glass substrates in the presence of an external magnetic field of 360 Oe. An oxidation solution containing 2 mM NaNO$_2$ and 17.5 mM CH$_3$COONa with a pH value of 8 to 9 and a precursor solution of NiCl$_2$+ZnCl$_2$+FeCl$_2$ with a pH value of 4 to 5 were sprayed simultaneously. The growth rate was ~40 nm/min. A detailed description of the spin spray deposition process is reported in chapter 2. Crystallographic and composition analyses of the films were done 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 $M$-$H$ loops were measured using a vibrating sample magnetometer (VSM), with an external magnetic field applied in-plane (easy and hard magnetic axis) and out of plane to the film axis. The complex permeability spectra of the films were measured using a broad band measurement technique which consists of a custom made permeameter using a coplanar waveguide connected to a network analyzer with a bandwidth of 0.045-10 GHz. Permeability calibration was done using a CoZrTa film with a known magnetization, in-plane anisotropy field and initial permeability.
The films show a pure polycrystalline spinel NiZn-ferrite phase, with no obvious preferential orientations, as typically shown in Fig 3.17(a). AFM images showed tightly packed atomic structures with grain size of about 0.1~0.3 µm and film roughness of about 100 nm. The surface SEM images also confirm tightly packed atomic structures with zero stress patterns (cracks) and growth defects present on the surface of the NiZn films. The surface SEM image for film 2 with x=0.06 is shown in Fig 3.17 (b) and is almost the same for films 1 and 3 with x=0.03 and 0.1 respectively.

Fig 3.17: (a) XRD pattern, (b) Surface SEM image of NiZn ferrite film with x=0.06 [28].
The films were magnetically isotropic in the inplane (easy and hard magnetic axis) direction, with no appreciable difference in the $M-H$ loops but exhibited magnetic anisotropy in the inplane and out of plane $M-H$ loops. As seen in table 3.2, the saturation magnetization, $M_s$, obtained from the $M-H$ loops decreases as Zn increases in concentration due to the increase in the ratio of the non-magnetic regions in the film, while coercivity however remains almost unchanged from $x=0.03$ to $x=0.06$ but decreased from $x=0.06$ to $x=0.1$ [20], [21], [27].

Table 3.2: Film composition and magnetic properties (saturation magnetization, $M_s$, inplane coercivity, $H_c$, real permeability at 300 MHz, $\mu_r'$, and FMR frequency, $f_r$) of the NiZn ferrite thin films [28].

<table>
<thead>
<tr>
<th>Film Composition</th>
<th>$M_s$ (emu/cc)</th>
<th>$H_c$ (Oe)</th>
<th>$\mu_r'$</th>
<th>$f_r$ (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 Ni$<em>{0.27}$Zn$</em>{0.03}$Fe$_{2.7}$O$_4$</td>
<td>557</td>
<td>21</td>
<td>66</td>
<td>2.8</td>
</tr>
<tr>
<td>#2 Ni$<em>{0.27}$Zn$</em>{0.06}$Fe$_{2.67}$O$_4$</td>
<td>517</td>
<td>22</td>
<td>110</td>
<td>2.7</td>
</tr>
<tr>
<td>#3 Ni$<em>{0.27}$Zn$</em>{0.1}$Fe$_{2.63}$O$_4$</td>
<td>358</td>
<td>11</td>
<td>150</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The initial permeability $\mu_{ri}$ at 300 MHz increases drastically from 66 to a very high 150 as $x$ increases from 0.03 to 0.1 but the FMR frequency
decreases from a high 2.8 GHz to 1.0 GHz as shown in table 3.2 and Fig 3.18 (a) to (c). This is because the anisotropy field, $H_k$, decreases more rapidly than the Ms of the films with increasing Zn concentration [27].

Fig 3.18: Permeability spectra of (a) $x=0.03$, (b) $x=0.06$, (c) $x=0.1$, NiZn ferrite films (d) $x=0.06$ (fabricated without an external magnetic field) NiZn ferrite film [28].
Fig 3. 19: Real permeability and resonance frequency of present NiZn ferrite bulk films compared with those of our NiZn ferrite thin films and previously published NiZn and NiZnCo (Nickel Zinc Cobalt) ferrite films (ref. 21 and 20 respectively).

It is noteworthy that these thin NiZn ferrite films can exhibit much higher FMR frequency and higher permeabilities at frequencies > 100 MHz than their bulk counterparts as well as those previously reported for spin spray deposited NiZn and NiZnCo (nickel zinc cobalt) ferrites as seen in Fig 3.19. The film with x = 0.06 showed a very high $\mu_r'$ of 100 up to 1 GHz (~ 50 times greater than that for bulk NiZn ferrite film) and >40 up to 2.7 GHz as seen from Fig 3.18 (b). Also, this NiZn film exhibited low magnetic losses, having $\tan\delta_m (\mu_r''/\mu_r')$ ~0.027 at 1 to 1.5 GHz. The x=0.1 film exhibited an extremely high $\mu_r' > 100$ up to 600 MHz and a high $\mu_r'$ of
~50 (which exceeds the Snoek’s limit of bulk NiZn films at 1 GHz by a factor of ~20) and \( \mu_r'' > 50 \) at 1 GHz as seen in Fig 3.18 (c). The \( \mu_r' \) spectrum of the NiZn films exhibited two peaks, more prominent in the \( x = 0.06 \) film, at 600 MHz and about 2.1 GHz. Fig 3.18 (d) shows the permeability spectra of the film with \( x=0.06 \) fabricated under the same processing conditions but without an external magnetic field. This film displayed a much lower initial \( \mu_r' \approx 41 \) at 300 MHz and an FMR frequency of 1.2 GHz compared to that fabricated in the presence of a magnetic bias field of 360 Oe. Clearly the strong magnetic bias field applied during the fabrication process may be responsible for the improved microwave magnetic properties in NiZn-ferrite films.

These properties are very useful for EMI suppression and also applicable to microwave devices such as antennas and inductors in the GHz range.
Reference


Chapter 4: Spin-spray Deposited Ferrite/Non-magnetic Multilayers

Bulk RF/microwave ferrite materials suffer from limited operating frequency (< 600 MHz) under self-bias condition (i.e. at zero bias magnetic fields) due to their well known Snoek’s limit. Spin-spray deposited ferrite thin films exhibit high permeabilities and high ferromagnetic resonance (FMR) frequency >5 GHz, exceeding the Snoek’s limit for bulk ferrite films [1-5]. One unique feature of spin-spray processing is its very low processing temperature (<100°C), which is much lower than that of other conventional ferrite synthesis processes (e.g. sputtering, molecular beam epitaxy, pulsed laser deposition, etc) requiring very high temperatures >600°C. This makes it is compatible with substrates like plastics, organic materials, RFIC and MMIC, etc. [6, 7].

Significantly enhanced performances have recently been reported in patch antennas, phase shifters and bandpass filters loaded with 2 µm thick spin-spray deposited ferrite films under self-bias conditions [8-10]. These performance enhancements in the ferrite film loaded RF/microwave devices could be further improved with thicker ferrite film loading. However, thick ferrite films with a high permeability, narrow ferromagnetic resonance linewidth and low magnetic loss tangent have been difficult to achieve. This is due to the degraded film quality caused by stress accumulation in thick ferrite films, the high out-of-plane anisotropy...
associated with their columnar polycrystalline microstructure, and their high eddy currents loss that degrade their RF performance. Ferrite/non-magnetic multilayers serve as a good approach to reducing the above problems associated with thick ferrite films. The non-magnetic insulating layer effectively relieves stress build up in the ferrite layer by interrupting the continuous growth of its out-of-plane columnar structure and could also reduce the eddy currents thus, leading to thick ferrite films with improved RF performance.

Metallic magnetic/non-magnetic multilayers have gained a lot of attention in the last several decades. Clow et al. [11] was the first to observe significantly reduced coercivity by 1 order of magnitude in Permalloy/SiO\textsubscript{x} multilayers, which was attributed to the reduced domain wall energy associated with the antiparallel magnetization in the multilayers. Slonczewski et al. [12] established the micromagnetics theory of magnetic/non-magnetic multilayers. He also predicted and experimentally demonstrated magnetic edge closure walls in metallic magnetic/non-magnetic multilayers that are ideal for self-biased RF/microwave magnetic devices. Besides reduced coercivity, metallic magnetic/insulator multilayers also exhibit significantly reduced eddy current loss and narrow FMR linewidth, providing great opportunities for performance enhancement in different integrated RF/microwave magnetic devices such as inductors, etc [13].
Similar to metallic magnetic/insulator multilayers, enhanced RF magnetic properties and reduced coercivity have been expected in ferrite/non-magnetic multilayers, but have not been reported. Abe et al. [14] reported on ferrite/organic multilayers of Ni-Zn ferrite/Dextran deposited on glass substrate for microwave integrated circuits by spin-spray deposition. These multilayers, however, exhibited degraded properties with increased coercivity and much broader FMR linewidth compared to their single layer counterparts.

In this work, ferrite/non-magnetic multilayer films with different ferrite compositions, thicknesses as well as numbers of periods were prepared by a low-temperature spin-spray deposition process, and their microstructure and magnetic properties were extensively characterized. All two-period ferrite/non-magnetic multilayers exhibited enhanced microwave magnetic properties compared to their single-layer ferrite film counterparts with the same composition and thickness; including reduced coercivity, narrower ferromagnetic resonance linewidth and enhanced permeability. The two-period \( \text{Ni}_{0.27}\text{Zn}_{0.3}\text{Fe}_{2.43}\text{O}_4/\text{Al}_2\text{O}_3/\text{Ni}_{0.27}\text{Zn}_{0.3}\text{Fe}_{2.43}\text{O}_4 \) multilayer exhibited a ferromagnetic resonance linewidth of 248 Oe at X-band, which was \(~15\%\) less than that of the single layer \( \text{Ni}_{0.27}\text{Zn}_{0.3}\text{Fe}_{2.43}\text{O}_4 \) film; and the \( \text{Fe}_3\text{O}_4/\text{Photoresist/Fe}_3\text{O}_4 \) multilayer showed \(~25\%\) enhancement in the initial permeability over its single-layer counterpart. The spin-spray deposited ferrite/non-magnetic multilayers constitute a unique approach to achieving thick (10 µm) ferrite films with enhanced RF/microwave
magnetic properties at a low temperature, which provide great opportunities for integrating thick ferrite films on RF integrated circuits and monolithic microwave integrated circuits.

\[ \text{Ni}_{0.27}\text{Zn}_{0.3}\text{Fe}_{2.43}\text{O}_4 \] (NZFO)/\text{Al}_2\text{O}_3/\text{Ni}_{0.27}\text{Zn}_{0.3}\text{Fe}_{2.43}\text{O}_4 \] and single layer NZFO thin films were fabricated at 90\(^\circ\)C by spin spray deposition onto commercially available 0.1mm thick alumina substrates. An oxidation solution containing 2mM NaNO\(_2\) and 140mM CH\(_3\)COONa with a pH value of 8-9 and a precursor solution of 0.58 mM Ni\(^{2+}\), 0.85 mM Zn\(^{2+}\) and 6.02 mM Fe\(^{2+}\) with a pH value of 4-5 were utilized. The growth rate was \(~40\text{nm/min}.\) A detailed description of the spin spray deposition process is available in chapter 2. After an approximate thickness of 0.6 \(\mu\)m, one of the substrates was taken out and 100 nm of Al\(_2\)O\(_3\) was deposited onto it using reactive dc sputtering in argon and oxygen at room temperature [15]. Another layer of NZFO was then deposited onto this insulating layer to complete the ferrite/non-magnetic multilayer film structure with a total thickness of \(~1.2\ \mu\)m. The second alumina substrate was left on to obtain a 1.2 \(\mu\)m thick homogenous single layer NZFO film which served as the NZFO control sample. The Fe\(_3\)O\(_4\)/Photoresist (PR)/Fe\(_3\)O\(_4\) multilayer films were also fabricated using the same process with the same processing conditions as described above but with a precursor solution containing 10 mM Fe\(^{2+}\) and a pH of 4-5. A thin layer of PR was deposited by spin coating at 2500 rpm for 30 seconds and then annealed at 100\(^\circ\)C for 10 min to form a 60 nm non-magnetic layer. Fe\(_3\)O\(_4\)/PR/Fe\(_3\)O\(_4\) sandwich structure.
and Fe$_3$O$_4$ single layer with a thickness of 1.4 µm were made on glass substrates. Much thicker multilayer films of Fe$_3$O$_4$/PR/Fe$_3$O$_4$, \{Fe$_3$O$_4$/PR\}$\times$4 multilayers and Fe$_3$O$_4$ single layers with total thicknesses of 10 µm were spin spray deposited onto 25 mil thick Roger’s RT/duroid 5880 dielectric substrates with a dielectric constant $K= 2.2$. All films exhibited strong adhesion to the substrates.

Chemical composition and crystal structure analyses of the films were done by x-ray diffraction (XRD) with a Cu K$_\alpha$ source ($\lambda=1.541$ Å), scanning electron microscope (SEM) and atomic force microscope (AFM) using contact force mode. AFM images were processed with Pico images to extract the height profile, which was used as a measure of the surface roughness. The magnetic properties of the films were measured using a vibrating sample magnetometer (VSM), with an external magnetic field applied parallel (inplane) and perpendicular (out of plane) to the film plane. The FMR spectrum of the films was determined using an electron paramagnetic resonance (EPR) system operating at X-band (9.6 GHz) with an external magnetic field applied parallel to the film plane, while the complex permeability spectra of the films were measured using a broad band custom-made permeameter consisting of a coplanar waveguide connected to a network analyzer with a bandwidth of 0.045-10 GHz. Permeability calibration was done using a Co-Zr-Ta film with a known magnetization, in-plane anisotropy field and initial permeability.
All samples demonstrated well defined $M-H$ loops when an external magnetic field was applied in-plane and out of plane to their film axis. A summary of the magnetic properties of the films is shown in table 1. The 2-period ferrite/non-magnetic multilayers all displayed reduced coercivities ($H_c$) compared to their single layer counterparts with the same total thicknesses, most prominent in the 10 µm Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer which showed ~14% reduction in $H_c$ from 96 Oe in the multilayer to 111 Oe in the Fe$_3$O$_4$ single layer. In contrast, the 4-period {Fe$_3$O$_4$/PR}$\times4$ multilayer film exhibited ~26% increased $H_c$ compared to the single layer counterpart, as seen in Fig 4.1. The XRD patterns of the 10 µm films are shown in Fig 4.2. The 10 µm single layer Fe$_3$O$_4$ film demonstrated a pure Fe$_3$O$_4$ phase with the (311) diffraction peak being the strongest, which is consistent with the standard powder diffraction data showing no obvious texture, whereas the Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer structure displayed a well defined (220) fiber texture with a single (220) diffraction peak. Conversely, {Fe$_3$O$_4$/PR}$\times4$ multilayer exhibited secondary phases besides the major phase of Fe$_3$O$_4$. The reason why the 2-period Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer shows a (220) texture is still under investigation. The increased $H_c$ of the 4-period Fe$_3$O$_4$/PR/Fe$_3$O$_4$ film is attributed to the presence of secondary phases Fe$_2$O$_3$ as observed in its XRD pattern.
Fig 4.1: Inplane magnetic hysteresis loops of the 10 µm Fe₃O₄ single layer, Fe₃O₄/PR/Fe₃O₄ and {Fe₃O₄/PR}×4 multilayers, and (Inset) enlarged inplane loops of the 10 µm films.
Table 4.1: Summary of film structure and magnetic properties (saturation magnetization, $M_s$, coercivity, $H_c$, real permeability at 300 MHz, $\mu'_r$, ferromagnetic resonance (FMR) frequency, $f_r$, and FMR linewidth $\Delta H$ at X-band (9.6 GHz)) of the ferrite/non-magnetic multilayers and the single layer films.

<table>
<thead>
<tr>
<th>Film Structure</th>
<th>Thickness ($\mu$m)</th>
<th>$M_s$ (emu/cm$^3$)</th>
<th>$H_c$ (Oe)</th>
<th>$\mu'_r$ (GHz)</th>
<th>$f_r$ (GHz)</th>
<th>$\Delta H$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$ Single</td>
<td>10</td>
<td>318</td>
<td>111</td>
<td>8</td>
<td>1.2</td>
<td>618</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PR/Fe$_3$O$_4$</td>
<td>10</td>
<td>318</td>
<td>96</td>
<td>10</td>
<td>1.3</td>
<td>589</td>
</tr>
<tr>
<td>(Fe$_3$O$_4$/PR)x4</td>
<td>10</td>
<td>302</td>
<td>140</td>
<td>5</td>
<td>2.1</td>
<td>1398</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ Single Layer</td>
<td>1.4</td>
<td>398</td>
<td>134</td>
<td>9</td>
<td>1.1</td>
<td>528</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/PR/Fe$_3$O$_4$</td>
<td>1.4</td>
<td>398</td>
<td>118</td>
<td>10</td>
<td>1.2</td>
<td>464</td>
</tr>
<tr>
<td>NZFO Single Layer</td>
<td>1.2</td>
<td>263</td>
<td>23</td>
<td>19</td>
<td>0.9</td>
<td>292</td>
</tr>
<tr>
<td>NZFO/Al$_2$O$_3$/NZFO</td>
<td>1.2</td>
<td>279</td>
<td>21</td>
<td>20</td>
<td>1.0</td>
<td>248</td>
</tr>
</tbody>
</table>
Ferromagnetic resonance (FMR) linewidth is an important figure of merit for RF/microwave magnetic materials. A lower FMR linewidth corresponds to a lower magnetic loss tangent at a specific operating frequency which is desired for RF/microwave magnetic devices. Conventional microwave spinel ferrites have FMR linewidth values ranging from 100 - 500 Oe at X-band. Similar to the $H_c$ values, the peak-to-peak FMR linewidth results of the two-period multilayers show reduced FMR linewidth values compared to their single layer counterparts; whereas the $\{\text{Fe}_3\text{O}_4/\text{PR}\}\times4$ multilayer exhibited a much broader FMR linewidth, as
shown in table 1. The NZFO/Al₂O₃/NZFO multilayer film displayed an inplane FMR linewidth of 248 Oe, which is 44 Oe (15%) less than that of the single layer NZFO (292 Oe) as shown in Fig 4.3(a). On the other hand, the {Fe₃O₄/PR}×4 multilayer displayed a considerably increase in FMR linewidth of 1398 Oe, which is more than twice the FMR linewidth of the single layer as seen in Fig 4.3(b).

It is notable that the reduction in the FMR linewidth of the multilayers shows a dependence on the ferrite layer thickness. As the ferrite layer thickness is increased, the FMR linewidth of the two-period multilayers approached that of the single layer. The Fe₃O₄/PR/Fe₃O₄ multilayer with a total layer of 10 µm demonstrated an FMR linewidth of 589 Oe, just 5% narrower than that of the 10 µm Fe₃O₄ single layer, unlike the 1.4 µm Fe₃O₄/PR/Fe₃O₄ multilayer that demonstrated a ~12% decrease in FMR linewidth compared to the single layer counterpart.
Fig 4.3: FMR absorption spectra (a) 1.4 µm NZFO single and NZFO/PR/NZFO multilayer on alumina substrate, and (b) 10 µm Fe$_3$O$_4$ single layer, Fe$_3$O$_4$/PR/Fe$_3$O$_4$ and (Fe$_3$O$_4$/PR)$\times4$ multilayers (with $\times4$ magnitude for (Fe$_3$O$_4$/PR)$\times4$ multilayer for clarity).
Enhanced permeability values were demonstrated for all 2-period multilayers over the single layers. The values of the real permeabilities of the films obtained at 300 MHz are given in Table 1. As shown in Fig 4.4, the 10 µm thick Fe₃O₄/PR/Fe₃O₄ multilayer displayed 25% enhancement over the 10µm Fe₃O₄ single layer. However, the {Fe₃O₄/PR}×4 multilayer displayed a 38% decrease in permeability values but a 75% increase in FMR frequency over the Fe₃O₄ single layer. Also, the {Fe₃O₄/PR}×4 multilayer exhibited an imaginary permeability, µᵣᵣ >8 in a wide band from 900 MHz-5 GHz which makes it very useful for EMI suppression in the GHz range.
Fig 4.4: I) Real and (II) imaginary permeability components of the 10 µm Fe$_3$O$_4$ single layer, Fe$_3$O$_4$/PR/Fe$_3$O$_4$ and {Fe$_3$O$_4$/PR}x4 multilayers.
Microstructural analysis on the multilayer samples were also carried out using the SEM and AFM, as shown in Fig 4.5 and 4.6. Examining the cross-section SEM images of the 10 µm samples in Fig 4.5(a)-(c), one can see well defined layers in the films. The PR layer was not discernable in the SEM image of the 10 µm samples but was obvious in the 1.4 µm Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayer where the substrate, glass, is much smoother and the ferrite layer is thinner than the 10 µm samples as seen in Fig 4.5(d). Fig 4.5(c) indicates a possible structure collapse in the \{Fe$_3$O$_4$/PR\}$\times$4 multilayer where the third and fourth layers combine together to form a layer with more than twice the thickness of the other two ferrite layers. The AFM images in Fig 4.6 (a)-(c) show that the 10 µm single ferrite and two-period multilayer films have similar morphology as well as surface roughness with particle sizes of 2.23+/-0.43 µm and 2.16+/-0.55 µm respectively. On the other hand, the \{Fe$_3$O$_4$/PR\}$\times$4 multilayer demonstrated a very different morphology with big clusters of 6.34+/-1.95 µm (~3 times larger in diameter) particle size. The difference in surface morphology and the presence of the secondary phase in the \{Fe$_3$O$_4$/PR\}$\times$4 multilayer are probable reasons for the degraded microwave magnetic properties. This again confirms that it is difficult to achieve ferrite/non-magnetic multilayers with more periods by spin spray deposition method [12].
Fig 4.5: Scanning electron microscope (SEM) images of 10 µm (a) Single layer Fe₃O₄, (b) Fe₃O₄/PR/Fe₃O₄ multilayer, (c) {Fe₃O₄/PR}x4 multilayer on Roger’s material, and (d) 1.4 µm Fe₃O₄/PR/Fe₃O₄ multilayer on glass substrate showing the photoresist (PR) layer.
Fig 4.6: Atomic force microscope (AFM) images of 10 µm (a) Single layer Fe$_3$O$_4$, (b) Fe$_3$O$_4$/PR/Fe$_3$O$_4$, and (c) (Fe$_3$O$_4$/PR)x4 multilayers on Roger’s material.
This low temperature fabricated ferrite/non-magnetic multilayers with enhanced microwave magnetic properties provide a viable route for achieving thicker ferrite films loading in RF/microwave devices without suffering from degraded microwave magnetic properties.
Reference


Chapter 5: RF Applications of Spin-spray

Ferrites

5.1 Ground Plane Immunity Enhancement of Dipole Antennas at GHz Range

In current wireless communication systems, there is a growing need for low profile antennas due to their small size and light weight. Dipole antennas, which can be used as low profile antennas, have gained a lot of attention because of their geometrical simplicity, linear polarization and omnidirectional radiation pattern. However, these antennas do not operate efficiently when placed horizontally close (less than a quarter wavelength of the working frequency) to a PEC (perfect electric conductor) ground plane due to the destructive interference between the radiated fields of the dipole and that of the ground plane which leads to a decrease in the radiation efficiency of the dipole.

Investigations into a suitable ground plane for this low profile application have been reported [1]-[3]. PMC (perfect magnet conductor)-like structures such as mushroom-like structures [3] and electromagnetic band gap (EBG) structure which may provide a PMC effect with a 0° reflection phase [2] have also been looked into. However, the EBG structure, as a periodic structure, would be relatively large and not suitable for communication systems. Also, due to the constructive effect
requirement of the EBG structure (reflection phase must be within $\pm 90^\circ$), it is not appropriate for wide band applications.

On the other hand, wave absorbing materials, which can absorb the back wave radiation at a very wide bandwidth, may perhaps be a better alternative to this problem. The microwave absorbing phenomena of ferrite materials have been reported [4], [5]. We also recently proposed the use of self-biased NiCo ferrite materials for antenna miniaturization [6].

For the purpose of enhancing the ground immunity of the dipole antenna, we have developed lossy ferrite thin films ($\text{Fe}_3\text{O}_4$); fabricated by the low cost, low temperature spin spray process, onto transparency materials. The $\text{Fe}_3\text{O}_4$ thin films are of light weight and small volume (only 1.5 $\mu$m thick) and thus, will not add weight and volume to the communication system. They also exhibit a large transmission loss of about -2.4dB at 5GHz which makes them good candidates as wave absorbers in low profile antenna design. The designed lossy ferrite film was placed between the dipole antenna and the copper ground plane. The fabricated antennas loaded with $\text{Fe}_3\text{O}_4$ lossy ferrite films showed greatly enhanced ground immunity, the reflection coefficient of -24.6 dB and -20.8 dB were obtained at the central frequency of antenna with one layer and two layers of ferrite films loading, respectively.

The length and diameter of the dipole arm was $\sim$25mm and 1mm respectively. A quarter wavelength of coaxial cable was adopted as a simplifier balun between the dipole and the feeding line. A 220 mm×250
A 95 mm rectangular copper ground plane was placed under the dipole antenna. The schematic of the dipole antenna is shown in Fig 5.1.

![Figure 5.1: Geometry of dipole antenna with Fe₃O₄ films loaded between antenna and PEC ground plane. A×B=220mm×250mm, a×b=51mm×51mm, D=2mm [7].](image)

1.5 µm thick Fe₃O₄ films were deposited onto 51×51 mm transparency by the spin-spray process as described in chapter 2. The hysteresis loops of the Fe₃O₄ film were measured and showed a coercivity
of 82 Oe and 177 Oe for the inplane and outplane respectively. The in-plane resistivity of the film was 6.5 Ω.cm. To measure the lossy characteristics of our new ferrite films, a coplanar waveguide circuit with 50 Ohm impedance matching on both terminals was employed, as shown in Fig 5.2 (a), with one layer of Fe₃O₄-ferrite film coated above the coplanar circuit, which as shown in Fig 5.2 (b). The measured insertion loss at 5 GHz was ~2.4dB as seen in Fig 5.3, which means that almost half of the transmission energy will be absorbed at 5 GHz. So it is a good candidate of absorbing material for low profile antenna design with enhanced ground immunity.
Fig 5.2: Coplanar waveguide (CPW) (a) without the ferrite film loading, and (b) with one layer of ferrite film loading [7].
Under the low profile condition of 2mm, four dipole antennas were designed and analyzed; one without the Fe$_3$O$_4$ film and PEC ground plane, one without the Fe$_3$O$_4$ film but with PEC ground plane, one with the PEC ground plane and one layer of Fe$_3$O$_4$ thin film loading and the other with two layers of the Fe$_3$O$_4$ film beneath the dipole. The distance between the films and the dipole was 0.5 mm.

The reflection coefficients were measured with the dipole antenna at a fixed position, while the ground plane and Fe$_3$O$_4$ ferrite films were added at different positions. From Fig 5.4, we can see that the central resonant frequency of the non-magnetic antenna is about 5.1 GHz, and the -10 dB bandwidth is 582 MHz. When a copper ground plane was
added beneath the dipole antenna at a distance of 2 mm, the reflection coefficient deteriorated to a value of about -6.0 dB at the central frequency. This indicates that at a short distance of 2 mm, the mutual coupling between the dipole antenna and the ground plane is very strong. In order to reduce the mutual coupling between the antenna and the ground plane, one layer of Fe₃O₄-ferrite film was added just under the dipole antenna. We observed that the resonant frequency shifted to 4.72 GHz, with a slightly enhanced reflection coefficient magnitude of -24.6 dB, indicating the mutual coupling was reduced with loading of lossy ferrite film, and the antenna bandwidth was 465 MHz. When two layers of Fe₃O₄-ferrite films were added beneath the dipole antenna, the resonant frequency was ~ 4.85GHz, with an $S_{11}$ magnitude of -20.8 dB. The antenna bandwidth was about 374 MHz. Clearly, the antenna loaded with lossy ferrite films can indeed enhance the ground immunity between the dipole antenna and the ground plane effectively. In both cases, there were slightly frequency shift, which may be caused by the change of antenna surrounding, i.e. we added the ferrite film at a very short distance, the film itself was a kind of high permittivity material. Therefore effective electric length of dipole with ferrite film was a little bit longer than the dipole without ferrite films. This in turn will result in the frequency shift.
Fig 5.4: Measured reflection coefficient of the antennas with the ground plane 2mm from the dipole [7].

Since the Fe$_3$O$_4$-ferrite film was deposited on the transparency, two dipole antennas with transparency were designed and fabricated in order to analyze the influence of the transparency on the dipole antennas. The transparency was loaded beneath the dipole, at a distance of 0.5mm, just like in the case of the ferrite films. As shown in Fig 5.4, the reflection coefficient of antenna with transparency is about -6.5 dB. This clearly shows that dipole antennas with one layer or two layers of Fe$_3$O$_4$-ferrite films can improve the ground immunity effectively, while their transparency counterparts have almost nothing to do with the reflection coefficient.
Increasing the distance between the dipole antenna and the ground plane to 3 mm, the reflection coefficients of the antennas were measured. As shown in Fig 5.5, the reflection coefficient is was ~5.15GHz, with an S11 magnitude of -9.5 dB, for the dipole antenna without the ferrite film loading. When one layer or two layers of transparency were added beneath the dipole antenna, the resonant frequency did not change too much. When two one layer or layers of Fe₃O₄-ferrite films were added under the dipole antenna, the resonant frequencies were ~4.75GHz and 4.62GHz, respectively. The antenna bandwidth of these two dipole antenna with Fe₃O₄ ferrite films was 500 MHz. Obviously, the antenna loaded with lossy ferrite films can effectively enhance the ground immunity between the dipole antenna and the ground plane.
Fig 5.5: Measured reflection coefficient of the antennas with the ground plane 3mm from the dipole [7].

The antenna radiation characteristics were measured in an anechoic chamber with the same input power to the antenna. For the investigation of lossy effects, we measured the received power of the dipole antenna without ground plane, dipole with 1 layer of Fe$_3$O$_4$ film beneath the dipole, and 2 layers of Fe$_3$O$_4$ beneath the dipole. The measured radiation patterns were normalized with the dipole antenna without ground plane, and plotted in Fig 5.6. The received power was about 4.56 mW for the dipole antenna without ground plane. For the ferrite films loading, the received powers were 3.93 mW and 3.69 mW for the 1
layer of Fe₃O₄ film and 2 layers of Fe₃O₄ film, respectively. This shows that the radiation characteristics are not too affected by the ferrite loading.

Conclusively, a new lossy ferrite film was successful introduced into the design of low profile dipole antenna to enhance its ground immunity by effectively reducing the mutual coupling between the antenna and the ground plane. Since the Fe₃O₄-ferrite film is very thin, it will neither add weight nor volume to the RF front circuit.
5.2 Improved Performance in GPS Antennas on High-K Materials

Recent widespread use of handheld and wireless communications systems has increased the great demand for smaller, inexpensive antennas [8]. While these requirements can easily be achieved at high frequency bands by using microstrip patch antennas, it may be a design challenge at frequencies in L-band or even lower, due to the relatively large resonant length of the patch. GPS (Global Positioning System) is one such application, where dual frequency operation, bandwidth and circular polarization pose major challenges when using traditional miniaturization techniques [8]-[12]. One of the effective methods to reduce the geometry dimension is by utilizing high permittivity material as the substrate, i.e. using a substrate with a permittivity of 20 or even higher [13]. However, probe-fed antennas with high-K materials exhibit several difficulties, especially for the circular polarization antennas, which require an excitation of two near-degenerate orthogonal modes with equal amplitude and 90° phase difference. In order to be practically feasible in miniature antenna applications, such as handheld wireless communication devices, it is important for antenna substrates to be comprised of self-biased magnetic materials, in which no external bias magnetic field is needed. Magnetic thin films provide a unique opportunity for achieving self-biased magnetic patch antenna substrates with $\mu_r > 1$ at frequencies $>1$ GHz. Magneto-dielectric substrates with thin magnetic films show great
potential in realizing electrically small tunable antennas with improved directivity and higher bandwidth than those realized on dielectric substrates [11]. In this work, we introduce self-biased magnetic films as a practical means to tune a patch antenna by loading a commercially available dielectric substrate.

Novel antenna designs with self-biased ferrite films deposited on Rogers’s substrate and High-k substrate were investigated. These magnetic patch antennas have improved the axial ratio from 1.57dB to 0.97dB with respect to the central frequency ranging from 1.575GHz to 1.562GHz, a large radiation frequency tunability of about 40% to 80% of the -10dB bandwidth, and a significantly enhanced directivity.

The antenna consists of a rectangular patch with a slot on the right side, and the width of the narrow side of the slot is 0.254 mm, the length is 4.38 mm. A metallic side-wall is adopted to improve the antenna's directivity, with the same height as the dielectric substrate. A circular ground plane with the radius of 101.6 mm is added at the back of the dielectric substrate. The feed point is located on the 45° diagonal, with a distance of 0.38mm along the x-axis. The substrate has relative permittivity of 91.7 and a thickness of 1.0 mm. All the other parameters are listed in the caption of Fig 5.7 (a). 2 µm thick nickel cobalt (Ni0.23Co0.13Fe2.64O4) ferrite film was deposited on the substrates by the spin-spray process as described in chapter 2. Using a PVD (physical vapor deposition) system, a 2 µm copper layer was deposited on top of
the ferrite layer. Photolithography was then used to develop this copper into the desired patch antenna shape. Finally more copper was added for each of the antennas ground plane. Based on this process four different antennas were designed as shown in Fig 5.7 (b) to (e); one with the ferrite layer above the patch, the second with the ferrite layer below the patch, the third with the ferrite layer above the ground plane and finally with two layers of ferrite film below the patch and above the ground plane. A rectangular patch antenna without any ferrite layer was used as control.
Fig 5.7: Schematic of (a) top and side views of the slot patch antenna with high-K substrate, (b) antenna with magnetic film above the rectangular patch, (c) magnetic film beneath the patch, (d) magnetic film above the ground plane, and (e) magnetic film both above the ground plane and beneath the patch. The thickness of the film is $h = 2 \, \mu m$ [17].
In order to prove the validity of this project we first ran detailed HFSS simulations on our material. Fig 5.8(a) shows that the central resonant frequency of the antenna without films is \( \sim 1.573 \text{ GHz} \), while the \( S_{11} \) peak magnitude is -14.5 dB. When the ferrite film was added above the patch, the resonant frequency shifted down to 1.572 GHz. With the ferrite film beneath the patch, the resonant frequency is 1.573 GHz with a peak magnitude of -19.4 dB, indicating a better impedance matching. In the third case, with the ferrite film above the ground plane, the central resonant frequency is 1.568 GHz with a magnitude of 20.7 dB, a shift of 5 MHz relative to the non-magnetic antenna. Finally with the two films both above the ground plane and beneath the patch, the resonant frequency shifted further down to 1.569 GHz. Therefore the patch antenna combined with ferrite films can improve the impedance matching and shift down the resonant frequency. Also the radiation patterns of these antennas were calculated with the help of HFSS, as shown in Fig 5.8 (b) and (c). We can see that the radiations are unaffected by the ferrite films, thus proving that the miniaturization does not compromise the antenna gain.
In this section we have shown that the addition of a spin-spray ferrite layer to the fabrication of a high permittivity substrate patch antenna can help to improve the impedance matching and resonance problems that are generally associated with patch antennas on high dielectric substrates. We have also shown that the microstrip antenna can be minimized by shifting down the resonance frequency with magnetic film loading [7].

5.3 Tunable Miniaturized Patch Antennas

Achieving relative permeability larger than 1 ($\mu_r > 1$) in antenna substrates can lead to antenna miniaturization, enhanced bandwidth,
tunable center frequency, polarization diversity, and beam steering [16]–[18]. Bulk ferrite materials [19], composites of ferrite particles in polymer matrix, metamaterials with embedded metallic circuits, etc., have been used as antenna substrates for achieving $\mu_r > 1$. However, these bulk ferrite materials or ferrite composites are too lossy to be used at frequencies > 500 MHz under self-bias condition, i.e., no bias magnetic field is needed, and large biasing magnetic fields are needed for these magnetic antennas to operate at higher frequencies. In order to be practically feasible in miniature antenna applications, such as handheld wireless communication devices, it is important for antenna substrates to be comprised of self-biased magnetic materials. However, it has been challenging to achieve self-biased magnetic materials for antenna substrate applications at >500 MHz.

Magnetic thin films provide a unique opportunity for achieving self-biased magnetic patch antenna substrates with $\mu_r > 1$ [20]–[22] and operating frequencies > 1 GHz. The strong demagnetization field for magnetic thin films, $II_{\text{demag}} = 4\pi M_s$, and large in-plane anisotropy field allow for self-biased magnetization with high ferromagnetic resonance (FMR) frequencies up to several GHz, a necessary condition for operations in the cellular and WLAN bands.

In this section, we report on a patch antenna miniaturized using single layer and multilayer self-biased nickel cobalt (NiCo) ferrite thin films on alumina substrate, thus essentially creating a magneto-dielectric
substrate for practical applications. Three different magnetic patch antennas are fabricated by loading the antenna with multilayer ferrite thin films adjacent to the patch. These antennas show enhanced bandwidth and significantly enhanced antenna efficiency. The -5 dBic gain beamwidth is increased from 140° to 155°, 156°, and 160°, for the three magnetic antennas, showing significantly improved omnidirectional performance.

Magnetic patch antennas with self-biased NiCo-ferrite magnetic films were designed, fabricated and tested at 2.1 GHz. The geometry of the patch antenna, designed for operation at 2.1 GHz, is shown in Fig 5.9 (a) and (b). It is a conventional line-fed microstrip patch on an alumina substrate with a thickness of 2 mm. The relative permittivity of the alumina substrate is \(\varepsilon_r=9.9\) and the relative permeability is 1. The copper patch for this non-magnetic antenna has a length \(L_3 = 22.2\) mm, width \(W_3 = 30\) mm and thickness of 3 \(\mu\)m. The width of the feed-line is 2.0mm and the length is 22.3mm. All the dimensions are noted in the caption of Fig 5.9.
Fig 5.9: Geometry of the non-magnetic rectangular patch antenna. (a) Top view, 
$L_1=8.0\text{mm}$, $L_2=14.3\text{mm}$, $L_3=22.2\text{mm}$, $W_1=2.0\text{mm}$, and $W_2=2.0\text{mm}$, $W_3=30.0\text{mm}$. (b) Side view, $H=2.0\text{mm}$ [7].

2 μm thick, self-biased spinel NiCo ferrite (Ni$_{0.23}$Co$_{0.13}$Fe$_{2.64}$O$_4$) films were deposited by spin-spray processing (as described in chapter 2), onto thin transparency. The films show a pure polycrystalline spinel NiCo-ferrite phase, with no obvious preferential orientations. The films were magnetically anisotropic in the inplane and outplane direction and demonstrated an inplane coercivity of 165 Oe. The in-plane resistivity of the film was $5.6 \times 10^3 \ , \text{Ω} \ \text{cm}$, the relative permittivity of the film was 13 and the permeability is ~10. The loss tangent of the NiCo-ferrite film is estimated to be about 0.05 at 2 GHz.

The self-biased NiCo-ferrite films were used for magnetic loading on the patch antenna. The large anisotropy field enables a low loss tangent of the ferrite films at several GHz frequencies. Three antennas with single layer and multilayer ferrite films are designed as follows; one layer of the 2 μm NiCo ferrite is introduced above the non-magnetic rectangular patch as shown in Fig 5.10 (a), the other two magnetic patch
antennas employ either two or three layers of the ferrite film above the patch, as shown in Fig 5.10 (b) and (c), respectively. All the four antennas were fabricated and tested.

Fig 5.10: Side view of rectangular patch antenna with ferrite films, (a) one layer of ferrite film above the patch, (b) two layers of ferrite film above the patch, and (c) three layers of ferrite film above the patch. $d = 2 \mu m$ [7].
The measured reflection coefficient for these three antennas with ferrite films is plotted in Fig 5.11, along with that of the non-magnetic patch for comparison. All the measured resonant frequencies and the bandwidth of these four antennas are listed in table 5.1.

Fig 5.11: Measured reflection coefficient of the patch antennas with/without ferrite films loading.
The non-magnetic patch shows a resonant frequency of 2.146 GHz, and 2:1 VSWR bandwidth of 18 MHz. When one layer of ferrite film is added above the patch; the resonance shifts down to 2.134 GHz, which indicates a tuning range of 12 MHz relative to the non-magnetic substrate. The bandwidth is 21 MHz with addition of the ferrite film, an increase of 3 MHz compared to non-magnetic antenna. As shown in Fig 5.11, the reflection coefficient also improves with an increase in ferrite film thickness. Clearly the ferrite film loading leads to enhanced bandwidth and improved matching. The addition of two layers of the ferrite film above the patch tunes the resonance down to 2.117 GHz with the minimum reflection coefficient of about -24 dB. The resonant frequency shift is 29 MHz compared with the non-magnetic antenna. Adding three layers of
ferrite film above the patch shifts the resonance down to 2.106 GHz, with the best reflection coefficient of -30 dB. We observe a central frequency shift about 40 MHz relative to the baseline non-magnetic patch, and an improved bandwidth of 29 MHz. As summarized in table 5.1, we can see that the antenna efficiency is increased from 41% of the non-magnetic antenna to 56%, 65%, and 74% for the latter three antennas. As mentioned above, superstrate loading is one of effective gain enhancement methods for microstrip antennas. The superstrate loading of ferrite films combined with the improved impedance matching are the main reasons for the improved efficiency. Also, the films are so thin (2 µm for each layer in our antennas) that the energy loss associated with the loss tangent is not a significant issue in such antennas with an alumina substrate thickness of 2 mm. The antenna gain is enhanced by 0.32, 0.77, and 1.1 dB, respectively, over the non-magnetic antennas. In order to evaluate the antenna gain at the different elevation angles, the gains of the patch antennas with/without ferrite films are plotted in Fig 5.12. From this figure we can see that the gains at the elevation angle of 80° are improved by 1.01, 1.03, and 1.36 dB in the H-plane, and 0.4, 0.74, and 1.0 dB in the E-plane relative to the unloaded patch, respectively, for the three antennas with ferrite films. The -5 dBic gain beamwidth is increased from 140° to 155°, 156° and 160°, for the three magnetic antennas, showing significantly improved omnidirectional performance.
Conclusively, single layer and multilayer self-biased ferrite magnetic films have been introduced as a practical means to tune a patch antenna operating at 2.1 GHz by loading a commercially available substrate. Measurements on magnetic patch antennas demonstrate that the central resonant frequency can be shifted downward over a tuning range of 12–40 MHz, which indicates that self-biased magnetic films do lead to minimized antenna by shifting down the resonance frequency. The antenna bandwidth of the magnetic antennas is enhanced by 3 MHz–11 MHz over the non-magnetic antenna. In addition, the antenna efficiency was increased from 41% to 56%–74% with multilayer ferrite films added onto the antenna. In summary, spin spray deposited self-biased ferrite
films provide a unique way of achieving self-biased magnetic antennas operating at GHz frequency range with significantly enhanced performance.
Reference


Chapter 6: Beyond RF Ferrites- Spin-spray

Deposited ZnO and Al doped ZnO

Microstructures

Zinc oxide is a direct wide band gap, hexagonal wurtzite structure semiconductor that has gained a lot of attention due to its high electrical and optical properties, and application in a wide variety of electronic, optoelectronic, spintronic and nanodevices [1]-[6]. One of its main advantages over other materials is its low growth temperature, low cost and toxicity, stability at high temperature and ease of patterning.

Several conventional growth methods have been investigated for ZnO structures including electrochemical, chemical vapor transport, vapor-phase growth, hydrothermal growth, chemical bath methods, sputtering, pulsed laser deposition etc [7]-[13]. Even though a lot of these conventional methods are low-temperature and cost effective, they have the disadvantages of requiring seed layers for film growth which necessitates additional deposition processes, have slow deposition rates which are too slow for industrial use, and produce very thin films. Currently, spin-spray technique, which was original developed for ferrite film fabrication [14], is been explored as a good candidate for ZnO film growth [15], [16]. The spin-spray technique is a low-temperature, low cost, direct deposition technique, with the added advantage that it requires no seed layer for film growth, has a continuous supply of fresh solution which
preserves the high concentrate of solute, and has a high deposition rate of up to 170nm/min, making it suitable for thick film development. Spin-spray process has been shown to produce high crystal quality ferrite films with good adhesion properties [17], excellent magnetic properties [18]-[21] and have been used for microwave devices such as antennas and filters [22]-[24].

It has been reported that the structural, electrical and optical properties of ZnO films depend on the deposition parameters, regardless of the method of growth [25]. Wagata et al. [16] showed that the 002 peak in the XRD pattern weakened with a change from spin-sprayed ZnO rod array to dense film and also how post annealing affected the UV luminescence of the microstructures. Since the practical application of ZnO depends on these properties, it is extremely necessary to investigate the effect of the deposition conditions on the growth and properties of ZnO structures by the spin-spray technique. Also, various elements can be doped into ZnO microstructures to control their properties [26]-[28]. In the last decade, doped ZnO thin films, especially Al-doped ZnO films have been intensely researched due to its exceptional electrical, luminescent and optical properties which make it applicable in transparent electrodes for photovoltaic devices, energy efficient flat panel display, light-emitting diodes etc, and also its high temperature stability [26], [28]-[34].

In this work, the influence of growth parameters of the spin-spray technique on the physical geometry and properties of ZnO microstructures
on glass substrates were investigated. This investigation was carried out by varying the pH and concentration of the solutions utilized. With increasing pH from 9-12, the scanning electron microscope (SEM) revealed a change in the microstructure of ZnO; from membrane-like structures with pH of 9, to single crystal rods with hexagonal ends with pH of 10, and to polycrystals with needle-like tips and random crystalline orientation with pH of 12. This change in structure was accompanied by a decrease in resistivity from $9 \times 10^4$ to $3.4 \times 10^4$ Ω cm. Increase in the additive sodium citrate decreased the distance between the individual rods thereby creating a film structure, with a decrease in thickness as expected. Further increase in the additive however, led to a rod array structure of the ZnO. Varying the concentration of the solution brought about a dramatic change in the crystal growth behavior and crystalline orientation, with the least concentration producing rods more oriented in the c-axis direction. Addition of Al dopant to the ZnO thin film further reduced the resistivity by an order of 3 magnitudes; from $3.4 \times 10^4$ to $14$ Ω cm. This investigation will enable optimized low temperature (<100°C) fabrication of ZnO films by the spin-spray technique with controllable properties based on their processing conditions.

ZnO microstructures of lengths/thicknesses 1 to 5 µm were fabricated onto commercially available 0.1mm thick glass substrates by the spin-spray deposition technique at 90°C. The glass substrates were cleaned in an ultrasonic with acetone and ethanol for 15 mins each. An
buffer solution containing 17.5 mM CH$_3$COONa, a pH buffer, with a pH value of 9-12 and a precursor solution contain varying concentration of ZnCl$_2$ with a pH value of 6-7 were sprayed simultaneously through separate nozzles onto the rotating glass substrates at 145 rpm. The growth rate of the ZnO structures was 66-333 nm/min. The pH of the buffer solution was tuned using NaOH solution. A detailed description of the spin-spray technique is described in chapter 2. Chemical composition and crystal structure analyses of the films were done by x-ray diffraction (XRD) with a Cu K$_\alpha$ source ($\lambda$=1.541 Å) and scanning electron microscope (SEM). Resistivity measurements were obtained using a four-point probe method.

6.1 Growth Characteristics

To investigate the effect of buffer pH on the ZnO microstructures, sample 1-3 were prepared with a fixed ZnCl$_2$ concentration of 10mM for the precursor solution, and a pH buffer solution with varying pH values of 9, 10 and 12 respectively. With increasing pH of the buffer solution, the SEM images as shown in Figure 1 revealed a drastic change in crystalline structure and orientation. Sample 1 with a pH of 9 exhibited a 300 nm thick membrane-like structure devoid of rod arrays as shown in Fig 6.1(a). Clearly, this pH is too low to initiate ZnO rod formation. Sample 2 with a pH of 10 however, demonstrated sparse, mostly single crystal rod arrays of lengths ~2-3 µm with hexagonal ends as seen in Fig 6.1 (b) and a slight orientation in the c-axis (perpendicular to the substrate) direction as
shown in Fig 6.1 (c), and (d). These ZnO single crystals are seen to grow out of the membrane-like structures which are still present in this case. Conversely, sample 3 with a pH of 12 displayed dense polycrystalline rod arrays of length ~3-4 µm with no membrane-like structures as seen in Fig 6.1 (e) and (f).

Looking closely at Fig 6.1 (e), one can see that after a certain length, additional rod arrays of length 1.2 µm and diameter 0.2 µm grew out of a single rod (base rod), which was not present in sample 2. These base rods were mostly oriented in the c axis direction as in the case of sample 2, while the additional rods were mostly perpendicular to the base rods on which they grew out from, that is, parallel to the substrate as demonstrated in Fig 6.1 (f). The diameter of the rods also increased from ~0.5 µm in sample 2 to ~0.8 µm (for the base rods) in sample 3. This shows that increase in pH, increases the growth rate of ZnO in the c axis and lateral directions.
Fig 6.1: SEM images of the ZnO microstructures; (a) sample 1 with pH of 9, (b) hexagonal end of sample 2 with pH of 10, (c) surface image of sample 2, (d) cross section image of sample 2, (e) surface image sample 3 with pH of 12, and (f) cross section image of sample 3.
Samples 4-7 were prepared by adding the additive sodium citrate, with varying concentration of 10, 18, 24 and 40 mM, to the pH buffer solution respectively. The resultant pH of this solution was maintained at 12. The additive sodium citrate has been shown to reduce the distance between the rod of ZnO by increasing the lateral growth of the rods while reducing the c axis growth to produce ZnO films with a decrease in thickness and a weakening of the 002 peak [16]. However, this film structure becomes porous and reverts back to a rod array structure with further citrate increase. As shown in Fig 6.1(d), with no citrate added, the ZnO film had a polycrystalline rod array structure. With an increase in sodium citrate, the distance between the rods is seen to decrease while the diameter of the rods increased from 0.8 µm to 2 µm as shown in Fig 6.1 (d) and Fig 6.2 (a)-(d). The thickness of the films also decreased from ~4 µm to 1.5 µm, while the uniformity of the rods increased with increase in sodium citrate. With a citrate concentration of 24mM, the ZnO microstructure is completely changed from a rod array to a dense film structure. With a further increase in sodium citrate to 40mM, the microstructure of the film was changed from a dense film structure back to a rod array of length 1.5 µm as shown in Fig 6.2 (d).
Fig 6.2: Surface SEM images of the ZnO microstructures with sodium citrate (a) 10mM –sample 4 (b) 18mM –sample 5, (c) 24mM –sample 6, and (d) 40mM –sample 7.

As examined by Wagata et al. [16], the citrate ions act to modify the crystal growth of ZnO. At low concentrations, the assimilation of the citrate ions hinders the growth of the ZnO microstructures in the c-axis direction, resulting in faster lateral growth and fatter rod structures with reduced thicknesses. For higher citrate concentration, ZnO growth is initiated by nucleation of randomly oriented ZnO nanosized grains. The ZnO grains grow and eventually form a film structure. However, since higher citrate concentration greatly impedes the c axis (perpendicular to the substrate)
growth of the rods, a film structure will not be formed as observed in sample 7.

The concentration of the precursor solution strongly affects the growth mechanism of the ZnO films as demonstrated in the SEM images shown in Fig 6.3 (a)-(f). To verify the precursor concentration effect on the growth mechanism of the microstructures, samples 8-10 were fabricated with a constant pH buffer + 10 mM sodium citrate with a pH of 12, and a varying precursor concentration of 20, 10 and 5 mM respectively. With a conc. of 20 mM, the ZnO film exhibited two distinct layers of rod arrays. The top layer as shown in Fig 6.3(a) and (b) are polycrystalline rods of 4-5 µm length with more rods of length ~ 3 µm growing out of these rods, thus forming a floral-like structure with oriented perpendicular to their base rod direction (the rod out of which they grew). In this case, the c-axis growth of the rods is more rapid than the lateral growth; hence, the rods are less dense than the bottom layer. The bottom layer shown in Fig 6.3(c) and (d) consists of well-defined tightly-packed hexagonal rods of length ~ 3 µm, mostly oriented in the c-axis direction. The rods on the bottom layer have well defined hexagonal plates at the ends. The distance between the rods are very close, forming a film-like structure as seen from the cross section image in Fig 6.3 (d). Since the rods are not of uniform length and thickness, they appear as rod arrays when viewed from the top, as shown in Fig 6.3 (c). With a decrease in conc. to 10 mM in Fig 6.3 (e), the SEM image revealed only one layer of densely-packed hexagonal rods of length
~ 3 µm, mostly oriented in the c-axis direction, while sample 10 with a concentration of 5 mM exhibited an almost film-like structure with little space between each rod. With a decrease in the precursor concentration, the hexagonal ends of the rods become less defined but the length and width of the rods become more uniform, producing a flat surface as in sample 10. With a decrease in concentrate, the diameter of the rods decreased from ~2 µm to 1 µm.
Fig 6.3: SEM images of the ZnO microstructures with varying precursor conc. (a) top layer of the 20 mM-surface image, (b) cross section of the top layer of the 20 mM, (c) bottom layer of 20 mM-surface image, (d) cross section of the bottom layer of the 20 mM, (e) surface image of the 10 mM, and (f) surface image of the 5 mM.
The XRD patterns of all the ZnO microstructures confirm pure wurtzite-type ZnO crystals with the (002) peak most prominent. With increasing pH of the buffer solution, the peaks are strengthened due to the increase in growth rate of the ZnO structures as seen in Fig 6.4 below. With an increase in pH from 9-12, the orientation of the ZnO structures become more random. This is because in sample 3, there were additional rods growing out of the base rods (the initial rods with orientation in the c axis) that were perpendicular to these base rods, and hence, parallel to the substrate. This is also the main reason why the other peaks are stronger in sample 3 than in sample 2 or 1 with no such growth property. The same is also true for samples 8-10 with varying precursor concentration as seen in Fig 6.4 (b).

![Fig 6.4: XRD patterns of the ZnO films with (a) varying pH of the buffer solution, and (b) varying precursor concentration.](image)
6.2 Electrical Properties

The variation of buffer pH influenced the resistivity of the ZnO microstructures. With increasing pH from 9 to 12, the resistivity decreased from $9 \times 10^4$ to $3.4 \times 10^4 \ \Omega \text{cm}$. This is probably due to the evolution of the ZnO rod arrays (carrier concentration) as the pH was increased. Since resistivity, $\rho = \frac{1}{\mu n q}$ (where $\mu$ is the Hall mobility, $n$ is the carrier concentration, and $q$ is an electron charge) the variation of the resistivity will depend on the evolution of the carrier concentration. However, increase in precursor and citrate concentration did not have much effect on the resistivity value which was maintained at $\sim 5.6 \times 10^4 \ \Omega \text{cm}$. This indicates that although the addition of sodium citrate and variation of precursor concentration induces changes in the growth mechanism of the films as previously shown, it does not affect the resistivity of the films. To further reduce the resistivity of the films, we doped the ZnO films with various amounts of Al. Zn$_{1-x}$Al$_x$O (with $x=0$-0.06) thin films of 1.5 µm thicknesses were fabricated on to commercially available 0.1 mm thick glass substrates using the spin-spray technique as described above. 24 mM of sodium citrate was also added to the buffer solution to obtain the film structure.

The resistivity of the films decreased about 3 order of magnitude with increase in Al from $5.6 \times 10^4 \ \Omega \text{cm}$ for $x=0$ to $14 \ \Omega \text{cm}$ for $x=0.02$. This is due to the increase in dopant concentration (in this case Al) in the films. However, the resistivity increased from $14 \ \Omega \text{cm}$ to $\sim 1 \times 10^4 \ \Omega \text{cm}$ from
x=0.02 to x=0.06. The plot of resistivity as a function of the Al concentration for x=0.002 to x=0.06 is shown in Fig 6.5.

![Graph](image)

**Fig 6.5:** Plot of resistivity as a function of Al concentration (for x=0.002 to 0.06) for the Zn$_{1-x}$Al$_x$O thin films.

In conclusion, we investigated the influence of growth parameters of the spin-spray technique on the physical geometry and properties of ZnO microstructures on glass substrates. This investigation was carried out by varying the pH and concentration of the solutions utilized. SEM
images revealed a change in the microstructure of ZnO; from membrane-like structures with pH of 9, to single crystal rods with hexagonal ends with pH of 10, and to polycrystals with needle-like tips and random crystalline orientation with pH of 12. This change in structure was accompanied by a decrease in resistivity from $9 \times 10^4$ to $3.4 \times 10^4 \ \Omega \ cm$. Varying the concentration of the solution brought about a dramatic change in the crystal growth behavior and crystalline orientation, with the least concentration producing rods more oriented in the c-axis direction. We were able to further reduce the resistivity by an order of 3 magnitudes; from $3.4 \times 10^4$ to $14 \ \Omega \ cm$ by doping with Al. This investigation will enable optimized low temperature ($<100^\circ\text{C}$) fabrication of ZnO films with controllable properties based on their processing conditions, by the spin-spray technique.
Reference


Chapter 7: Conclusion

7.1 Summary

In this dissertation, we presented novel RF ferrites by the low temperature spin-spray deposition process. These ferrites demonstrated strong interface adhesion required for strong coupling, thus providing a viable route to low temperature synthesis of novel high quality multiferroic materials. Also, strong magnetoelectric (ME) coupling leading to record-high electrostatic field induced ferromagnetic magnetic resonance (FMR) field change of 860 Oe, microwave ME coefficient of 108 Oe cm/kV and FMR microwave tunability of 1450 Oe were achieved in Fe$_3$O$_4$/PZN-PT multiferroic heterostructure. We reported on Ni$_{0.27}$Zn$_x$Fe$_{2.73-x}$O$_4$ (with $x = 0.03$-$0.1$) thin films that exhibited high permeabilities that exceeded the Snoek limit for bulk NiZn-ferrite films and those previously reported for spin spray deposited ferrites. The NiZn-ferrite film with $x=0.06$ was low in magnetic losses, having $\tan\delta_m (\mu_r'/'/\mu_r)$ $\sim$0.027 from 1 to 1.5 GHz, and a high ferromagnetic resonance (FMR) frequency of 2.7 GHz, while the $x=0.1$ film exhibited a high $\mu_r'$ of $\sim$50 and $\mu_r'' > 50$ at 1 GHz. These properties are ideal for microwave applications such as antennas, inductors and electromagnetic interference (EMI) suppression in the GHz range.

Ferrite/non-magnetic multilayers, an approach to thicker film loading, were also examined in this dissertation. We developed
Fe$_3$O$_4$/PR/Fe$_3$O$_4$ multilayers up to 10 µm thick with ~14% reduction in coercivity and 25% enhancement in their permeability spectra compared to their single layer counterparts. These spin-spray deposited ferrite/non-magnetic multilayers constitute a unique approach to achieving thick ferrite films with enhanced RF/microwave magnetic properties at a low temperature, which provide great opportunities for integrating thick ferrite films on RF integrated circuits and monolithic microwave integrated circuits.

To explore the RF performances of these spin-sprayed novel ferrites, various types of antennas were designed and developed. Fe$_3$O$_4$, a lossy ferrite film was successful introduced into the design of low profile dipole antenna to enhance its ground immunity by effectively reducing the mutual coupling between the antenna and the ground plane. Since the Fe$_3$O$_4$-ferrite film is very thin (only 1.4 µm thick), it will neither add weight nor volume to the RF front circuit. We also demonstrated how the addition of spin-spray ferrite layer(s) to the fabrication of high permittivity substrate antennas can help to improve the impedance matching and resonance problems that are generally associated with these antennas, and in addition induce shifting down of the resonance frequency; which enables antenna miniaturization. The antenna bandwidth and efficiency were also improved, thus confirming that spin spray deposited self-biased ferrite films provide a unique way of achieving self-biased miniaturized magnetic
antennas operating at GHz frequency range with significantly enhanced performance.

Although the spin-spray technique was originally designed for ferrite fabrication, it is currently being explored as an approach to semiconductor material fabrication. This dissertation investigated the influence of the process conditions for zinc oxide (ZnO) and Al doped ZnO microstructure growth.

7.2 Further Research

Despite the progress made in this dissertation, further work is needed to fully understand the inter-grain behavior of the spin-spray ferrite/non-magnetic multilayers. For example, for RF/Microwave applications, characterization of electrical resistivity at high frequency of these multilayers is crucial for providing explicit information about the electrical transport properties.

Also, investigation into the development of other types of materials, e.g. ferromagnetic semiconductor, could bring about further advancement in the device industry.