## Growth and Characterization of Epitaxial Thin Films and Multiferroic Heterostructures of

Ferromagnetic and Ferroelectric Materials

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Physics College of Arts and Sciences University of South Florida

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# **DEDICATION**

I dedicate this dissertation to my parents, Mr. Soumendra Nath Mukherjee and Mrs. Gouri Mukherjee, and my grandfather, Late Benoy Krishna Chakraborty.

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#### ABSTRACT

Multiferroic materials exhibit unique properties such as simultaneous existence of two or more of coupled ferroic order parameters (ferromagnetism, ferroelectricity, ferroelasticity or their anti-ferroic counterparts) in a single material. Recent years have seen a huge research interest in multiferroic materials for their potential application as high density non-volatile memory devices. However, the scarcity of these materials in single phase and the weak coupling of their ferroic components have directed the research towards multiferroic heterostructures. These systems operate by coupling the magnetic and electric properties of two materials, generally a ferromagnetic material and a ferroelectric material via strain. In this work, horizontal heterostructures of composite multiferroic materials were grown and characterized using pulsed laser ablation technique. Alternate magnetic and ferroelectric layers of cobalt ferrite and lead zirconium titanate, respectively, were fabricated and the coupling effect was studied by X-ray stress analysis. It was observed that the interfacial stress played an important role in the coupling effect between the phases. Doped zinc oxide (ZnO) heterostructures were also studied where the ferromagnetic phase was a layer of manganese doped ZnO and the ferroelectric phase was a layer of vanadium doped ZnO. For the first time, a clear evidence of possible room temperature magneto-elastic coupling was observed in these heterostructures. This work provides new insight into the stress mediated coupling mechanisms in composite multiferroics.

#### CHAPTER 1:

#### **INTRODUCTION**

In 1865, James Clerk Maxwell had proposed four equations governing the dynamics of electric fields, magnetic fields and electric charges [1]. This was the first time that magnetic interactions and motion of electric charges, which were previously thought to be independent phenomena, were shown to be intrinsically coupled to each other. This was followed by the some pioneering work, in 1888, by Rontgen [2] and in 1894, by Curie [3] that discovered the magnetoelectric (ME) effect in solids. The ME effect in its most common definition describes the coupling between magnetic and electric fields in matter [4]. However, the search for materials that displayed ME effect was difficult and the field remained elusive for a long time. This was primarily due to the complex mechanisms involved and the different origins of ferroelectricity and magnetism in solids, which did not guarantee a strong coupling between the two behaviors [5 - 8]. In the mean time, research on magnetic and electronic materials had found their way into every aspect of modern technology [9]. The huge amount of data generated by consumer electronics everyday is frequently stored in modern memory devices such as Magnetoresistive Random Access Memory (MRAM) and Ferroelectric Random Access Memory (FeRAM) [10, 11]. However, the ever increasing trend towards device miniaturization led to renewed increased interest in combining the magnetic and electric properties into multifunctional materials, so that a single device element can perform

more than one task [9]. Multiferroics materials might hold the future for a new generation of memory devices that could be electronically written and magnetically read [12]. Major discoveries such as the four state multiferroic memory devices brought the research one step closer in that direction [13].

Recent years have seen a flurry of research focused on multiferroic materials where both magnetism and ferroelectricity coexist [4, 14 - 16]. The revival of modern multiferroics was possible not only due to recent theoretical breakthroughs in understanding the coexistence of magnetic and electrical ordering but also advances in thin film growth techniques and experimental methods for observing magnetic and electric domains [4].

Probably, the most important factor that rejuvenated the "quiet" and "abstruse" field of multiferroics was the broader realization that combining magnetism and ferroelectricity in different ways in a single material could create new technical applications like the electric field control of magnetic memory and vice versa.

#### **1.1. Materials Overview**

Before we go into the details of multiferroic behavior a review of the basic properties of magnetic and ferroelectric materials is presented.

### 1.1.1. Magnetic Materials

Magnetic materials exhibit long range alignment of the atomic moments resulting in a spontaneous net magnetization (M) even in the absence of an external magnetic field (H) [14]. The important magnetic parameters can be obtained from the M versus H hysteresis loop as shown in Figure 1.1.1. The coercivity (H<sub>c</sub>) is the reverse field that reduces M to zero from saturation magnetization (M<sub>s</sub>). The remnant magnetization (M<sub>r</sub>) is the value of M at H = 0. Magnetic memory devices should have high H<sub>c</sub> and squareness (M<sub>r</sub>/M<sub>s</sub>) to ensure that a majority of domains have similar switching fields.

#### 1.1.1.1. Spinel-type Ferrite: CoFe<sub>2</sub>O<sub>4</sub>

The ferrites include the complete family of Fe-containing oxides such as the spinels (AFe<sub>2</sub>O<sub>4</sub>), garnets (AFe<sub>5</sub>O<sub>12</sub>), hexaferrites (AFe<sub>12</sub>O<sub>19</sub>), and orthoferrites (RFeO<sub>3</sub>) where A or R is a metal or a rare-earth element, respectively [14]. Among them the spinel-type ferrites have attracted considerable research interest over the years for possible applications in diverse fields [17 - 19]. Spinel ferrites have found applications in microwave magnetic devices [20 - 23], magneto-optic data storage appliances [24 - 26], and for potential biological applications in drug delivery [27, 28]. They have also found applications in magnetic tunnel junctions [29], magneto elastic devices [30], spintronic devices and composite multiferroic heterostructures [31].



Magnetic Field (H)

Figure 1.1.1. Typical hysteresis loop of a ferromagnetic material showing the saturation magnetization  $(M_s)$ , remnant magnetization  $(M_r)$  and coercive field  $(H_c)$ .

Cobalt ferrite (CFO), having a chemical formula  $CoFe_2O_4$ , is an important member of the spinel type ferrite family. CFO is a hard magnetic material with high degree of magnetic anisotropy and magnetostriction [17]. The unique magnetic properties of this material can be understood from its electronic and structural configurations. The  $Co^{2+}$  and  $Fe^{3+}$  are located on the octahedral and tetrahedral sites, respectively, as in an inverse spinel structure as shown schematically in Figure 1.1.2. In a normal spinel structure (AB<sub>2</sub>O<sub>4</sub>), the A<sup>2+</sup> cations occupy the tetrahedral sites whereas the B<sup>3+</sup> cations occupy the octahedral sites. However, in an inverse spinel structure, half of the octahedral coordination sites are occupied by A<sup>2+</sup> cations and the remaining half as well as all the tetrahedral coordination sites are occupied by the B<sup>3+</sup> cations. A unit cell of CoFe<sub>2</sub>O<sub>4</sub> (CFO) which is a face-centered cubic (fcc) structure with lattice parameter ( $a_o$ ) of 8.39 Å, consists of 8 formula units (Figure 1.1.2) [17]. The eight Fe<sup>3+</sup> ions in tetrahedral sites are aligned antiferromagnetically with respect to the remaining eight Fe<sup>3+</sup> ions via super-exchange interactions mediated by oxygen ions. Thus the uncompensated Co<sup>2+</sup> ions which have three unpaired electrons in their d-orbitals give a theoretical saturated magnetization value of 3  $\mu_B$  per formula unit or per Co site.



Figure 1.1.2. Schematic diagram of unit cell and subunits in  $CoFe_2O_4$  inverse spinel structure (Adapted from Ref. [32]).

However, the experimental value of the saturated magnetization in CFO is found to be around 4  $\mu_B$ . This discrepancy between the theoretical and experimental values could be attributed to two factors [17]. First, the calculation was done by neglecting the contribution from the orbital motion of electrons. Secondly, the Fe<sup>3+</sup> moments were assumed to be aligned perfectly anti-parallel, but in reality they may be canted. In addition, the distribution of different ions may not be as perfect as assumed. This creates the intriguing magnetic properties of CFO thin films as compared to bulk powders. In this work, CFO was chosen as a promising magnetic material for growing thin films and heterostructures.

### 1.1.1.2. Magnetic Anisotropy

When the magnetization (M) of a magnetic material changes with the direction of the applied magnetic field (H), it is said to exhibit magnetic anisotropy. This behavior, primarily observed in thin films, makes their magnetic properties quite different from those of the bulk. In CFO thin films, due to their unique structural properties, the magnetic moments prefer to lie in an energetically favorable direction, called the easy axis of magnetization. Figure 1.1.3 (a) shows an idealized M versus H hysteresis loop for a thin film having the easy magnetization axis parallel to the film plane. When H is applied parallel to the film plane (in-plane), the M-H loop exhibits easy magnetization to saturation. Contrarily, when H is applied perpendicular to film plane (out-of-plane), a much larger field is necessary to fully magnetize the sample. Figure 1.1.3 (b) shows a schematic diagram of the direction of easy axis of magnetization with respect to the magnetic moments in the microstructure of the film.

For thin films with uniaxial magnetic anisotropy, the overall magnetic anisotropy coefficient (K<sub>u</sub>) is given by [33]:

$$K_{u} = K_{int} + K_{sh} + K_{\sigma} \tag{1.1}$$

where  $K_{int}$  is the intrinsic magneto-crystalline,  $K_{sh}$  is the shape, and  $K_{\sigma}$  is the stress anisotropies, respectively.



Figure 1.1.3. (a) Ideal M - H loop and (b) schematic diagram of magnetic moments for a thin film with the easy axis of magnetization along the film plane, respectively.

The microscopic origin of the intrinsic magnetocrystalline anisotropy is related to the spin state of the magnetic moments and by the symmetry of their arrangement in the crystal lattice that involves spin-lattice coupling. The  $K_{int}$  for a simple cubic symmetry crystal such as CFO is given by [34]:

$$K_{int} = K_1 \left( \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 \right) + K_2 \left( \alpha_1^2 \alpha_2^2 \alpha_3^2 \right) + \dots$$
(1.2)

where  $K_i$  (i = 1, 2, ...) is the anisotropy constant and  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are the direction cosines of M and the a, b, and c axes of crystal system.

The source of the shape anisotropy is the demagnetization energy associated with the shape of the sample. This favors the alignment of the moments along the largest extent of sample (parallel to the film). For a film whose thickness is much less than its other dimensions, shape anisotropy is given by [34]:

$$K_{\rm sh} = -2\pi M_{\rm s}^2 \tag{1.3}$$

Thin films invariably grow with in built stresses during the deposition process. The stress anisotropy is given by [34]: Magnetostriction is another property of magnetic materials associated with the change in dimensions upon magnetization [35, 36]. As a result, elastic strains are developed in the crystal lattice that change the alignment of the magnetic moments and create the magnetoelastic effect in the material [37, 38].

### 1.1.2. Ferroelectric Materials

Ferroelectric materials exhibit long range alignment of electric dipoles resulting in a net polarization under an applied electric field. The unit cell of a ferroelectric crystal has a polar axis that causes spontaneous electric dipole moment even in the absence of an electric field [34]. The existence of a spontaneous polarization implies that there is a preferred special orientation in the crystal. Just like in magnetic materials the important parameters for a ferroelectric material can be obtained from the polarization (P) versus electric field (E) hysteresis loop as shown in Figure 1.1.4.

Ferroelectric thin films have found applications in micro-electro-mechanical (MEMs) devices, non-volatile memories, and high frequency electrical components [39]. An exhaustive review of applications can be found in Ref. [40] and the articles therein [40]. The principle of nonvolatile ferroelectric random access memories (FeRAMs) is based on the polarization reversal in ferroelectric thin film capacitors under the influence of an external applied electric field. The computational "0" and "1" are represented by the nonvolatile storage of the negative or positive remnant polarization state, respectively [40].



Figure 1.1.4. Typical hysteresis loop of a ferroelectric material showing the saturation polarization ( $P_s$ ), remnant polarization ( $P_r$ ) and coercive field ( $H_c$ ).

#### 1.1.2.1. Ferroelectric Perovskite: PZT

Ferroelectric perovskites, such as  $Pb(Zr_x,Ti_{1-x})O_3$  (PZT), BaTiO<sub>3</sub> (BTO), and BiFeO<sub>3</sub> (BFO) have always attracted significant interest due to their simple crystal structure, better ferroelectric and mechanical properties [14], and their potential application in ultrahigh density memory devices [41]. Among them, PZT has remained the material of choice for its outstanding ferroelectric properties [42].

Lead zirconium titanate (PZT) is a solid solution of PbTiO<sub>3</sub> and PbZrO<sub>3</sub> compounds [43]. The Curie temperature (T<sub>c</sub>) of PZT can vary from 230 °C to 490 °C depending on the composition (i.e. 1 > x > 0). Above T<sub>c</sub>, PZT is cubic (Figure 1.1.5) and has no electric dipole moment. However, below T<sub>c</sub>, structural changes make the crystal non-centro-symmetric. The Ti/Zr ion shifts from its central location along one of several

allowed directions (Figure 1.1.5). This slightly distorts the crystal lattice into a perovskite structure (tetragonal/rhombohedral shape), and produces an electric dipole. If it is then subjected to an electric field, the domain dipoles align in the direction of the field causing polarization. The dipoles maintain this orientation even after the field is removed which gives the remnant polarization.

In this work, PZT has been selected as a ferroelectric material for growing thin films and heterostructures. Solid solutions of PZT with different compositions exhibit an unusual phase boundary which divides ferroelectric regions with different structures. PZT shows anomalously high ferroelectric response near such morphotropic phase boundary (MPB). For this reason, in this work, the PZT composition was kept constant at  $PbZr_{0.52}Ti_{0.48}O_3$  it is in the vicinity of the MPB [44].



Figure 1.1.5. Schematic diagram of PZT unit cell showing off-centering of Zr/Ti ion under an external applied electric field (Adapted from C. Kittel [45]).

Also, the direct epitaxial growth of PZT on Si substrates is inhibited due to interdiffusion and larger lattice mismatch [44]. Hence the PZT films have been grown on single crystal MgO and SrTiO<sub>3</sub> substrates in this work.
## **1.1.3. Multiferroic Materials**

By definition, multiferroic materials are those that simultaneously display more than one ferroic or corresponding antiferroic properties such as ferroelectricity, ferromagnetism, ferroelasticity, or antiferroelectricity, and antiferromagnetism [46]. Multiferroic materials can be divided into two categories. If the co-existence of the ferroic properties occur in the same material, it is called a single phase multiferroic. On the other hand, if the ferroic behaviors exist individually within separate phases, it is called a composite multiferroic.

# 1.1.3.1. Scarcity of Single Phase Materials

There is a scarcity of single phase multiferroic materials. Only a small group of materials that show magnetic and electric polarization are either ferromagnetic or ferroelectric. Within these select materials, a very small subgroup exhibits multiferroic behavior. The overlap required for multiferroic materials is shown schematically in Figure 1.1.6.

In order to understand why these materials are so rare, one has to look into the microscopic mechanisms of magnetism and ferroelectricity in these materials. Although the ferromagnetic and ferroelectric materials both exhibit similar behaviors in term of hysteresis, their origins are completely different. While on one hand ferroelectric materials are insulators with unfilled d orbitals, ferromagnets need conduction electrons and have incompletely filled d shells [14]. Thus there exists an apparent inconsistency between the usual mechanism of off-centering in a ferroelectric materials and the formation of magnetic order in a magnetic material. This also explains the scarcity of ferroelectric-ferromagnetic multiferroics [48].



Figure 1.1.6. Schematic diagram showing the overlap required to achieve multiferroic properties in a single material (Adapted from Ref. [47]).

# **1.1.3.2. Magnetoelectric Effect**

Magnetoelectric (ME) effect is the phenomenon of the induction of magnetization by an electric field or polarization by a magnetic field [4, 14]. In general, the ME effect depends on temperature. From applications viewpoint, the real interest in multiferroic materials is in observation of the strong ME coupling at room temperature. In general terms ME coupling typically refers to the linear ME effect. However, the effect could also be non-linear.

This can be understood from the expansion of free energy (F) of a material given by:

$$F(\overline{E}, \overline{H}) = F_0 - P_i^{S} E_i - M_i^{S} H_i - \frac{1}{2} \varepsilon_0 \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j \dots - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \dots$$
(1.5)

with  $\overline{E}$  and  $\overline{H}$  as the electric and magnetic fields, respectively.

Differentiation leads to the polarization

$$P_{i}(\overline{E},\overline{H}) = -\frac{\delta F}{\delta E_{i}}$$
$$= P_{i}^{S} + \varepsilon_{0}\varepsilon_{ij}E_{j} + \alpha_{ij}H_{j} + \frac{1}{2}\beta_{ijk}H_{j}H_{k} + \gamma_{ijk}H_{i}E_{j} + \dots$$
(1.6)

and to magnetization

$$M_{i}(\overline{E},\overline{H}) = -\frac{\delta F}{\delta H_{i}}$$
$$= M_{i}^{S} + \mu_{0}\mu_{ij}H_{j} + \alpha_{ij}E_{j} + \beta_{ijk}E_{i}H_{j} + \frac{1}{2}\gamma_{ijk}E_{i}E_{k} + \dots$$
(1.7)

where  $P_i^s$  and  $M_i^s$  are the spontaneous polarization and magnetization, and  $\varepsilon$  and  $\mu$  are the electric and magnetic susceptibilities. The coefficient  $\alpha$  in Equations (1.6, and 1.7) is designated as the linear ME coefficient. Experimentally,  $\alpha$  is generally expressed as  $\alpha_E = \Delta E/\Delta H$ , called the ME voltage coefficient. The SI unit of  $\alpha$  is (s/m), although often it is expressed in amore practical unit of (mV/cmOe).

## **1.2. Thin Film Multiferroics**

One aspect of fundamental interest in multiferroic research is the production of high quality thin films of multiferroic materials. Epitaxial thin films provide an additional degree of freedom compared to bulk samples through the 'strain engineering' between the substrate and the film. Multiferroic thin films and nanostructures have been fabricated using a wide variety of growth techniques including sputtering, spin coating, pulsed laser deposition, sol–gel processes, metal-organic, chemical vapor deposition, and molecular beam epitaxy [14].

# 1.2.1. Single Phase Multiferroic Thin Films

Thin films of perovskite BiFeO<sub>3</sub> (BFO) have received the most attention for their multiferroic behavior among all the single phase multiferroics [49]. BFO thin films have shown simultaneous ferroelectricity, ferroelasticity and weak ferromagnetism [50, 51]. However, direct evidence of strong ME coupling at room temperature has not been observed.

The next important group includes hexagonal multiferroics formed by the ferroelectric antiferromagnetic manganites RMnO<sub>3</sub> with R = Sc, Y, In, Ho, Er, Tm, Yb, Lu [4]. However, they show multiferroic behavior with high ferroelectric ordering temperature (> 590 K) and low magnetic ordering temperature (70 K – 120 K) making them still unsuitable for device applications. Thin films of BiMnO<sub>3</sub> were also investigated for potential multiferroic applications. However, they showed ferroelectricity below 450K and ferromagnetism at 105 K [52], both temperatures being impractical.

A number of other single phase multiferroic materials have been studied over the years. Some of the notable ones are BiCrO<sub>3</sub> [53] displaying weak antiferromagnetic-

ferromagnetic coupling around 120 K – 140 K, or BiCoO<sub>3</sub> or PbVO<sub>3</sub> or double perovskites like Bi<sub>2</sub>NiMnO<sub>6</sub>[4, 14]. However the ME coefficients ( $\alpha_E = \Delta E/\Delta H$ ) in most single phase materials are still small in magnitude ( $\alpha_E \sim 20$  mV/cm Oe) for any potential applications [4]. Despite a concerted 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.

### **1.2.2.** Composite Multiferroic Thin Films

The scarcity of single phase multiferroic materials and the weak coupling of order parameters in the existing materials have directed research towards composite multiferroic thin films. These systems operate by coupling the magnetic and electric properties of two materials, generally a ferromagnetic material and a ferroelectric material via strain [14, 15]. The ME effect in composite materials is shown schematically in Figure 1.2.1. 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 [15]. 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 [15]. Thus the ME effect is the cross interaction in the two phases. It is product of the magnetostrictive effect in the magnetic phase and the electrostrictive effect in the electric phase.

The composite ME effect can therefore be described as follows [4, 15]:

$$Direct ME \ effect = \frac{Magentic}{Mechanical} \times \frac{Mechnical}{Electric}$$
(1.8)



Figure 1.2.1. Schematic diagram of strain-mediated ME effect in a composite system consisting of ferromagnetic layer (pink) and ferroelectric layer (blue) (Adapted from Ref. [15]).

There are three main kinds of ME composite nanostructures that have been studied so far. As shown schematically in Figures 1.2.2 (a, b, and c) they are denoted as 2-2 horizontal heterostructures, 1-3 vertical nanostructures, and 0-3 nano-particle embedded films, respectively [15]. The pair of numbers preceding the names refer to the dimensionalities of the two phases. The first kind is the 2-2 horizontal heterostructure with alternating ferroelectric (2 dimension) layers and magnetic (2 dimension) layers, or simply a ferroelectric (or magnetic) thin film grown on a magnetic (or ferroelectric)

substrate. The second kind is the 1-3 vertical heterostructure with one-phase nanopillars (1 dimension) embedded in a matrix of another phase (3 dimensions). Finally, the third kind is the 0-3 particulate nanocomposite films with magnetic particles (0 dimensions) embedded in a ferroelectric film matrix (3 dimensions).



Figure 1.2.2. Schematic diagram of the three main kinds of ME composite nanostructures (a) horizontal heterostructures, (b) vertical nanostructures, and (c) nano-particle embedded films, respectively. (Adapted from Ref [15])

The ferroelectric component materials often used include BaTiO<sub>3</sub> (BTO), PbTiO<sub>3</sub> (PTO), Pb(Zr,Ti)O<sub>3</sub> (PZT) and BiFeO<sub>3</sub> (BFO), and the magnetic component materials include CoFe<sub>2</sub>O<sub>4</sub> (CFO), NiFe<sub>2</sub>O<sub>4</sub> (NFO), Fe<sub>3</sub>O<sub>4</sub>, La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> (LSMO) and metals.

## **1.2.2.1.** Horizontal Heterostructures

Horizontal multilayered films (Figure 1.2.2 a) of alternate ferroelectric perovskite and ferromagnetic spinel phases are the most widely investigated composites due to their ease of fabrication. In recent years a large number of composite horizontal multilayered structures have been investigated. These experiments have shown that these composite thin films have great potential for device applications. The observed ME effects were comparable to those of their bulk counterparts. High quality ferroelectric-magnetic PZT/Ni<sub>0.8</sub>Zn<sub>0.2</sub>Fe<sub>2</sub>O<sub>4</sub> multilayer films [54], BaTiO<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> and PZT/La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> bilayer films [55, 56], respectively, have been reported to have coexisting ferroelectric and ferromagnetic behaviors. The ME coefficient in these composite films ranges from 3 mV/cm Oe to 30 mV/ cm Oe. Heterostructures of CFO and BaTiO<sub>3</sub> have exhibited ME voltage coefficient  $\alpha_E$  ( $\Delta E/\Delta H$ ) of 66 mV/cmOe [57]. Recently, simple heterostructures of epitaxial Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub> films on La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> single crystal substrates have exhibited ME coefficient as high as 600 mV/cmOe depending on growth conditions [58]. One of the drawbacks of horizontal heterostructures is that the ME effects are weakened due to the large in-plane constraint (or clamping) from the substrate [59].

## 1.2.2.2. Vertical Nanostructures

One way to avoid the substrate clamping is to grow vertical nanostructures (Figure 1.2.2 b). There have been some reports of vertical nanostructured film in which ferrimagnetic CFO nanopillars are embedded in a BFO film [60, 61]. It was shown that an electric field could change the magnetic configuration of the CFO pillars. The strength of the ME coupling between the ferroelectric matrix and the ferrimagnetic nanopillars, was estimated from the electric field-induced change of magnetization ( $\Delta M$ ) which gave  $\alpha = \Delta M/\Delta E = 0.126$  Oe cm V<sup>-1</sup>. The mechanism responsible for the electric field-induced changes in magnetization was due to the intimate lattice coupling between CFO and BFO. This was possible due to the three-dimensional heteroepitaxial growth in such vertical structures. In vertical nanostructures as described above, the shape of the piezoelectric matrix changes with the application of an electric field through the inverse piezoelectric

effect (Figure 1.2.1). This alters the magnetic anisotropy of the ferromagnetic pillars via magnetostriction giving rise to the observed ME effect.

#### 1.2.2.3. Nano-particle Embedded Films

Wan et al., [62] used a sol-gel technique to grow composite films with CFO nanoparticles dispersed in PZT matrix (Figure 1.2.2. c). Zhong et al. [63] employed an analogous method to grow composite films of CFO nanoparticles in a ferroelectric phase of  $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$  (BNTO). Both films exhibited ferroelectric and ferromagnetic behaviors, and ME coefficients were measured in both studies. Murugavel et al. [64] prepared (100)-oriented PZT/NiFe<sub>2</sub>O<sub>4</sub> composites on (001) SrTiO<sub>3</sub> substrates by PLD where the NFO nanoparticles were randomly dispersed in the PZT matrix. However, the maximum values of  $\alpha_E$  for these composites were of the order of 10 mV/cmOe which is lower than that reported for bulk PZT/NFO particulate composites [18]. This might be due to lattice clamping effects by the substrate.

In all these structures it interfacial strain was always found to play a crucial role that determined the effectiveness of the coupling mechanism. The ultimate goal for multiferroic device fabrication would be a new single-phase or composite material with strong coupling between ferroelectric and ferromagnetic order parameters making for simple control over the magnetic nature of the material with an applied electric field at room temperature. Multiferroic memories when fully functional would offer the possibility of combining the best qualities of FeRAMs and MRAMs: fast low-power electrical write operation, and non-destructive magnetic read operation.

# **1.3. Chapter Summary**

In conclusion it can be said that high-quality thin films of composite multiferroic materials hold huge prospect for the rational design of new device functionalities. Preliminary experiments have shown that strong ME coupling at room temperatures can be achieved by the proper interfacial strain engineering in these composite heterostructures.

With this in mind, the work on the growth and characterization of 2-2 horizontal heterostructures of CFO and PZT was undertaken. CFO and PZT were chosen as the respective ferromagnetic and ferroelectric phases for their excellent room temperature magnetic and ferroelectric properties. Along the way, a single phase heterostructure using doped ZnO thin film was also fabricated and characterized for the first time. The following section gives a brief outline of the dissertation.

# **1.4. Dissertation Outline**

Chapter 2 describes the experimental and measurement techniques used in this work. It includes a description of the process of pulsed laser deposition of the thin films and heterostructures. It also discusses the measurement tools and how they were used to characterize the material properties of the deposited films. Chapter 3 and 4 describes the details of the results obtained from the experiments. Chapter 3 discusses the role of epitaxial thin films in controlling the ferromagnetic/ferroelectric properties of CFO/PZT bilayer films. Chapter 4 describes the interesting properties of doped ZnO thin films and how they can be manipulated to observe magneto-elastic coupling mechanisms. Chapter 5 will give a brief account of future directions and conclusions.

# **CHAPTER 2:**

### METHODOLOGY

This chapter describes the experimental setups and measurement techniques used in this work. The entire work was done at the Department of Physics, University of South Florida (USF). Thin film fabrication using pulsed laser deposition (PLD) and characterization was performed at Laboratory for Advanced Material Science and Technology (LAMSAT) at USF. The PLD set up used in this work was assembled under the guidance of R. Hyde. The structural characterization was done using X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscope (AFM). Some of the XRD scans and the AFM scans were performed at Nanotechnology Research and Education Center (NREC) at USF. The magnetic measurements were performed at Functional Materials Laboratory (FML) at USF. For the ferroelectric measurements a home-made micro-pole-station and ferro-tester set up was built at LAMSAT.

## 2.1. Pulsed Laser Deposition of Thin Films.

Pulsed laser deposition (PLD) is a versatile technique for thin-film and multilayer research [65]. During the last decade PLD has been extensively used to grow thin films of oxides and other complex materials [66].

Although the underlying ablation process is complex, PLD is conceptually and experimentally simple [65]. A ultra-violet KrF (wavelength of 248 nm, pulsed width of 20-25 ns) excimer laser beam is focused with an energy density (fluence) in the range 1 J/cm<sup>2</sup> to 6 J/cm<sup>2</sup> onto a rotating target inside a vacuum chamber as shown in the schematic diagram in Figure 2.1.1. The deposition chamber is equipped with a multi-target "carousel" (changer) and a substrate heater. For multilayer deposition, multiple targets can be sequentially exposed to the incident laser beam, thereby enabling the insitu growth of hetero-structures and super lattices with relatively clean interfaces.



Figure 2.1.1. Schematic diagram of the single laser deposition set up.

PLD is often described as a three-step process consisting of (i) laser-target interaction and vaporization of a target material, (ii) plasma plume formation and its

transport towards the substrate, and (iii) nucleation of the ablated species and growth of thin film on the substrate surface [67].

When the laser beam strikes the rotating target, the UV laser radiation is absorbed by the outermost layers of the target surface. This causes rapid heating and vaporization of the target material to form dense plasma. The highly energetic ablated species travel towards the substrate, crystallizing into a film with a composition typically identical to that of the target material [68].

PLD has several characteristics that distinguish it from other film-growth processes and provide special advantages for the growth of oxides, doped semiconductors and multicomponent materials.

- *Congruent (stoichiometric) transfer of materials.* Under the proper choice of laser fluence films have the same composition as the target. This sets PLD apart from incongruent-transfer methods such as thermal evaporation and sputtering.
- *Capability for reactive deposition in ambient gases.* Since the deposition chamber does not require any electron beam or hot filament, ambient gases can be used. Energetic species of the ablated plasma react with ambient gas molecules facilitating the deposition of multicomponent ceramic materials.
- *Growth of multilayered epitaxial heterostructures.* These thin films are composed of layers of materials of different compositions, but all layers share a common continuous crystal structure. With the revival of multiferroics such layered structures have been researched a lot to investigate magneto-electric coupling between the layers [9].

The ablation process has some characteristic limitations depending on the materials being ablated.

- Particulates. PLD films invariably have some particulates with diameters ranging from 0.1 to 10 μm (with most < 1 μm). These particulates are undesirable for multilayer structures where they lead to unacceptable scattering mechanism and surface roughness of films [69, 70].</li>
- Uniform film thickness. Due to the highly forward directed nature of the laser ablated plume, PLD films are uniformly thick only in a narrow region. To overcome this problem, all the films in this work were grown on small area (1 cm x 1 cm) substrates where uniform thicknesses were achieved.
- *Preferential ablation of elements for complex oxides*. For multi-component oxides such as PZT laser ablation is complicated by the high volatility of one of the elements i.e. Pb. Due to the high vapor pressure of Pb in PZT, at high growth temperatures the films are often obtained as Pb depleted with poor ferroelectric properties. [42].

These shortcomings of PLD can be overcome using a Dual Laser Deposition (PLD<sub>DL</sub>) technique [71]. The dual laser ablation technique used in this work has been described in more details elsewhere [72 - 75]. Figure 2.1.2 shows a schematic diagram of the PLD<sub>DL</sub> system. Briefly, the KrF excimer laser output is combined with a CO<sub>2</sub> laser (wavelength 10.6  $\mu$ m, pulse duration 500 ns) output. The laser beams are spatially and temporally overlapped on to a rectangular spot size of 6 mm<sup>2</sup> on the target. An intensified charge-coupled detector (ICCD) system is aligned normal to the plume propagation direction to image the visible wavelength emission from the laser induced plume. The

excimer laser and ICCD camera are triggered through the digital delay generator which is used to control the peak-to-peak (p-p) inter-pulse delay ( $\Delta t$ ) between the two lasers (Figure 2.1.2) [72 - 75].



Figure 2.1.2. Schematic diagram of the dual laser deposition set up.

The p-p delay is adjustable in the range -70 ns to 250 ns, relative to the peak of the excimer laser pulse. The temporal profiles of the two laser pulses are directly observed on a 400 MHz, 2 G-sample/sec oscilloscope through the use of a UV photodiode and an IR pyroelectric detector, thereby allowing a precise adjustment of the required inter-pulse delay [76]. The ICCD imaging and emission spectroscopy of the ablated plumes in  $PLD_{DL}$  are used in determining the optimum coupling of the laser outputs and optimizing the growth parameters for film deposition.



Figure 2.1.3. Photograph of the custom built PLD system at LAMSAT.

At the optimum coupling condition of laser energies enhanced plume excitation and expansion is observed that facilitates the growth of very smooth, particulate-free, and uniform films over large area. Figure 2.1.3 shows a photograph of the custom built PLD system at LAMSAT used in this work. The individual parts have been labeled.

A general scheme followed for the deposition of all the thin film in this work. The target to substrate distance was always kept constant at 6 cm. Thin films were deposited on various single crystal substrates such as Si (100), c-cut sapphire (Al<sub>2</sub>O<sub>3</sub>) (0001), MgO (100) and SrTiO<sub>3</sub> (STO) (100). The substrates were firstly cleaned using ultrasonic cleaning in acetone, methanol, rinsed with de-ionized water, and then dried with high purity N<sub>2</sub> gas before loading into the deposition chamber. The base pressure in the deposition chamber was kept constant at  $10^{-6}$  T. High purity O<sub>2</sub> gas was used as the background ambient gas during deposition. After the deposition, the films were cooled down to room temperature gradually in the same partial O<sub>2</sub> pressure (pO<sub>2</sub>).

In the following chapters the deposition conditions for the films will be summarized in a tabular form. As an example Table 2.1 lists the deposition condition for a film named 'Sample A'.

Sample	Substrate	Laser Fluence (J/cm <sup>2</sup> )	Growth Temperatures $T_s$ (°C)	$O_2$ Pressure pO <sub>2</sub> (mT)	Film Thickness (nm)
Sample A	Si	2	600	10	200

Table 2.1. Summary of deposition conditions of a thin film named Sample A.

# 2.2. Structural Characterization

This section is devoted to explain the basic principles and the techniques that were used for the structural characterization of the thin films. Structural characterization helped in optimizing the growth conditions required for producing high quality thin films. It also helped in investigating the micro structural properties of the films such as crystallinity and surface morphology and how they were related to their material properties such as magnetization, polarization, conductivity, etc. Crystal structure and phase of the thin films were determined from the X-ray Diffraction (XRD) analysis. Chemical purity and stoichiometry were confirmed by the Energy Dispersive X-ray Spectroscopy (EDS). Surface morphology of the thin films was studied using the Scanning Electron Microscope (SEM) and the Atomic Force Microscope (AFM).

### 2.2.1. X-ray Diffraction

X-ray diffraction (XRD) is a widely used, simple yet versatile tool that can all issues related to the crystal structure of thin films, including lattice parameters, identification of unknown materials, orientations of single crystalline films, preferred orientations of polycrystalline films, defects, stress, etc. Since the wavelength of X-rays (approx. 0.1 to 1 Å) is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms in a wide range of materials. XRD is non destructive and does not require elaborate sample preparation [77].

The basic principle is based on Bragg's law given by:

 $2d\sin\theta = n\lambda$  (2.1)

where  $\theta$  is the angle of incidence of the X-rays,  $\lambda$  is the wavelength of the X-rays, and n is a positive integer representing the order of the diffraction peak. Figure 2.2.1 shows an

incident beam of parallel X-rays impinging the crystal surface at an angle  $\theta$ , and getting reflected from the parallel planes of atoms formed by the crystal lattice of the material. The atoms, represented as spheres in all the figures, can be viewed as forming different sets of planes in the crystal. Two consecutive reflected beams have a phase difference because they travel a different path. Constructive interference of the reflected rays occurs only when their path difference is an integer multiple of the wavelength of X-ray as given in Equation 2.1. A characteristic diffraction pattern is produced and plotted as intensity (I) versus 2 $\theta$  graph. The measured pattern can be then compared with a known database of reference patterns to determine the crystal structure of the film.



Figure 2.2.1. X-ray reflection from lattice planes illustrating Bragg's law.

Polycrystalline films generate XRD patterns with all the possible crystal orientations of the material similar to the bulk powders. However, preferred oriented or textured films demonstrate XRD patterns with certain Bragg reflections more pronounced than the others. Figures 2.2.2 (a, b, and c) show schematic diagrams of randomly orientated crystallites in a polycrystalline film, textured film with preferred weak

orientation, and epitaxial film with strong orientation, respectively. The preferred crystallographic directions lead to anisotropic properties in thin films [78].



Figure 2.2.2. Schematic diagram of crystallites in a (a) polycrystalline film with random orientation, (b) textured film with preferred weak orientation, (c) epitaxial film with strong orientation, respectively. (Adapted from Ref. [78])

The XRD scans were carried out with Cu K $\alpha$  radiation using Bruker D8 Focus Xray Diffractometer equipped with a position sensitive Lynx Eye detector (PSD). Figure 2.2.3 shows a photograph of the equipment and its major components. The four major components in the system are: X-ray source consisting of a Cu anode, LynxEye X-ray detector (five times more resolution power than scintillation detectors), goniometer with sample holder, and control computer. The system can perform all linear scans such as  $\theta$ - $2\theta$  scans,  $2\theta$ -  $\omega$ , asymmetric or detector scans, and rocking curves.

The following sections briefly describe the various types of scans that were performed during this work.

During  $\theta$ -2 $\theta$  scan, the angle of incidence ( $\theta$ ) and the angle of detection (2 $\theta$ ) are continuously varied but kept  $\theta$  and 2 $\theta$ , respectively, in a locked-coupled mode. Figure 2.2.4 shows an example of a  $\theta$ -2 $\theta$  scan performed on an epitaxial (100) film grown on a (100) single crystal substrate.



Figure 2.2.3. Photograph of Bruker D8 X-ray Diffractometer at LAMSAT showing the individual parts.

The Bragg reflections occur only from the (100) planes that are parallel to the substrate planes. The out-of-plane lattice parameter  $(a_{\perp})$  can be calculated for the cubic system of crystals using the relation:

$$a = d_{(hkl)} \sqrt{\left(h^2 + k^2 + l^2\right)}$$
(2.2)

which gives  $a_{\perp} = d_{(100)}$  (i.e. d spacing for (100) plane).



Figure 2.2.4. Schematic diagram of X-ray reflections from the parallel crystal planes of a (100) oriented film grown on a (100) single crystal substrate.

Asymmetric scans are used in order to calculate the in-plane lattice parameter  $(a_{II})$ in epitaxial films. In asymmetric scans the incident x-ray is set at a characteristic diffraction angle  $\theta$  corresponding to a plane other than the epitaxial plane. The reflected beam is then traced by the detector which scans from 0 to 2 $\theta$ . The XRD peak occurs when the Bragg condition is satisfied for the plane for which the incident angle is initially set. This is illustrated in Figure 2.2.5 which shows the asymmetric scan being performed about the (111) plane for an epitaxial (100) film grown on a (100) single crystal substrate. When the detector reaches the correct 20 values for the (111) plane, the Bragg reflection occurs. This allows for the calculation of d spacing (d<sub>(111)</sub>). The in-plane lattice parameter (a<sub>II</sub>) is calculated using equation (2.2) which gives  $a_{II} = \sqrt{3} d_{(111)}$ .



Figure 2.2.5. Schematic diagram of asymmetric scan or detector scan performed about the (111) plane of an epitaxial (100) oriented film grown on single crystal (100) substrate.

Thin films inevitably have in built stresses due to the deposition process. For an unstressed cubic crystal the bulk lattice parameter  $(a_0)$  is same in all directions. However, in a thin film the out-of-plane  $(a_{\perp})$  and in-plane  $(a_{\parallel})$  lattice parameters could be different depending on whether the film grows with compressive or tensile (expansive) strains. As shown schematically in Figure 2.2.6, if the bulk lattice parameter  $(a_0)$  of the material is greater than that of the substrate  $(a_{substrate})$  or  $a_0 > a_{substrate}$ , then in order to match the

smaller lattice parameter of the substrate the film gets compressed in-plane and extended out-of-plane making  $a_{\perp} > a_{\parallel}$ . In this case the film is said to be under in-plane compressive strain. The situation is opposite when  $a_0 < a_{substrate}$ , then the film gets extended in-plane and compressed out-of-plane making  $a_{\perp} < a_{\parallel}$ . In this case the film is under in-plane tensile strain.



Figure 2.2.6. Schematic diagrams of films grown under compressive and tensile strains.

The out-of-plane and in-plane strains ( $\epsilon$ ) at room temperature can be calculated by using the formula:

$$\varepsilon = \frac{a - a_o}{a_o} \tag{2.3}$$

where *a* is the out-of-plane  $(a_{\perp})$  or in-plane  $(a_{\parallel})$  lattice parameters and  $a_o$  is the bulk unstressed lattice parameter, respectively. The out-of-plane and in-plane and stresses  $(\sigma)$ in the film were calculated using Hook's law,  $Y = \sigma/\epsilon$ , relating the in-plane strain values  $(\epsilon)$  and the Young's modulus (Y) value for the material.

The residual stress in a thin film is generally caused by the lattice mismatch between film and substrate or post-deposition processing or external influences like differences in thermal expansion coefficients between the film and the substrate, or the microstructure of the film [79]. The stress analysis is especially critical in multiferroic heterostructures since the magneto-electric effect is mediated through interfacial stress [9].

To quantify the residual stress in a thin film one can use the  $\sin^2\psi$  technique of stress measurement. The  $\sin^2\psi$  technique is a standard non-destructive technique to measure residual stress in a material. In this work the  $\sin^2\psi$  technique was performed using a Philips X'Pert X-ray Diffractometer equipped with a 3 dimensional (pole-figure) goniometer as shown in Figure 2.2.7 (a). This allows the rotation of the sample in three degrees of freedom about the angles  $\theta$ ,  $\varphi$  and  $\psi$  as shown in Figure 2.2.7 (b). In  $\sin^2\psi$ technique, a highly textured film is scanned in the vicinity of a Bragg reflection plane. A shift in the Bragg reflection (20) is observed if a strained film is tilted by an angle  $\psi$  [80]. The scan is performed in the continuous scan mode with the incident angle  $\theta$  and the detector fixed at 20 for the plane under investigation, while changing the  $\psi$  angle at the same time but keeping the  $\varphi$  angle at 0°.

Due to the residual stress the lattice parameter and consequently the d-spacing of the parallel crystal planes change causing a shift in the  $2\theta$  peaks. When the film is under

compression the 2 $\theta$  peaks show a shift to higher angles due to the decrease in d-spacing following Bragg's law. The 2 $\theta$  value for each  $\psi$  angle was used to calculate the d values using Equation 2.1. The shift in d values ( $\Delta$ d) are calculated using  $\Delta$ d = d –d<sub>o</sub> where d<sub>o</sub> is the unstrained lattice spacing of the film.



Figure 2.2.7. (a) Photograph of Philips X'Pert X-ray Diffractometer. (b) Schematic diagram showing the angles  $\theta$ ,  $\phi$  and  $\psi$  with respect to the thin film sample and the incident X-ray beam.

For biaxial residual stress the d-spacing versus  $\sin^2 \psi$  graph follows a linear relationship. Hence the residual stress ( $\sigma_R$ ) is calculated from the slope of the linear fit of  $\Delta d/d_o \text{ vs } \sin^2 \psi$  graph following the equation [80]:

$$\sigma_{R} = \frac{1}{2} \left( \frac{Y}{1+\nu} \right) \left( \frac{\partial d}{\partial \sin^{2} \Psi} \right) \left( \frac{1}{d_{o}} \right)$$
(2.4)

where  $d_0$  is the value at  $\psi = 0^\circ$ , Y is the Young's modulus and v is the Poison's ratio for the film.

If the residual stress is not biaxial the sample has to be rotated to different  $\varphi$  angles and the sin<sup>2</sup> $\psi$  technique has to be repeated at each  $\varphi$  angle. The equations used are as follows [80]:

$$\frac{d_{\phi\psi} - d_0}{d_0} = \frac{1 + \upsilon}{E} \sigma_{\phi} \sin^2 \Psi - \frac{\upsilon}{E} (\sigma_{11} + \sigma_{22})$$
(2.5)

$$\sigma_{\phi} = \sigma_{11} \cos^2 \phi + \sigma_{22} \sin^2 \phi \tag{2.6}$$

The  $\sin^2 \psi$  technique is unique compared to other XRD scans as it gives a quantitative value for the residual stress.

Rocking curves ( $\omega$ -scans) are used to estimate the degree of in plane orientation in textured films can be investigated using rocking curves. The rocking curve scans are always performed about the plane of preferred orientation. The detector is fixed on the  $2\theta_0$  position of the Bragg plane under investigation, and the sample is tilted (rocked) about the vicinity of the angle  $\theta_0$  as shown in Figure 2.2.8. The FWHM obtained from the rocking curve reveals the degree of film orientation. A narrow peak indicates of a high degree of in-plane orientation of the crystallites. For a perfect single crystal, the ideal rocking curve peak is a  $\delta$  function [78]. The rocking curves of a highly oriented thin films generally show a finite peak width (< 1°).



Figure 2.2.8. Schematic diagram of the X-ray rocking curve measurement where the sample is tilted (rocked) about the plane of orientation.

Azimuthal scans ( $\varphi$  scans) are used to determine the crystal symmetry and epitaxial growth in thin films. The  $\varphi$  scans in this work were performed using the Philips X'Pert X-ray Diffractometer. Figure 2.2.9 (a) shows the initial set up for a typical  $\varphi$  scan to be performed to confirm the cubic symmetry of an epitaxial (100) thin film. Although the epitaxial (100) planes give Bragg reflection at incident angle  $\theta$ , there are other sets of parallel planes for example (111) that could also satisfy Bragg condition provided the sample is mounted at some other incident angle  $\theta_0$ . In order that Bragg's condition is satisfied for the plane (111) the sample is rotated by  $\psi = 45^\circ$  which is the angle between the (111) and (100) planes.



Figure 2.2.9. Schematic diagram of  $\phi$  scan performed to determine the cubic symmetry of a (100) oriented thin film.

The  $\psi$  angle is calculated using the formula:

$$\Psi = \cos^{-1} \left[ \frac{hh_e + kk_e + ll_e}{\sqrt{h^2 + k^2 + l^2} \sqrt{h_e^2 + k_e^2 + l_e^2}} \right]$$
(2.7)

where (hkl) and ( $h_ek_el_e$ ) are the Miller indices for the two planes under consideration for a cubic crystal system. Now with the incident beam fixed at  $\theta_o$  (Bragg angle for (111) plane) and the detector fixed at  $2\theta_o$  and  $\psi = 45^\circ$  the sample is rotated about the  $\phi$  angle from 0 to 360°.

If there are only four peaks in the  $\varphi$  spectra that are separated by equal intervals of 90° it confirms the four fold symmetry of the cubic system and the in plane epitaxy. As shown later, both for cobalt ferrite and PZT the  $\varphi$  spectra peaks occur at 90° intervals, since both crystals exhibit four fold symmetry.

## 2.2.2. Scanning Electron Microscope

Scanning Electron Microscope (SEM) is one of the most widely used techniques to characterize the surface morphology and cross-section of the thin films. In this work all the imaging was performed using a JOEL JSM-6390LV SEM. Figures 2.2.10 (b, c, and d) show the major components of the SEM: the electron gun column, specimen chamber and control console. Figure 2.2.10 (a) shows a schematic diagram of path of the electron beam inside the electron gun column. The electron gun column consists of an electron gun and magnetic lenses (Figure 2.2.10 a). The control console consists of a LCD viewing screen and a control computer. At the base of the column is the specimen chamber (Figure 2.2.10 c) which is evacuated to about 10<sup>-6</sup> Torr during operation. The electron gun consists of three components: tungsten wire filament serving as cathode, grid cap and anode (Figure 2.2.10 a).



Figure 2.2.10. (a) Schematic diagram of electron gun column. (b, c, and d) Photographs of the JOEL SEM at LAMSAT with the major components identified.

The tungsten filament is heated by a current to a temperature of 2000-2700 K which results in thermionic emission of electrons and accelerates them to energy in the range 0.1–30 keV. A series of magnetic lenses focuses the electron beam to a small spot on the specimen. When the focused electron beam interacts with the specimen various signals including secondary electrons (SEs), backscattered electrons (BSEs), Auger

electrons, X-rays, cathodoluminescence are generated. SEs are mostly used for imaging as they mainly indicate the information about the specimen surface. However, BSE imaging provides compositional information as they interact with the positively charged nucleus of the specimen and are scattered at large angles (0° to 180°). The JOEL JSM-6390LV SEM is equipped with both the BSE and SE detectors. The machine has a maximum resolution power of 3 nm at an acceleration voltage of 30 kV and working distance (WD) of 8mm. The magnification could be varied from 5x to 300,000x.

### 2.2.3. Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray Spectroscopy (EDS) is a type of electron spectroscopy, which uses the unique energy levels of the characteristic X-rays emitted from the atoms of the sample under investigation. Figure 2.2.11 (a) shows the major components of the EDS detector from Oxford Instruments INCA X-sight 7582M that was attached to the JOEL SEM described in Section 2.2.2. The working principle for EDS is very simple. As shown in Figure 2.2.11 (b), when the high energy primary electron beam from the SEM interacts with the atoms of sample it creates an "interaction volume," typically several microns in diameter. Several signals are generated along with characteristic X-rays, which are fingerprints of the individual atoms encountered. These X-rays can penetrate through the material, allowing them to escape and be detected by the EDS detector. Because the intensity of the individual X-ray is related to the quantity of the "parent atom" in the interaction volume, quantitative elemental analysis can be obtained from the sample. From the EDS spectra one can investigate the elementary composition of the materials and the presence of any foreign impurity in the sample. The stoichiometry of

the sample is also tested from the elementary analysis of the EDS spectrum. In this work, the EDS scans were always performed using Cu calibration.



Figure 2.2.11. (a) Photograph of the Oxford Instruments EDS detector that was attached to JOEL SEM. (b) Schematic diagram of signals generated when electron beam from SEM interacts with the sample.

## 2.2.4. Atomic Force Microscope

Atomic Force Microscope (AFM) is a very high resolution scanning probe technique that can be used to analyze the surface of the thin films. The AFM works much the same way as a phonograph or a profilometer, only on a much smaller scale [81]. As shown in Figure 2.2.12 (a), a very sharp tip (few nm) that is attached to a cantilever is dragged on the sample surface. During the scan, the probing tip is brought in close proximity to the sample surface and gets affected by Van der Waals forces between the atoms of tip and the surface. This causes a vertical deflection of the cantilever reflecting the topography of the surface. The deflection is recorded as a change in the direction of a reflected laser beam from the top of the cantilever picked up by a photodiode [81]. By collecting the height data for a succession of lines it is possible to form a three dimensional map of the surface features. Figure 2.2.12 (b) shows the major components of the Digital Instruments III Atomic Force Microscope that was used to scan the surfaces of the thin films in this work.



Figure 2.2.12. (a) Schematic diagram of the basic working principle of a typical AFM. (b) Photograph of Digital Instruments III Atomic Force Microscope.

# 2.3. Electrical Characterization

The electrical properties of the films were measured using the Van der Pauw technique [82 - 84]. Since the thicknesses of the films were much smaller than their length and breadth, and they were grown on symmetrical (1 cm x 0.5 cm) substrates, the Van der Pauw method could be successfully applied. The electrical contacts were made with silver epoxy and gold wires. They were placed on the periphery of the film as shown in the schematic diagram in Figure 2.3.1 (a).



Figure 2.3.1. Schematic diagrams of Van der Pauw technique of thin film (a) resistivity and (b) Hall measurements, respectively.

During the Hall measurements the magnetic field (H) was applied perpendicular to the film plane as shown in the schematic diagram in Figure 2.3.1 (b). The electromagnet could provide a maximum field of 0.5 T. This was kept constant for all measurements. For measuring the temperature dependence of resistivity and carrier concentration the samples were cooled in a continuous He flow cryostat which could reach temperatures as low as 30 K.
## 2.4. Magnetic Characterization

All the magnetic measurements in this work were performed using a commercial Physical Property Measurement System (PPMS) from Quantum Design equipped with a Vibrating Sample Magnetometer. As shown in Figure 2.4.1, the PPMS consists of two major components: a liquid Helium Dewar with a 7 T longitudinal superconducting magnet and a temperature controller which can operate in the range 1.9 K to 400 K. The orientation of the thin film sample with respect to the magnetic field inside the PPMS can be varied.



Figure 2.4.1. Photograph of the magnetic measure system, PPMS from Quantum Design.

The sample surface can be positioned either parallel or perpendicular to the applied magnetic field to measure the in-plane and out-of-plane magnetizations. Such

measurements are required for identification of the easy or hard axis of magnetization in thin films. If the easy axis of magnetization is parallel to the film plane then in-plane magnetization would shows saturation at lower applied fields than out-of-plane magnetization and vice versa. In this work, all the magnetization measurements were carried out at 10 K or 300 K in range of magnetic fields from -5 T to 5 T.

#### 2.5. Ferroelectric Characterization

The ferroelectric properties of the thin films were measured using a specially designed and assembled experimental set-up. As shown in Figure 2.5.1 the set-up consists of a Precision LC Materials Analyzer, an optical microscope with video monitor, a probe station, and control PC. The Precision LC Materials Analyzer from Radiant Technologies is the ferro-electric tester component. The optical microscope is from Zeiss equipped with a Sanyo color CCTV camera and video monitor. The probe station includes sample stage holder, micro-manipulators and pole pieces. The micro-manipulators on the probe station are KRN-01A 'DC' positioners from J-Micro Technology. The manipulators have a 0.3 inch movement range in x, y, and z directions which sets a limit to the separation between the electrodes on the film. The manipulator's base is magnetic which helps in reducing noise due to mechanical vibrations during measurement.

For the proper polarization of the ferroelectric capacitors, very small electrodes were fabricated (approx. 100  $\mu$ m diameter) which could be seen only through the microscope and in the video monitor screen (Figure 2.5.1). The needles like pole pieces have a 20  $\mu$ m tip and are made from tungsten or Pd alloy. They are used to connect the electrodes on the film to the ferro-tester (Figure 2.5.1). The Precision LC ferro-tester includes many features such as +/- 10 V options, minimum pulse width of 50  $\mu$ s, minimum rise time @ 5 V of 40  $\mu$ s with 10 kHz Fatigue Frequency and minimum Hysteresis loop of 10s. The various tests that can be preformed include Hysteresis, Leakage Current, Charge, Retention, I (V), C (V), Fatigue, PUND, and imprint.



Figure 2.5.1. Photographs of the home-made set-up used for ferroelectric measurements of thin films.

For Hysteresis measurement the Precision LC uses an in built modified Sawyer-Tower circuit as shown in Figure 2.5.2 [85].



Figure 2.5.2. Block diagram of Sawyer-Tower circuit used for hysteresis measurement of ferroelectric thin film.

The circuit has been modified to avoid noise by applying virtual ground [86] The FE thin film capacitor is usually fabricated using top and bottom electrodes as shown in Figure 2.5.2. By measuring the potential (V) across a reference capacitor in series with the FE thin film capacitor (FEC) one can determine the charge (Q) on the FEC using the relation [86]:

$$Q = \int I dt = \int j\omega C V_0 e^{j\omega t} dt = CV$$
(2.8)

when the input voltage is  $V = V_0 e^{j\omega t}$  and C is the capacitance of reference capacitor. When two capacitors are in series the charge on each capacitor must be the same (ideally), so the electric charges on the reference capacitor and the FEC are the same. Since the reference capacitor has a very high capacitance, most of the voltage drops across the FEC. Thus the signal V in the display represents the voltage across the sample. The P signal is proportional to the charge on the FEC. In the FEC there is a remnant polarization, i.e., the electric dipole moments remain aligned in the direction it was poled by the applied field even after this field has been removed. Thus a plot of P versus V displays hysteresis [87].

In order to confirm the accuracy of the polarization measurements using the custom built ferroelectric tester, the system was calibrated using a standard capacitor (RT040903T018-SKTBD) from Radiant Technologies. Figure 2.5.3 (a) shows a photograph of the reference standard capacitors. Figure 2.5.3 shows a schematic diagram of the cross-section. The standard capacitor is a PZT thin film grown on Si substrate having a top and bottom electrode configuration. The known values of polarization of the standard capacitor provided in the specification data sheets were compared with the values obtained from the measurement. The same values were obtained. This validated the polarization values obtained for the deposited films.



Figure 2.5.3. (a) Photograph of the standard FE capacitor used for calibration of the ferrotestor. (b) Schematic diagram of the cross-section of the standard FE capacitor.

# 2.6. Chapter Summary

This chapter gave an outline of the experimental methods and procedures used in this work. High quality thin films were prepared using PLD. Structural characterization was studied using XRD, SEM, EDS and AFM. Magnetic measurements were performed using PPMS. Measurements of ferroelectric properties required fabrication of a homemade ferro-tester system. Following chapters elaborate on the results obtained from these experiments.

#### CHAPTER 3:

#### **CFO-PZT BILAYER THIN FILMS**

In recent years there have been numerous reports of the magneto-electric (ME) effect in layered CFO-PZT structures mostly grown on Pt/Ti/SiO<sub>2</sub>/Si substrates [88-93] and some on MgO [94] or STO [95] substrates. It is considered that the ME effect in such composite structures is mediated mechanically by the mutual interaction between the constituent elastic, magnetic and electric components [89, 94]. However the structure property relationships in such composite thin films have remained elusive. Hence a systematic study on the growth of these multiferroic composite structures was undertaken.

In this thesis, composite bilayered thin films consisting of CFO and PZT as ferromagnetic and ferroelectric phases, respectively, were chosen and fabricated. Horizontal bilayer configuration was selected for the ease of fabrication. Moreover the layered structures allowed for the effective separation of the conducting magnetic phase so as to enhance the polarization in the insulating ferroelectric layer. More importantly, the lattice strain and interlayer interaction was investigated with ease in such horizontal heterostructures [89, 96, and 97]. The coupling effect between the CFO and PZT was investigated through the stress analysis of the constituent layers using high resolution X-ray diffraction. The first two sections of the chapter discuss the CFO and PZT single layer films. The third section describes the CFO-PZT bilayer films.

#### 3.1. Cobalt Ferrite (CFO) Thin Films

Cobalt ferrite, CoFe<sub>2</sub>O<sub>4</sub>, belongs to the family of spinel-type ferrites and is one of the important magnetic materials with high coercivity, moderate magnetization and highest magnetostriction coefficient [17, 35 - 38]. The magnetocrystalline anisotropy constant (K<sub>1</sub>) at room temperature for CFO is  $2 \times 10^6 \text{ erg/cm}^3$ , which is one of the highest for ferrites [98, 99]. However, the direction of anisotropy in CFO thin films can change depending on the growth conditions [100, 101], the choice of substrate, and whether the film is grown under compression or tension [102, 103]. Stress anisotropy comes from stresses produced in the CFO films during the deposition process, or by thermal expansion differences, or lattice mismatch between substrates and films [37]. If grown under tension, CFO thin films have a tendency to grow with the easy axis perpendicular to the substrate which makes it an attractive material for applications in magneto-optic recording [17]. CFO has a very high magnetostriction coefficient ( $\lambda_{100} = -200 \times 10^{-6}$  to -590 x 10<sup>-6</sup>) [98]. For this reason CFO has been extensively explored as a promising magnetostrictive material for applications in actuators, sensors, and transducers [104 – 107]. CFO is considered as a key component for multiferroic multilayers or composites [96]. Epitaxial CFO/PZT composites [108] have exhibited multiferroicity. CFO has also found applications in microwave devices due to its high resistivity (~10<sup>7</sup> $\Omega$ .cm) and large permeability at high frequency (~1000MHz) [11]. Due to the good insulating properties and high Curie temperature, it has been used in magnetic tunnel junctions [109].

To summarize, CFO thin films have great potential for technological applications varying from magnetic recording to microwave devices. Hence a systematic study of the magnetic properties of CFO thin would be beneficial.

#### **3.1.1. Experimental Details**

The CFO target was prepared by standard pressing-sintering technique. Weighed amount of high purity CFO powder was uniformly grinded and then pressed into a disc with a diameter of 30 mm and thickness of 5 mm. This disc was sintered in a furnace at 1000°C for 2 hours to obtain a dense hard target. The target density was calculated to be 4.5 g/cm<sup>3</sup>.

CFO films were grown on various single crystal substrates such as Si (100), c-cut sapphire ( $Al_2O_3$ ) (0001), MgO (100) and SrTiO<sub>3</sub> (STO) (100). Table 3.1 summarizes the deposition conditions of the CFO films. The deposition rate under these conditions was 0.1 nm/s.

Sample	Substrate	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Film Thickness	
		$(J/cm^2)$	$T_s(^{\circ}C)$	$pO_2(mT)$	(nm)	
CFO-Si	Si (100)	2	450	10	50, 100, 200	
CFO-Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> (001)	2	450	10	200	
CFO-MgO	MgO (100)	2	450	10	200	
CFO-STO	STO (100)	2	450	10	200	

Table 3.1. Deposition conditions of CFO films on different substrates.

### **3.1.2. Results and Discussions**

The following sections describe the structure-property relationships of epitaxial CFO thin film on MgO and STO substrates. A detailed discussion on polycrystalline CFO films grown on Si and Al<sub>2</sub>O<sub>3</sub> substrates has been included in Appendix A.

## **3.1.2.1. Structural Properties**

The microstructure of the CFO target surface was first studied. Figure 3.1.1 shows

SEM images of the prepared target surface exhibiting tetragonal crystals of CFO.



Figure 3.1.1. SEM images of CFO target surface.

Table 3.2 shows the Co/Fe ratio in the CFO target and the deposited films on different substrates, obtained from the EDS analysis. The average Co/Fe ratio is close to 2 confirming the proper stoichiometry.

Table 3.2. Ratio of Co/Fe in CoFe<sub>2</sub>O<sub>4</sub> target and thin films, obtained by EDS analysis.

Sample	Co/Fe ratio
CFO target CFO- Si CFO- MgO CFO- STO	$\begin{array}{c} 1.96 \pm 0.11 \\ 2.04 \pm 0.08 \\ 2.01 \pm 0.06 \\ 2.04 \pm 0.08 \end{array}$

## 3.1.2.1.1. Epitaxial CFO thin films

The small lattice mismatches of CFO (face-centered cubic, lattice parameter, a = 8.391 Å) with MgO (face-centered-cubic, 2 x lattice parameter = 8.42 Å); and STO (primitive cubic, 2 x lattice parameter = 7.81 Å), respectively, allow for the epitaxial growth of CFO-MgO and CFO-STO films. The lattice mismatch at room temperature

was calculated using the relation  $(a_s - a_o)/a_s$  (%) where  $a_s$  and  $a_o$  are the lattice parameters of the substrate and the bulk powder. The calculated values of lattice mismatches for CFO-MgO and CFO-STO are 0.34% and -7.4%, respectively.

The surface morphology of CFO-MgO film was examined using AFM. Figure 3.1.2 (a) shows an AFM image of the CFO surface. The as-deposited film exhibits a uniform and flat surface with a root-mean-square value of surface roughness ( $R_{rms}$ ) of 2.084 µm. The average grain size is around 50 nm. Figure 3.1.2 (b) shows a section analysis of the film surface where the height of surface features is plotted against a horizontal line scan. It is evident that the surface features are small (<5 nm) indicating a highly flattened surface. Such a flattened surface could be indicative of a layer by layer growth mechanism as reported earlier [110].



Figure 3.1.2. (a) AFM image of CFO film on MgO substrate. (b) Section analysis of CFO film on MgO. Horizontal and vertical distances between red markings are  $3.008 \mu m$  and  $1.288 \mu m$ , respectively.

Figures 3.1.3 (a, b, and c) show the XRD  $\theta$ -2 $\theta$  scans for the CFO powder, CFO-STO and CFO-MgO films, respectively. The CFO powder XRD pattern (Figure 3.1.3 a) shows all the characteristic peaks of CFO [111]. The peaks match with the face-centered cubic phase with space group Fd-3m (227). The XRD patterns for CFO-STO and CFO-

MgO films (Figures 3.1.3 b, and c) show only the (400) peak of CFO with no trace of any impurity peaks even in the logarithmic scale. This demonstrates the epitaxial growth. The inset to Figure 3.1.3 (c) shows a close-up view for the CFO (400) and MgO (200) peaks. Due of the larger lattice mismatch (7.4 %) for CFO film grown on STO, CFO (400) peak is shifted significantly to lower  $\theta$  values (Figure 3.1.3 b) compared to the corresponding powder peak (Figure 3.1.3 a). This peak shift indicates that the lattice structure of the CFO film lattice is possibly tetragonally distorted as reported earlier [112, 113].



Figure 3.1.3. XRD patterns of (a) CFO powder target, and epitaxial CFO films grown on (b) STO (100), and (c) MgO (100) substrates, respectively. The inset to (c) shows the details of MgO (200) (left) and CFO (400) (right) peaks.

In order to verify the epitaxial relationship,  $\phi$  scans and rocking curves were performed for the CFO-STO and CFO-MgO films. Figures 3.1.4 (a, and d) show the  $\phi$  scans for CFO films on STO and MgO substrates, respectively.



Figure 3.1.4. Left column of graphs (blue) (a, b, c) represent the film grown on STO and the right column (red) (d, e, f) represents films grown on MgO. (a, and d)  $\varphi$  scan spectra from (311) CFO reflection. (b, and e) Rocking curves of CFO (400) peaks. (c, and f) Asymmetric scans of the (511) and (440) planes of the CFO films.

The  $\phi$  scan measurements were conducted using Bragg's reflection from the (311) plane of CFO. In both cases the peaks of the  $\phi$  spectra occur at intervals of 90°

confirming the cubic symmetry and in plane epitaxial growth. Figures 3.1.4 (b, and e) show the rocking curves ( $\omega$ -scans) about the (400) plane of CFO-STO and CFO-MgO, respectively. The FWHM value for CFO-MgO film is 0.076°, which confirms an excellent crystallographic texture along (100) direction. However, FWHM in the case of CFO-STO film is larger (0.915°) (Figure 3.1.4 b). This is due to the larger lattice mismatch between CFO and STO as mentioned earlier. Figures 3.1.4 (c, and f) show the asymmetric scans of the CFO (511) and (440) planes.

#### 3.1.2.1.2. Residual Stress in CFO thin films

In the unstressed bulk CFO powder both the out-of-plane  $(a_{\perp})$  and in-plane  $(a_{n})$ lattice parameters are same in all directions. However in the CFO thin film due to the strains induced by lattice mismatches between substrates and the films, the  $a_{\perp}$  and  $a_{n}$  values are different. In order to study the effect of strain on CFO films, the  $a_{\perp}$  and  $a_{n}$  were calculated. The out-of-plane lattice parameters  $(a_{\perp})$  were calculated from the XRD  $\theta$ -2 $\theta$ scans (Figure 3.1.3). The in-plane lattice parameters  $(a_{n})$  were calculated from the asymmetric scans about the CFO (511) and (440) planes (Figures 3.1.4 c, and f). Table 3.3 summarizes all the lattice parameters and calculated strains. The in-plain strain ( $\epsilon$ ) was calculated by using the formula  $\epsilon = (a_{n} - a_{0})/a_{0}$  where  $a_{0}$  is the unstressed bulk lattice parameter for CFO ( $a_{0} = 8.391$  Å). The in-plane stress ( $\sigma$ ) was calculated using  $\sigma = Y\epsilon$ where Y is Young's modulus [98] for CFO along the (100) or in-plane direction ( $Y_{100} =$ 1.5 x 10<sup>12</sup> dyne/cm<sup>2</sup>). Stress anisotropy constant ( $K_{a}$ ) was estimated using  $K_{a} = (3/2) \lambda_{100}$  $\sigma$ , where  $\lambda_{100}$  for CFO [98, 100] is -590 x 10<sup>-6</sup>. From the listed values in Table 3.3 it is observed that in case of CFO-MgO film,  $a_{n}$  and  $a_{\perp}$  differ by only 0.15%. However  $a_{n}$  (8.401 Å) is slightly larger than  $a_{\perp}$  (8.388 Å) which implies that there is a small lateral stretching along the film surface.

Table 3.3. In plane and out of plane lattice parameters obtained from x-ray diffraction (XRD) peaks and the strain calculated using in plain lattice parameters. In plane stress calculated using Young's modulus  $Y= 1.5 \times 10^{12} \text{ dyne/cm}^2$ . Anisotropy calculated using stress.

Out-of-plane	In-plane	In-plane	In-plane	Stress Anisotropy
lat. par.	lat. par.	Strain	Stress	$(K_a)$
$a_{\perp}$	a <sub>II</sub>	3	$(x10^{9})$	$(x10^{6})$
(Å)	(Å)		(dyne/cm <sup>2</sup> )	(erg/cm <sup>3</sup> )
8.388	$8.401\pm0.002$	$0.0013 \pm 0.0002$	$1.9 \pm 0.4$	$1.8 \pm 0.3$
8.486	$8.297\pm0.009$	$-0.011 \pm 0.001$	$-16.5 \pm 0.1$	$14.6 \pm 1.4$
	Out-of-plane lat. par. a⊥ (Å) 8.388 8.486	Out-of-plane         In-plane           lat. par.         lat. par. $a_{\perp}$ $a_{\parallel}$ (Å)         (Å)           8.388         8.401 ± 0.002           8.486         8.297 ± 0.009	Out-of-plane         In-plane         In-plane           lat. par.         lat. par.         Strain $a_{\perp}$ $a_{\mu}$ $\epsilon$ (Å)         (Å)           8.388 $8.401 \pm 0.002 \ 0.0013 \pm 0.0002$ $8.486$ $8.297 \pm 0.009 \ -0.011 \pm 0.001$	Out-of-plane         In-plane         In-plane         In-plane           lat. par.         lat. par.         Strain         Stress $a_{\perp}$ $a_{\parallel}$ $\epsilon$ $(x10^9)$ (Å)         (Å)         (dyne/cm <sup>2</sup> )           8.388         8.401 ± 0.002 0.0013 ± 0.0002 $1.9 \pm 0.4$ 8.486 $8.297 \pm 0.009$ $-0.011 \pm 0.001$ $-16.5 \pm 0.1$

This indicates that the CFO film on MgO grows under subtle tensile strain (0.13 %) with respect to bulk powder. On the other hand for the CFO-STO film, the  $a_{\perp}$  (8.486 Å) is larger than  $a_{\mu}$  (8.297 Å) which implies that there is a compression along the film plane. The CFO-STO film grows with a larger compressive strain (1.1%) with respect to bulk powder. This difference between the  $a_{\perp}$  and  $a_{\mu}$  values results in a tetragonal distortion in the film grown on STO. Figure 3.1.5 shows a schematic diagram of the different strain situations that the CFO film undergoes under different lattice mismatches.



Figure 3.1.5. Schematic diagrams show the (a) unstressed CFO bulk powder (b) CFO lattice under in-plane tensile stress on MgO substrate with  $a_{II} > a_{\perp}$  and (c) CFO lattice under high in-plane compressive stress causing tetragonal distortion  $a_{\perp} > a_{II}$ .

To further emphasize the importance of stress anisotropy in epitaxial CFO films the  $\sin^2\psi$  technique (Section 2.2.1) of residual stress calculation was used. Figure 3.1.6 shows the 20 scans of CFO-MgO film for various  $\psi$  tilts. The plot of lattice spacing d as a function of  $\sin^2\psi$  is shown in the inset of Figure 3.1.6. The good linear fit of data points indicates that the residual stress within the area under scan is nearly homogeneous. The stress ( $\sigma$ ) calculated from slope of the linear fit for CFO-MgO film is  $\sigma = -12.19 \times 10^9$ dyne/cm<sup>2</sup>. Due to the proximity of the substrate and the film peak, a background due to MgO substrate was subtracted from the slope. The values Y, v and d<sub>0</sub> used were as follows for CFO: Y = 1.5 x 10<sup>12</sup> dyne/cm<sup>2</sup>, v = 0.26 [114] and d<sub>0</sub> = 2.0979 Å. The stress anisotropy (K<sub>a</sub>) is obtained from K<sub>a</sub> = (3/2)  $\lambda_{100} \sigma$ , where  $\lambda_{100}$  for CFO is -590 x 10<sup>-6</sup> and  $\sigma = -12.19 \times 10^9$  dyne/cm<sup>2</sup>, to be 10.79 x 10<sup>6</sup> erg/cm<sup>3</sup>. This value of K<sub>a</sub> is larger than the magnetocrystalline anisotropy of bulk CFO (2 x 10<sup>6</sup>erg/cm<sup>3</sup>). The value of Y and  $\lambda$  are specific for (100) direction and thus are good estimates for epitaxial films. A possible error in the calculation could be due to the bulk Poisson's ratio (v) used. However, by changing v by 25%, the value of anisotropy (K<sub>a</sub>) only changes by around 5%. The anisotropy field (H<sub>a</sub>) of the film grown on MgO is determined to be about 66.8 kOe, which is lower compared to that of the film grown on STO (H<sub>a</sub>=72.5 kOe).



Figure 3.1.6. XRD  $\theta$ -2 $\theta$  scan about  $2\theta = 43.006^{\circ}$  by varying the  $\psi$  angle from 0 to  $15^{\circ}$  keeping the  $\varphi$  at  $0^{\circ}$  on the CFO films on MgO (100) substrate. The legend shows the values of  $\sin^2 \psi$ . The inset shows the plot of d vs.  $\sin^2 \psi$  and a linear fit to the data points.

#### **3.1.2.2. Magnetic Properties**

The magnetic measurements were conducted both at 300 K and 10 K in magnetic fields up to 50 kOe. The in-plane and out-of-plane configurations symbolized by  $\parallel$  and  $\perp$ , respectively, represent the application of the magnetic fields parallel and

perpendicular to the film planes. All the hysteresis loops were obtained after subtracting the diamagnetic contribution from the substrates.

Figures 3.1.7 (a, and c) and (b, and d) show the M-H loops measured at 10 K and 300 K for CFO-STO and CFO-MgO films, respectively. The films have the same thicknesses of 200 nm. The CFO-MgO film with a lattice mismatch of 0.34% shows out-of-plane anisotropy with well saturated loop in the out-of-plane direction. On the other hand, the CFO-STO film with a lattice mismatch of 7.4% displays in-plane anisotropy with well saturated loop in the in-plane direction. Table 3.4 summarizes the saturation magnetization ( $M_s$ ), ratio of remnant magnetization ( $M_r$ ) to  $M_s$  and the coercivity ( $H_c$ ) for all the samples at 300 K and 10 K.

Table 3.4. Saturation magnetization ( $M_s$ ), ratio of remnant magnetization ( $M_r$ ) to  $M_s$  (squareness), and coercive field ( $H_c$ ) measured at 300 K and 10 K for in-plane and out-ofplane configurations for 200 nm thick CFO films on MgO and STO substrates. The symbols  $\parallel$  and  $\perp$  denote the in-plane and out-of-plane configurations respectively.

				300 K				
Sample	$M_s \parallel$	$M_s \parallel$	$M_r\!/M_s\parallel$	$H_c \parallel$	$M_s \perp$	$M_s \perp$	$M_r\!/M_s\!\perp$	$H_c \perp$
	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)
CFO-MgO	$304 \pm 5$	2.4	37.6	3.8	$310 \pm 6$	2.5	<13.9	< 0.03
CFO-STO	$478\pm5$	3.8	53.9	3.5	> 164	> 1.3	>21.6	3.0
				10 K				
Sample	$M_{s}\parallel$	$\mathbf{M}_{\mathbf{s}} \parallel$	$M_r\!/M_s\parallel$	10 K H <sub>c</sub>	$M_{s} \bot$	$M_{s} \bot$	$M_r/M_s \perp$	H <sub>c</sub> ⊥
Sample	$M_s \parallel$ (emu/cm <sup>3</sup> )	$\begin{array}{c} M_{s}\parallel\\ (\mu_{B}/Co^{2^{+}})\end{array}$	M <sub>r</sub> /M <sub>s</sub> ∥ (%)	10 K H <sub>c</sub> ∥ (kOe)	$M_s \perp$ (emu/cm <sup>3</sup> )	$\begin{array}{c} M_{s}\bot \\ (\mu_{B}/Co^{2^{+}}) \end{array}$	$M_r/M_s \perp$ (%)	H <sub>c</sub> ⊥ (kOe)
Sample	$M_s \parallel$ (emu/cm <sup>3</sup> )	$\begin{array}{c} M_{s}\parallel\\ (\mu_{B}/Co^{2^{+}})\end{array}$	M <sub>r</sub> /M <sub>s</sub> ∥ (%)	10 K H <sub>c</sub> ∥ (kOe)	$M_{s} \perp$ (emu/cm <sup>3</sup> )	$\begin{array}{c} M_{s}\bot \\ (\mu_{B}/Co^{2^{+}}) \end{array}$	$M_r/M_s \perp$ (%)	H <sub>c</sub> ⊥ (kOe)
Sample CFO-MgO	M <sub>s</sub> ∥ (emu/cm <sup>3</sup> ) >497	$M_{s} \parallel (\mu_{B}/Co^{2^{+}})$ 3.9	M <sub>r</sub> /M <sub>s</sub> ∥ (%) >41.3	10 K H <sub>c</sub> ∥ (kOe) 10	$\begin{array}{c} M_{s} \bot \\ (emu/cm^{3}) \end{array}$ $441 \pm 12$	$\begin{array}{c} M_{s} \bot \\ (\mu_{B}/Co^{2^{+}}) \end{array}$	$M_{r'}M_{s}\perp$ (%) 30.9	$\begin{array}{c} H_c \bot \\ (kOe) \end{array}$
Sample CFO-MgO CFO-STO	$M_{s} \parallel$ $(emu/cm^{3})$ $>497$ $541 \pm 9$	$\begin{array}{c} M_{s} \parallel \\ (\mu_{B}/Co^{2^{+}}) \\ 3.9 \\ 4.3 \end{array}$	$M_r/M_s \parallel$ (%) >41.3 63.1	10 K H <sub>c</sub> ∥ (kOe) 10 11	$\begin{array}{c} M_{s} \bot \\ (emu/cm^{3}) \end{array}$ $\begin{array}{c} 441 \pm 12 \\ > 164 \end{array}$	$M_{s} \perp$ ( $\mu_{B}/Co^{2^{+}}$ ) 2.5 > 1.3	$M_r/M_s \perp$ (%) 30.9 14.6	H <sub>c</sub> ⊥ (kOe) 0.3 0.7

The  $M_r/M_s$  ratio provides an estimate of the degree of squareness of the loops. Although the M-H loop for CFO-MgO film suggests an out-of-plane anisotropy the easy axis of magnetization is not well defined because the  $M_s \perp$  and  $H_c \perp$  are smaller than  $M_s \parallel$ 

and  $H_{c}$ , atypical of easy axis (Table 3.4). However, the easy axis of magnetization for CFO-STO film is along the plane of the film (Figures 3.1.7 a, and c). The M<sub>s</sub> value for CFO-STO film at 300 K is around 478 emu/cm<sup>3</sup> which corresponds to 3.8  $\mu_{\rm B}$  per Co-site. The magnetic moment per Co-site was calculated taking into account the unit cell volume (V) of fcc structure where  $V = a_0^3 = (8.391 \text{ Å})^3 = 590.99 \text{ Å}^3$  and 8 Co sites per unit cell. This value is around 2.6 µ<sub>B</sub> per Co-site in case of CFO-MgO film. However, at low temperature (10 K), the M<sub>s</sub> is closer to the bulk value of the CFO (3  $\mu_{\rm B}$  per Co-site) [17]. The  $M_r/M_s \parallel$  is about 54% in CFO-STO film suggesting a high degree of squareness at 300 K. The high degree of squareness and coercive field H<sub>c</sub>ll both at 300 K and 10 K for CFO-STO film indicate the strong in-plane magnetic anisotropy as reported earlier [113].On the other hand the M-H loops for CFO-MgO show lower M<sub>r</sub>/M<sub>s</sub> values compared to those for CFO-STO. According to earlier reports the magnetic anisotropy in CFO-MgO films is highly dependent on the film thickness [115]. The observed out-ofplane anisotropy in this case is consistent with previous reports for similar film thicknesses [33, 110, 116, and 117].

The difference in magnetic anisotropy for CFO-MgO and CFO-STO films could have arisen from the fact that the CFO films grow with tensile strain on MgO substrate and undergo compression when grown on STO. Thus, the lattice mismatch stress may have played a significant role in the observed anisotropy.



Figure 3.1.7. (a, and c) M-H loops measured at 300 K and 10 K respectively of the 200 nm thin film grown on STO (100) for in plane and out of plane configuration. (b, and d) M-H loops measured at 300 K and 10 K respectively of the 200 nm thin film grown on MgO (100) for in plane and out of plane configurations.

To address this, the uniaxial anisotropy was calculated by using the difference between the in-plane and out-of-plane magnetization values from Figure 3.1.7. The uniaxial magnetic anisotropy is given by [38]

$$K_{u} = \int_{0}^{M_{s}} (H_{eff}^{out} - H_{eff}^{in}) dM$$
(3.1)

where  $H_{eff} = H_{ex} - NM$ , N = demagnetization factor, M = magnetization and H<sub>ex</sub> is the external field applied and M<sub>s</sub> is the saturation magnetization. The superscript *out* and *in* correspond to the out-of-plane and in-plane orientation of the films with respect to the applied magnetic field.

For the case of a thin film with uniform magnetization in all x, y and z direction, Equation (3.1) reduces to

$$K_{u} = H_{ex}^{out} M_{s}^{out} - H_{ex}^{in} M_{s}^{in} - \frac{1}{2} (M_{s}^{out})^{2}$$
(3.2)

The uniaxial magnetic anisotropy (K<sub>u</sub>) calculated for the CFO-MgO film is K<sub>u</sub>=  $9.13\pm0.34 \times 10^6 \text{ erg/cm}^3$ . This value of K<sub>u</sub> is 3 times larger than the intrinsic magnetocrystalline anisotropy of bulk CFO ( $2 \times 10^6 \text{erg/cm}^3$ ) [98, 100]. The value of the anisotropy (K<sub>u</sub>) thus obtained is very close to that calculated earlier using the  $\sin^2 \psi$  technique (K<sub>u</sub>= 10.79 x 10<sup>6</sup> erg/cm<sup>3</sup>). The consistency of these two independent methods clearly indicates that the large anisotropy seen in the CFO-MgO film arises from the presence of large stress due to the mismatch between the film and the substrate.

For the case of the CFO-STO film, the out-of-plane magnetization is not saturated up to an applied field of 50 kOe (Figure 3.1.7). Therefore, it is not precise to use Equation 3.2 to estimate the magnetic anisotropy for this film. Alternatively, the magnetic anisotropy of CFO-STO film was estimated by using the difference between the lattice parameter of bulk ( $a_0 = 8.39$  Å) CFO and the corresponding thin film ( $a_{II} = 8.297$ Å). The strain ( $\epsilon$ ) due to the difference between the  $a_0$  and  $a_{II}$  is -0.011 (Table 3.3). The in-plane stress ( $\sigma$ ) is -16.50 x 10<sup>9</sup> dyne/cm<sup>2</sup> (Table 3.3). Magnetoelastic stress anisotropy constant ( $K_a$ ) is 14.6 x 10<sup>6</sup> erg/cm<sup>3</sup>. This value is larger compared to that obtained for the film grown on MgO (100). This is consistent with the fact that stress is larger for the film grown on STO than for the film grown on MgO. It is the presence of larger stress in the film grown on STO that causes a larger shift in the (400) Bragg reflection compared to the bulk (Figures 3.1.6 a, and b). The anisotropy field (H<sub>a</sub>) of the film grown on STO is estimated to be about 59.6 kOe, using the expression  $H_a=2K_a/M_s$ .

## **3.1.3.** Conclusions

To summarize, the magnetic anisotropies in epitaxial CFO thin films were investigated. Epitaxial films on MgO (100) with a lattice mismatch of 0.35% showed outof-plane anisotropy whereas the films on STO (100) with a lattice mismatch of 7.4% displayed in-plane anisotropy. Stress anisotropy calculated from angle-dependent x-ray diffraction analysis confirmed that the change in anisotropy originates from the lattice mismatch strains.

#### 3.2. Lead Zirconium Titanate (PZT) Thin Films

Ferroelectric thin films of PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub> (PZT) have attracted enormous research interest in recent years for a wide variety of applications in memory and microelectromechanical (MEMs) devices [39, 43]. PZT has also been used as a component of multiferroic structures [96]. Thin film deposition techniques, such as sputtering [119], pulsed laser deposition (PLD) [120], molecular beam epitaxy [121], metal-organic chemical vapor deposition [122], and sol-gel processing [123] have been extensively used to fabricate PZT thin films and hetero-structures.

PLD offers unique advantages in terms of stoichiometric transfer of material from multi-component targets to the as-deposited films; high deposition rate, and inherent simplicity for growth of multilayered structures with precise control of composition and crystallinity (see Chapter 2, Section 2.1). However, laser ablation of PZT causes preferential evaporation of the volatile element Pb from the target. PZT films require deposition temperatures ( $T_s$ ) between 500°C to 600°C for good crystallinity [124]. At such high temperatures the films are Pb depleted due to the high vapor pressure of Pb [42]. This Pb deficiency is responsible for the coexistence of a meta-stable pyrochlore (non-ferroelectric) phase with the perovskite PZT structure, thereby degrading the ferroelectric properties of the films [43]. To compensate for the Pb loss, a common practice is to add excess PbO during the preparation of the targets. The composition of PZT films also depends strongly on the laser energy density or fluence and partial pressure of ambient  $O_2$  (pO<sub>2</sub>) [43]. Generally, a high pO<sub>2</sub> (~200-400 mTorr) and high KrF fluence (> 3.5 J/cm<sup>2</sup>) are used during deposition [44, 121]. At such high fluences and  $pO_2$ , the highly forward directed laser-induced plume gives rise to non-uniform and

particulate laden films which are undesirable in heterostructure growth. To overcome these adverse effects a dual-laser deposition ( $PLD_{DL}$ ) process was adopted [72 - 76] that significantly reduced the thickness variation and particulate density on the deposited films. This led to the growth of smooth uniform films with enhanced ferroelectric properties.

### **3.2.1. Experimental Details**

PZT films were grown on single crystal MgO (100) and SrTiO<sub>3</sub> (STO) (100) substrates using both single (PLD<sub>SL</sub>) and dual laser deposition (PLD<sub>DL</sub>) (see Chapter 2, Section 2.1). The laser-target interactions were studied using two targets, namely a stoichiometric (PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>) PZT target and a PZT target with 30 atomic (at.) % excess PbO. Henceforth in the text, the nomenclature PZT<sub>ST</sub> and PZT<sub>PbO</sub> will denote stoichiometric PZT (PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>) and PZT with 30 atomic (at.) % excess PbO. The PZT targets were purchased from Kurt J. Leskar Company (1" Dia. x 0.25" Thick, Density 7.41 g/cm<sup>3</sup>). All the films were deposited at 550 °C under a pO<sub>2</sub> of 500 mT using the PZT<sub>PbO</sub> target.

#### **3.2.2. Results and Discussions**

The crystallinity of the PZT targets was characterized using XRD. Figure 3.2.1 shows the XRD scans for the  $PZT_{ST}$  and  $PZT_{PbO}$  targets. Both the scans match with the tetragonal  $PbZr_{0.52}Ti_{0.48}O_3$  phase with no other impurity phases besides PbO. Due to tetragonal perovskite crystal structure of PZT and almost same lattice parameters (a=b= 4.036 Å, c= 4.146 Å), the equivalent perpendicular planes are in close occurrence to each other in the XRD spectra (Figure 3.2.1).



Figure 3.2.1. XRD patterns of stoichiometric PZT target and PZT target with excess PbO.

### 3.2.2.1. Laser-target interaction and Plume Diagnostics

In order to investigate the Pb depletion during ablation, the laser-target interactions and the ablated plumes were studied. A general procedure was followed to systematically investigate the events that occur during the laser-target interaction. The target surface was irradiated by 1000 laser pulses at a pulse rate of 10 Hz for various fluences in pO<sub>2</sub> of 500 mT. The target was kept stationary during this time. The repeated ablation by the focused laser beam created a rectangular 2 mm x 3 mm spot or laser-target interaction site (Figure 3.2.2 a). Henceforth the nomenclature LTIS will be used to denote laser-target interaction site, in the text. When viewed under SEM, uniformly distributed conical features were revealed near the center of the LTIS (Figure 3.2.2 b). Multiple EDS scans were performed estimate the average composition of the target after ablation. The conical structures were imaged in detail as shown in Figure 3.2.2 (d). The physical transformation of the target surface after ablation can be seen by comparing

Figure 3.2.2 (d) to the unablated target surface in Figure 3.2.2 (c), both imaged under the same magnifications.



Figure 3.2.2. SEM images of the PZT target surface after irradiation by 1000 laser pulses showing (a) the rectangular spot size, (b, and d) conical features near the center of the interaction site and (c) the unablated target surface, respectively.

### 3.2.2.1.1. Single KrF laser ablation

Figure 3.2.3 (a) shows a typical SEM image of the  $PZT_{ST}$  target surface near the center of a LTIS after irradiation by a single KrF laser at a low fluence of 1 J/cm<sup>2</sup>. The conical structures are characterized by a smooth, globular cone-tip and a distinct cone-body underneath. All the cones have a common orientation and point in the direction of the incoming laser beam. EDS measurements were performed randomly at various locations on different cone tips and cone bodies.



Figure 3.2.3 (a) SEM image of conical structures formed on a PZT target surface after repeated ablation by KrF excimer laser. (b) Histogram of at. % ratios of Pb/(Zr+Ti), Zr/(Zr+Ti) and Ti/(Zr+Ti) at random locations on the cone tips and bodies.

Figure 3.2.3 (b) shows a histogram of at. % ratios of Pb/(Zr+Ti), Zr/(Zr+Ti) and Ti/(Zr+Ti) obtained from EDS analysis. It is seen that the at. % ratios of Pb are significantly lower in the cone tips as compared to the cone bodies. However the Zr and Ti ratios remain almost the same. In other words, the cone tips are extremely Pb deficient as compared to their bodies. This suggests that the cone tip originates from the melt and solidification of the cone on the top end and after the laser pulse. One of the theories that

explain these cone formations is the so-called 'impurity shielding mechanism' [68]. This mechanism attributes the cone formation to vaporization-resistant impurities which in this case are Zr (melting point, mp =1865 °C) and Ti (mp = 1668°C), which have higher melting temperatures as compared to Pb (mp = 327.5 °C). The materials surrounding the impurities (i.e. Pb) are preferentially removed during ablation. As a result of this erosion-formation process, cones grow in length as the laser exposure increases [125]. This effect generally leads to the non-stoichiometry in the films [126].

Figure 3.2.4 shows the SEM images of LTISs on the PZT<sub>ST</sub> target surface after irradiation by the KrF laser with increasing fluences from 1 to 6 J/cm<sup>2</sup>, denoted as KrF 1 to 6 J/cm<sup>2</sup>. Severe surface melting and formation of columnar structures are observed. Two types of cones can be identified: one type with a well defined cone tip and body at fluences KrF 1 to 2 J/cm<sup>2</sup> (Figures 3.2.4 a, and b) as explained earlier, and the other type having only the cone tip at fluences KrF 3 to 5 J/cm<sup>2</sup> (Figures 3.2.4 c to f).Unlike the cones formed at low fluences (Figures 3.2.4 a, and b) which point towards the incoming laser beam, the cones formed at higher fluences (Figures 3.2.4 c to f) are oriented with the cone axis almost perpendicular to the target surface. Also the space between the cone tips is larger than those at 1 and 2 J/cm<sup>2</sup>. These differences suggest that the formation mechanism of the cones in Figures 3.3.4. (c - f) is different from the impurity shielding mechanism and are not associated with preferential ablation.

Several models have been proposed to explain the cones formed at higher fluences (Figures 3.2.4 c to f). Among them, the hydrodynamic sputtering mechanism proposed by Kelly et al. [127] and the capillary wave instability mechanism proposed by Brailovsky et al. [128] are the most acceptable ones. All these models attribute the cone formation to instabilities on the melted target surface created by the laser pulse. The motion of the melted surface creates aspirates which subsequently solidify to form the cones. The SEM images of the  $PZT_{PbO}$  target after ablation also showed similar structures.



Figure 3.2.4. SEM images of PZT target after irradiation by 1000 pulses of a KrF laser beam in 500 mT  $O_2$  ambient at laser fluences of (a)  $1J/cm^2$ , (b)  $2J/cm^2$ , (c)  $3J/cm^2$ , (d)  $4J/cm^2$ , (e)  $5J/cm^2$ , and (e)  $6J/cm^2$ , respectively, denoted as KrF  $1J/cm^2$  to  $5J/cm^2$ .

Figures 3.2.5 (a, and b) show the variation of at. % ratios of Pb/(Zr+Ti), Zr/(Zr+Ti) and Ti/(Zr+Ti), obtained from EDS, at the LTISs for the PZT<sub>ST</sub> and the

 $PZT_{PbO}$  targets, respectively. Here 0 J/cm<sup>2</sup> represent the target compositions before ablation. For the  $PZT_{ST}$  target (Figure 3.2.5 a), the at. % ratio of Pb decreases from  $\approx 0.93$ at 0 J/cm<sup>2</sup> to  $\approx 0.66$  at 1 J/cm<sup>2</sup> and reaches saturation at higher fluences. However, the Zr and Ti ratios remain almost constant. On the other hand, for the  $PZT_{PbO}$  target, the at. % ratio of Pb decreases from  $\approx 1.3$  at 0 J/cm<sup>2</sup> to  $\approx 0.83$  at 1 J/cm<sup>2</sup> with almost no change in the Zr and Ti ratios. However, above 3 J/cm<sup>2</sup>, the at. % ratio of Pb reaches saturation at  $\approx$ 1.0, with the Zr and Ti ratios still the same. This suggests that above the threshold fluence of 3 J/cm<sup>2</sup>, congruent ablation occurs from the  $PZT_{PbO}$  target. Hence the PZT films were grown using the excess PbO target.



Figure 3.2.5. Chemical compositions using EDS analysis of the ablated target surfaces as a function of KrF laser fluence for (a) stoichiometric PZT and (b) PZT (30 at.% PbO) target.

In order to study the effect of ambient gas pressure on the film stoichiometry, PZT films deposited on Si substrates at room temperature by varying the  $pO_2$  in the

chamber. Figure 3.2.6 shows the variation of at. % of Pb, Zr, and Ti on the PZT films obtained from EDS analysis. It is evident that high  $pO_2$  (~500mT) is facilitates more Pb incorporation in the deposited PZT films.



Figure 3.2.6. Chemical compositions using EDS analysis of PZT films deposited on Si substrates at room temperature by varying the ambient  $O_2$  pressures.

The visible emissions from the laser-induced plumes were captured using ICCD imaging. The ICCD imaging system was aligned normal to the plume propagation to image the axial (on-axis) and transverse plume expansion. Figure 3.2.7 (a) shows a schematic diagram of the arrangement of target and the ablated plumes as imaged by the ICCD camera. The FWHMs of the plumes were measured 1 cm away from the target as shown in Figure 3.2.7 (a). Initial studies of the plasma plumes showed that using the detector with zero gain the visible plumes lasted for about 11  $\mu$ s. Figure 3.2.7 (b) shows an ICCD image of the particulates ejected from the PZT<sub>PbO</sub> target surface during ablation

using high KrF fluence of 5 J/cm<sup>2</sup>. These particulates get deposited on the film surface as molten spherical droplets. This is called "splashing". The particles ejected from the target become visible only after the intense plume disappears (duration time ~ 11  $\mu$ s). Thus the image was obtained using a 500  $\mu$ s gate or exposure time on the camera.



Figure 3.2.7. (a) Schematic diagram of the arrangement of target and the ablated plume as viewed by the ICCD camera. (b) ICCD image the particulates ejected from the PZT (30 at. % excess Pb) target surface during ablation using high KrF fluence of 5 J/cm<sup>2</sup>.

In order to capture the total emitted light from the plumes, a 20  $\mu$ s exposure time was set in the camera. Figure 3.2.8 shows the ICCD images for the total visible emission spectra of the single KrF laser-ablated plumes at various fluences in pO<sub>2</sub> of 500 mT. With higher fluence the plasma is more excited as evident from the axial and transverse expansion of the plumes.

To summarize, from the single KrF laser ablation studies it is observed that the preferential evaporation of Pb from the target is suppressed at high fluences (>  $3 \text{ J/cm}^2$ ) where the high energy facilitates the congruent evaporation of materials from the target surface. Further, high O<sub>2</sub> ambient during deposition restricts the Pb loss. The results are consistent with earlier reports [43, 44].



Figure 3.2.8. ICCD images of total visible emission spectra of single laser plumes varying the KrF fluences as (a) 1 J/cm<sup>2</sup> (b) 2 J/cm<sup>2</sup> (c) 3 J/cm<sup>2</sup>, and (d) 4 J/cm<sup>2</sup> under 500 mT  $pO_2$ .

## 3.2.2.1.2. Dual (KrF and CO<sub>2</sub>) laser ablation

The most crucial requirement in  $PLD_{DL}$  is the correct choice of the KrF and CO<sub>2</sub> laser fluences. From the  $PLD_{SL}$  study, a KrF fluence of 3 J/cm<sup>2</sup> was chosen. The CO<sub>2</sub> fluence was chosen such that it was lower than the ablation threshold of the target material but enough to melt the target surface [72]. Figure 3.2.9 shows a series of ICCD images of total visible spectra of CO<sub>2</sub> laser ablated plumes with increasing CO<sub>2</sub> fluences from 1 J/cm<sup>2</sup> to 3 J/cm<sup>2</sup>. It is evident that at 3 J/cm<sup>2</sup> ablation occurs. Thus, a CO<sub>2</sub> fluence of 2 J/cm<sup>2</sup> was chosen. For all PLD<sub>DL</sub> films throughout this work, it will be assumed that the CO<sub>2</sub> fluence is 2 J/cm<sup>2</sup> if not mentioned.



Figure 3.2.9. ICCD images of total visible emission spectra of  $CO_2$  laser ablated plumes with increasing  $CO_2$  fluences from 1 J/cm<sup>2</sup> to 3 J/cm<sup>2</sup>.

In order to find the optimum condition for the efficient coupling of the CO<sub>2</sub> and KrF laser outputs, the laser-target interaction were studied using PLD<sub>DL</sub> with a KrF fluence of 3 J/cm<sup>2</sup> but varying the peak-to-peak (p-p) inter-pulse delay ( $\Delta$ t). Figure 3.2.10 shows the KrF and CO<sub>2</sub> pulse waveforms at various p-p inter-pulse delays. Figure 3.2.10 (c) represents the situation when the KrF pulse arriving at the target about 50 ns after the onset of the CO<sub>2</sub> pulse.



Figure 3.2.10. KrF and CO<sub>2</sub> pulse waveforms at (a) 250 ns, (b) 145 ns, (c) 100 ns, (d) 50 ns, (e) 0 ns, and (f) – 50 ns of peak-to-peak inter-pulse delays ( $\Delta$ t), respectively.

Figure 3.2.11 shows SEM images of the LTISs on the PZT<sub>ST</sub> target at various p-p inter-pulse delays ( $\Delta t$ ). The surface features are distinctly different depending on the delay ( $\Delta t$ ). For  $\Delta t = 250$  ns and 145 ns (Figures 3.2.11 a, and b), the ablated surface shows typical conical features indicating preferential evaporation. At such large delay times (145 ns <  $\Delta t$  < 250 ns), the CO<sub>2</sub> laser energy is totally absorbed by the preceding KrF induced plasma, increasing the plasma temperature [72]. The higher plasma
temperature coupled with the high pO<sub>2</sub> keeps the molten region on the target surface in a liquid state for a larger time. During this time, the volatile Pb escapes from the molten pool leaving behind columnar structures. However, from Figures 3.2.11 (c, and d) it is observed that surface features indicate congruent ablation similar to high fluence PLD<sub>SL</sub> (Figures 3.2.4 c to f). This probably indicates an optimum coupling of the laser energies. At delay times (50 ns <  $\Delta t$  < 100 ns), the rising edge of CO<sub>2</sub> pulse (Figures 3.2.10 c, and d) first preconditions the target to produce a shallow, transient, molten layer, from which the slightly delayed KrF pulse then initiates the ablation. The receding end of the CO<sub>2</sub> pulse is absorbed by the KrF induced plasma to produce higher ionization. However, the situation is quite different for delay times in the range -50 ns <  $\Delta t$  < 0 ns (Figures 3.2.10 e, and f). When the CO<sub>2</sub> pulse arrives at the target much earlier than the KrF pulse, it completely melts the target surface and facilitates preferential evaporation of Pb. The delayed KrF pulse ablates this completely liquid target surface with low Pb content.

This is confirmed by analyzing the chemical composition using EDS of the LTISs as shown in Figure 3.2.12. The at. % of Pb at the LTIS is the least in the range of delay times, -50 ns <  $\Delta t < 0$  ns, as explained earlier. For a delay time  $\Delta t > 50$  ns, the at. % of Pb reaches saturation. The Zr and Ti content remains almost constant. The SEM and EDS analysis of the PZT<sub>PbO</sub> also showed similar results. Thus, from the study of p-p interpulse delay times in PLD<sub>DL</sub> it is concluded that the optimum coupling of the laser outputs and congruent ablation condition is achieved in the range, 50 ns <  $\Delta t < 100$  ns. This was supported by ICCD imaging of the plasma plumes at various delays. It was observed that the transverse cross-sectional expansion of the plumes was the largest in the range, 50 ns <  $\Delta t < 250$  ns.



Figure 3.2.11. SEM images of laser-target interaction sites on the stoichiometric PZT target using KrF (3 J/cm<sup>2</sup>) and CO<sub>2</sub> (2 J/cm<sup>2</sup>) lasers by varying the peak-to-peak interpulse delay ( $\Delta$ t) as (a) 250 ns, (b) 145 ns, (c) 100 ns, (d) 50 ns, (e) 0 ns, and (f) -50 ns, respectively.



Figure 3.2.12. Chemical compositions using EDS analysis of the ablated stoichiometric PZT target surfaces using KrF (3 J/cm<sup>2</sup>) and CO<sub>2</sub> (2 J/cm<sup>2</sup>) lasers by varying the peak-to-peak inter-pulse delay ( $\Delta t$ ).

The effect of the varying the KrF laser fluence but keeping the CO<sub>2</sub> fluence at 2  $J/cm^2$  was studied using 50 ns and 100 ns delays. Figures 3.2.13 and 3.2.14 show SEM images of LTISs on the PZT<sub>ST</sub> target at 50 ns and 100 ns delay, respectively. From the target surface features in Figures 3.2.13 and 3.2.14, it is obvious that a minimum KrF fluence of 3  $J/cm^2$  is required for congruent ablation. However, overall there is no difference in the surface morphologies between the two delay times as seen in Figures 3.2.13 and 3.2.14. The surface features for the LTISs on the PZT<sub>PbO</sub> target also showed similar structures and followed the same trend.



Figure 3.2.13. SEM images of laser-target interaction sites on the stoichiometric PZT target using CO<sub>2</sub> fluence at 2 J/cm<sup>2</sup> but varying the KrF fluence as (a) 1 J/cm<sup>2</sup>, (b) 2 J/cm<sup>2</sup>, (c) 3 J/cm<sup>2</sup> and (d) 4 J/cm<sup>2</sup>, respectively keeping the peak-to-peak inter-pulse delay ( $\Delta$ t) at 50 ns.



Figure 3.2.14. SEM images of laser-target interaction sites on the stoichiometric PZT target using CO<sub>2</sub> fluence at 2 J/cm<sup>2</sup> but varying the KrF fluence as (a) 1 J/cm<sup>2</sup>, (b) 2 J/cm<sup>2</sup>, (c) 3 J/cm<sup>2</sup> and (d) 4 J/cm<sup>2</sup>, respectively keeping the peak-to-peak inter-pulse delay ( $\Delta$ t) at 100 ns.

Figures 3.2.15 (a, and b) show chemical compositions of the LTISs on  $PZT_{PbO}$  target at delay times of 50 ns and 100 ns, respectively. Although there are no structural differences as observed in SEM images (Figures 3.2.13 and 3.2.14) it is evident from Figure 3.2.15 that the Pb depletion is higher for 50 ns delay above a fluence of 3 J/cm<sup>2</sup>. Therefore, the interpulse delay was fixed as 100 ns in PLD<sub>DL</sub>.



Figure 3.2.15. Chemical compositions using EDS analysis of the ablated PZT (30 at. % excess PbO) target surfaces using CO<sub>2</sub> fluence at 2 J/cm<sup>2</sup> but varying the KrF fluence at the peak-to-peak delay ( $\Delta$ t) of (a) 50 ns and (b) 100 ns, respectively.

Figure 3.2.16 compares the chemical compositions obtained from EDS analysis of the ablated  $PZT_{PbO}$  target surfaces using  $PLD_{DL}$  and  $PLD_{SL}$ . It is evident that the at. % of Pb loss is less in  $PLD_{DL}$  compared to  $PLD_{SL}$ . From the laser-target interaction study, it can be concluded that  $PLD_{DL}$  minimizes the Pb loss during ablation.



Figure 3.2.16. Chemical compositions using EDS analysis of the ablated PZT target surfaces with excess PbO, using dual and single laser ablations.

This can be associated with the more expanded plume in  $PLD_{DL}$  due to higher ionization [72]. Figure 3.2.17 shows the ICCD images for the total visible emission spectra of the  $PLD_{DL}$  ablated plumes at various KrF fluences. With higher fluence the plasma is more excited as evident from the axial and transverse expansion of the plumes with higher laser energies. Further the  $PLD_{DL}$  plumes (Figure 3.2.17) have broader transverse expansion as compared to  $PLD_{SL}$  plumes (Figure 3.2.7).



Figure 3.2.17. ICCD images of total visible emission spectra of dual laser plumes varying the KrF fluences as (a) 1 J/cm<sup>2</sup> (b) 2 J/cm<sup>2</sup> (c) 3 J/cm<sup>2</sup>, and (d) 4 J/cm<sup>2</sup> but keeping the CO<sub>2</sub> fluence at 2 J/cm<sup>2</sup> and the inter-pulse delay at 100 ns under 500 mT pO<sub>2</sub>.

Figures 3.2.18 (a, and b) shows the ICCD images of the laser-induced plasma plumes for the PLD<sub>DL</sub> and (b) PLD<sub>SL</sub>, respectively, using KrF fluence of 3 J/cm<sup>2</sup>. In order to compare the images, the intensities were normalized to the PLD<sub>SL</sub> plume (Figure 3.2.18 b). The overall total intensity of the PLD<sub>DL</sub> plume was 145% greater than that of PLD<sub>SL</sub> emission. Also, the broader transverse expansion, measured on-axis 1 cm from the target (Figure 3.2.7 a), of the plume in dual-laser (28.0 mm FWHM) compared to single–laser (18.7 mm FWHM) clearly exhibits coupling of the laser energies in dual-laser ablation. This allowed the growth of more uniform film over a larger area and led to enhanced film properties.



Figure 3.2.18. Time integrated ICCD images of the visible emission spectra of laserinduced plumes in 500 mTorr ambient  $O_2$  for (a) dual-laser ablation using KrF and  $CO_2$ laser fluences of 3 J/cm<sup>2</sup> and 2 J/cm<sup>2</sup> respectively, with the inter-pulse peak-to-peak delay of 100 ns, and (b) the KrF single-laser ablation with a fluence of 3 J/cm<sup>2</sup>. The scale bar represents 10 mm.

## **3.2.2.2. Structural Properties**

The single and dual laser processed PZT films were characterized using XRD, SEM and AFM. Henceforth in the text, the nomenclature  $PZT_{DL}$  and  $PZT_{SL}$  refer to duallaser and single-laser deposited PZT films, respectively. Figures 3.2.19 (a, b, and c) show XRD scans of  $PZT_{SL}$  films deposited using KrF fluence of 2 J/cm<sup>2</sup> and 5 J/cm<sup>2</sup> and a  $PZT_{DL}$  film using KrF 1 J/cm<sup>2</sup> and CO<sub>2</sub> 2 J/cm<sup>2</sup> ( $\Delta t = 100$  ns) on STO substrates, respectively. The films are highly epitaxial with peaks only from the [100] planes of tetragonal PZT structure. There are no observed peaks from secondary phase formation even in the log-scale intensity. From Figures 3.2.19 (a, and b) it is can be concluded that the crystallinity  $PZT_{SL}$  films is improved with higher fluence as evident from the higher peak intensities at 5 J/cm<sup>2</sup> (Figure 3.2.19 b) compared to 2 J/cm<sup>2</sup> (Figure 3.2.19 a). However, the  $PZT_{DL}$  film (Figure 3.2.19 c) shows improved crystallinity with the high peak intensities although grown at lower KrF fluence. All the films have the same thickness of about 350 nm.



Figure 3.2.19. XRD scans of PZT<sub>SL</sub> films deposited using KrF fluence of (a) 2 J/cm<sup>2</sup> and (b) 5 J/cm<sup>2</sup> and a (c) PZT<sub>DL</sub> film using KrF 1 J/cm<sup>2</sup> and CO<sub>2</sub> 2 J/cm<sup>2</sup> ( $\Delta t = 100$  ns) on STO substrates, respectively. The substrate peaks are denoted by \*.

In order to further confirm the in plane epitaxy, rocking curves were performed about the PZT (200) plane for the PZT<sub>SL</sub> at 5J/cm<sup>2</sup> and PZT<sub>DL</sub> films as shown in Figure 3.2.20. Both films have excellent in plane epitaxy indicated by the narrow FWHM of the rocking curves. The FWHMs of the rocking curves for the PZT<sub>SL</sub> at 5J/cm<sup>2</sup> and PZT<sub>DL</sub> films are 0.536° and 0.541°, respectively. EDS analysis of the films revealed that the at. % ratio of Pb for PZT<sub>SL</sub> films deposited at 2J/cm<sup>2</sup> and 5 J/cm<sup>2</sup> was 0.39 and 0.85, respectively. However, the PZT<sub>DL</sub> film had high Pb content of 0.84.



Figure 3.2.20. Rocking curves about PZT (200) plane for single and dual laser grown PZT films on STO substrates.

Figures 3.2.21 (a, b, and c) show AFM images of the of  $PZT_{SL}$  films deposited using KrF fluence of 2 J/cm<sup>2</sup> and 5 J/cm<sup>2</sup> and  $PZT_{DL}$  film using KrF 1 J/cm<sup>2</sup> and CO<sub>2</sub> 2 J/cm<sup>2</sup> ( $\Delta t = 100$  ns) on STO substrates, respectively. The  $PZT_{SL}$  film at 5 J/cm<sup>2</sup> (Figure 3.2.21 b) exhibits a rougher surface and high density of larger particulates as compared to the  $PZT_{SL}$  film at 2 J/cm<sup>2</sup> (Figure 3.2.21 a). The root-mean-square surface roughness ( $R_{rms}$ ) values for  $PZT_{SL}$  films at 5 J/cm<sup>2</sup> and 2 J/cm<sup>2</sup> are 12 nm and 3 nm, respectively. However, a drastic reduction in particulate density and surface roughness is observed in  $PZT_{DL}$  film (Figure 3.2.21 c). The  $R_{rms}$  value  $PZT_{DL}$  film is 2 nm. This confirms the effectiveness of dual laser ablation in growing high Pb content, particulate free and smooth PZT films with the desired perovskite structure and no impurity phases.



Figure 3.2.21. AFM images of PZT films deposited using single laser ablation (a) at 2 J/cm<sup>2</sup> and (b) at 5 J/cm<sup>2</sup> and (c) dual laser ablation. All scan areas are 5  $\mu$ m x 5  $\mu$ m.

Figures 3.2.22 (a, b, and c) show SEM images of  $PZT_{SL}$  films grown using low fluence of at 2 J/cm<sup>2</sup>, high fluence of 5 J/cm<sup>2</sup>, and  $PZT_{DL}$  film deposited using KrF 1 J/cm<sup>2</sup> and CO<sub>2</sub> 2 J/cm<sup>2</sup> ( $\Delta t = 100$  ns) on STO substrates, respectively. Although the  $PZT_{SL}$  film at 2J/cm<sup>2</sup> (Figure 3.1.22 a) shows a relatively clean surface, the low Pb content degraded the ferroelectric properties. On the other hand, the  $PZT_{SL}$  film at 5 J/cm<sup>2</sup> (Figure 3.2.22 c) had good crystallinity (Figure 3.2.19) and the proper Pb content, however the high density of particulates on the film surface make it unsuitable for heterostructure growth. On the contrary, the  $PZT_{DL}$  film not only had the good crystallinity and proper Pb content, it exhibited low particulate density compared to  $PZT_{SL}$  at 5 J/cm<sup>2</sup>. Figure 3.2.22 (d) shows the details of one of the particulates of  $PZT_{SL}$  film at 2 J/cm<sup>2</sup>. The spherical shape of the particle is a clear indication that it was "splashed" as a molten droplet on the film surface [66]. Thus, the origin of these particulates is from the target surface during ablation.



Figure 3.2.22. SEM images of  $PZT_{SL}$  films deposited at 550 °C on STO substrates at (a) low fluence of 2 J/cm<sup>2</sup> and (b) high fluence of 5 J/cm<sup>2</sup>, and (c)  $PZT_{DL}$  film, respectively. (d) SEM image of details of one of the particulates on  $PZT_{SL}$  film at 2 J/cm<sup>2</sup>.

Although the  $PLD_{DL}$  films deposited using low KrF fluence of 1 J/cm<sup>2</sup> as described above, exhibited particulate free surface with high Pb content, their ferroelectric properties were not as high as films deposited at high KrF fluence. Thus, in

order to enhance the ferroelectric properties,  $PZT_{DL}$  films were deposited using a high KrF fluence of 3 J/cm<sup>2</sup>, keeping other parameters constant. For comparison,  $PZT_{SL}$  films were also deposited under the same conditions. Further to test the polarization of the PZT capacitors, metallic oxide La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSMO) electrodes were used. The growth and characterization of LSMO electrodes are described in Appendix B.

## 3.2.2.1. LSMO/PZT/LSMO capacitor

The following paragraphs describe structural properties of LSMO/PZT/LSMO capacitors grown on STO and MgO substrates. A schematic diagram of the capacitor structure is shown in Figure 3.2.23. The thicknesses of the individual LSMO and PZT layers are 100 and 500 nm, respectively.



Figure 3.2.23. Schematic diagram of PZT thin film capacitor fabricated using LSMO top and bottom electrodes.

The crystallinity of the PZT capacitors was examined by XRD. Figures 3.2.24 (a, and b) show the XRD patterns for LSMO/PZT<sub>DL</sub>/LSMO/STO and LSMO/PZT<sub>SL</sub>/LSMO/STO, respectively. In both cases, only strong (l00) (l = 1, 2, and 3) diffraction peaks of LSMO and PZT are observed along with those of the single-crystal STO (100) substrate. This implies that the individual layers have an epitaxial relationship with each other. The films are highly textured without any secondary impurity phases

even in log scale. The PZT peaks were indexed with the tetragonal phase with space group P4mm (99). The (200) planes of LSMO and STO substrate are shown in detail in the inset (I) of Figure 3.2.24 (a). Inset (II) of Figure 3.2.24 (a) and inset (III) of Figure 3.2.24 (b) show rocking curves ( $\omega$  scans) about the PZT (100) plane for PZT<sub>DL</sub> and PZT<sub>SL</sub>, respectively. The smaller FWHM value for PZT<sub>DL</sub> (0.1°) as compared to PZT<sub>SL</sub> (0.5°) relates to better in-plane orientation for the dual-laser deposited film.



Figure 3.2.24. XRD  $\theta$ -2 $\theta$  scans of LSMO/PZT/LSMO capacitors on STO (100) substrates grown using (a) dual and (b) single-laser ablations, respectively. Inset (I) shows the details of STO (200) and LSMO (200) peaks around 2 $\theta$  values of 46°. Inset (II) shows the rocking curve of the PZT (100) peak with FWHM value of 0.1°. Inset (III) shows the rocking curve of the PZT (100) peak with the FWHM value of 0.5°. The PZT (*l*00) (1 = 1, 2, 3) reflections are denoted by  $\alpha$ ,  $\beta$ ,  $\gamma$  and the LSMO/STO (001) peaks are denoted by \*.

Figures 3.2.25 (a, and b) show AFM images of the surfaces of  $PZT_{DL}$  and  $PZT_{SL}$  films on STO substrates, respectively. Clearly,  $PZT_{DL}$  (Figure 3.2.25 a) exhibits a smoother surface and smaller grain size with a root mean square ( $R_{rms}$ ) roughness value of 1.6 nm compared to 11.5 nm for  $PZT_{SL}$  (Figure 3.2. 25 b).



Figure 3.2.25. AFM images of the PZT surface for the LSMO/PZT/LSMO capacitors on STO substrates deposited using (a) dual-laser ablation and (b) single-laser ablation. The  $R_{rms}$  surface roughness values for (a) and (b) are 1.6 nm and 11.5 nm, respectively.

Since the surface features on the  $PZT_{DL}$  film were much smaller those on the  $PZT_{SL}$  film, the z-height for the AFM scan for  $PZT_{DL}$  had to be set as two times smaller than that for the  $PZT_{SL}$  (Figures 3.2. 25 a, and b), in order to make the surface features

observable. The surface features for  $PZT_{DL}$  have been shown in detail for a smaller scan area in the lower panel of Figure 3.2.25.

Figures 3.2.26 (a, and b) show the XRD  $\theta$ -2 $\theta$  scans for LSMO/PZT<sub>DL</sub>/LSMO/MgO and LSMO/PZT<sub>SL</sub>/LSMO/MgO, respectively.



Figure 3.2.26. XRD  $\theta$ -2 $\theta$  scans of LSMO/PZT/LSMO capacitors on MgO (100) substrates grown by (a) dual and (b) single-laser ablation, respectively. Insets (I) and (II) in Figure 3.2.30 (a) and (b) show the details of PZT(100)/LSMO(100) peaks and MgO(200)/PZT(200)/LSMO(200) peaks, respectively. The small peaks denoted by \* are artifacts from the MgO substrates.

The XRD patterns indicate an epitaxial relationship between the films and the substrate. The insets (I) and (II) in Figure 3.2.26 (a) show the details of PZT(100)/LSMO(100) peaks and MgO(200)/PZT(200)/LSMO(200) peaks, respectively. The corresponding peaks for the  $PZT_{SL}$  films have been shown in the inset (I) and (II) in Figure 3.2.26 (b). The better in-plane epitaxy in the  $PZT_{DL}$  film compared to  $PZT_{SL}$  film is confirmed from the rocking curves about the PZT (100) plane as shown in Figure 3.2.27.



Figure 3.2.27. XRD rocking curves about the PZT (100) plane for the LSMO/PZT/LSMO capacitors on MgO (100) substrates grown by (a) dual and (b) single-laser ablation, respectively.

Although both the films have the same thickness (500  $\mu$ m), the higher intensity counts and lower FWHM value (Figure 3.2.27 a) in the PZT<sub>DL</sub>-MgO films demonstrate the better crystallinity compared to PZT<sub>SL</sub>-MgO film.

Figures 3.2.28 (a, and b) show AFM images of the surfaces of  $PZT_{DL}$  and  $PZT_{SL}$  films on MgO substrates, respectively. The smoother surface of  $PZT_{DL}$  film is not as apparent as seen earlier for PZT-STO films (Figure 3.2.25). Nevertheless, the root mean surface roughness values is smaller ( $R_{rms} = 16.7 \text{ nm}$ ) for  $PZT_{DL}$  as compared to  $PZT_{SL}$  ( $R_{rms} = 22.6 \text{ nm}$ ).



Figure 3.2.28. AFM images of the PZT surface for the LSMO/PZT/LSMO capacitors on MgO substrates deposited using (a) dual-laser ablation and (b) single-laser ablation, respectively. The  $R_{rms}$  surface roughness values for (a) and (b) are 16.7 nm and 22.6 nm, respectively.

#### **3.2.2.3 Ferroelectric Properties**

The requirements of a good ferroelectric thin film capacitor for memory applications include high remnant polarization ( $P_r$ ), low coercive field ( $E_c$ ) allowing operation at low voltages, well saturated square hysteresis loop, short switching times, good retention, and fatigue properties [40, 129]. The following section will describe the

ferroelectric properties of epitaxial PZT films on STO and MgO substrates. However, polycrystalline PZT films were also deposited on LSMO/Si(100) substrates for comparison. Figure 3.2.29 (a) shows the room temperature polarization versus electric field (P-E) hysteresis loop for a 400 nm thick  $PZT_{SL}$  film on LSMO/Si(100) substrate denoted as  $PZT_{SL}$ (400 nm)-Si.



Figure 3.2.29. (a) P-E hysteresis loop and (b) XRD pattern for  $PZT_{SL}$  film on LSMO/Si(100) substrate, respectively.

The maximum polarization ( $P_{max}$ ) of 36  $\mu$ C/cm<sup>2</sup>,  $P_r$  of 24  $\mu$ C/cm<sup>2</sup> and  $E_c$  of 180 kV/cm was observed using a maximum driving voltage of 40 V. Figure 3.2.29 (b) shows

the XRD pattern of the film exhibiting the polycrystalline nature. The results are consistent with earlier reports on PZT/LSMO/Si films [130, 131].

Figure 3.2.30 shows the P-E loops for PZT<sub>SL</sub> films deposited at varying KrF fluences of 2 J/cm<sup>2</sup>, 3 J/cm<sup>2</sup>, and 5 J/cm<sup>2</sup> on STO and MgO substrates. All the films have the same thickness of 500 nm. The measurements were performed with 9 V driving voltage at various hysteresis periods from 100 ms to 1000 ms. From Figures 3.2.30 (a, and b) it is evident that the PZT<sub>SL</sub>-STO and PZT<sub>SL</sub>-MgO films at low KrF fluence of 2 J/cm<sup>2</sup> have poor ferroelectric behavior. As described earlier, this is due to the poor Pb content in the films. PZT<sub>SL</sub> films deposited at higher fluences (Figures 3.2.30 c to f) have better P-E hysteresis loops with the P<sub>r</sub> values much higher than polycrystalline PZT films (Figure 3.2.30). The polarization values increase with KrF fluence from 3 J/cm<sup>2</sup> to 5  $J/cm^2$ . This is possibly due to the higher Pb content in the films grown with increasing fluences. The PZT<sub>SL</sub> films grown using KrF fluence of 5 J/cm<sup>2</sup> (Figures 3.2.30 e, and f) exhibit the highest polarization, however, the P-E loops changed drastically with the change of hysteresis periods or frequency which makes them not suitable for device application. Thus, it appears that PZT<sub>SL</sub> films at KrF 3 J/cm<sup>2</sup> (Figures 2.2.30 c, and d) exhibit the most acceptable ferroelectric behavior with better frequency response, among all the films. However, from Figures 3.2.30 (b, and d) it is seen that the loops are positively biased. This voltage shift means that an internal bias field has built up in the  $PZT_{SL}$  film which is again inappropriate for device applications [132]. All these adverse effects were overcome in the PZT<sub>DL</sub> films.



Figure 3.2.30. P-E hysteresis loops for  $PZT_{SL}$  films at KrF fluences of (a, b) 2 J/cm<sup>2</sup>, (c, d) 3 J/cm<sup>2</sup>, and (e, f) 5 J/cm<sup>2</sup> on STO and MgO substrates, respectively, measured at 9V driving voltage and varying the hysteresis period from 100 to 1000 ms.

The following paragraphs will describe the ferroelectric properties of  $PZT_{DL}$  films deposited on MgO and STO substrates using KrF fluence of 3 J/cm<sup>2</sup> and CO<sub>2</sub> fluence of 2 J/cm<sup>2</sup> with 100 ns p-p delay. For comparison  $PZT_{SL}$  films were also grown under the same conditions. Figure 3.2.31 shows the P-E loops for  $PZT_{SL}$  and  $PZT_{DL}$  capacitors deposited on MgO and STO substrates.



Figure 3.2.31. P-E hysteresis loops for  $PZT_{SL}$  and  $PZT_{DL}$  films on STO and MgO substrates, respectively, at various maximum driving voltages.

All the films have the same thicknesses (500 nm) and LSMO top bottom electrode configurations. All the loops were measured using a range of driving voltages from 1 V to 9 V at 1Hz. From Figure 3.2.34 it is evident that the P-E loops for  $PZT_{DL}$  films (Figures 3.2.31 b, and d) show well saturated square behavior at lower voltages as compared to  $PZT_{SL}$  films (Figures 3.2.31 a, and c). Further the  $PZT_{DL}$  films show enhanced polarization compared to  $PZT_{SL}$  films.

Figures 3.2.32 shows the P-E loops for  $PZT_{DL}$ -MgO and  $PZT_{SL}$ -MgO films measured at an applied voltage of 9 V. Similarly, Figures 3.2.33 shows the P-E loops for  $PZT_{DL}$ -STO and  $PZT_{SL}$ -STO films at 9V. The polarization values have been summarized in Table 3.5. The coercive field (E<sub>c</sub>) was calculated using  $E_c = |(V_c(+)+V_c(-))|/2d$  where  $V_c$  is the nominal voltage required for switching.

Table 3.5. Summary of maximum polarization ( $P_{max}$ ), remnant polarization ( $P_r$ ), nominal switching voltage ( $V_c$ ), coercive field ( $E_c$ ) and leakage current density  $J_L$  (A/cm<sup>2</sup>) for PZT<sub>SL</sub> and PZT<sub>DL</sub> films grown on MgO and STO substrates. Data measured at 9 V driving voltage at 1 Hz.

Sample	Substrate	P <sub>max</sub>	Pr		V	2	Ec	$J_{L}$
		$(\mu C/cm^2)$	$(\mu C/cm^2)$	)	(V	)	(kV/cm)	$(A/cm^2)$
			(+)	(-)	(+)	(-)		x 10 <sup>-9</sup>
PZT <sub>SL</sub>	MgO	64	45	-39	2.09	-1.91	40.0	0.43
PZT <sub>DL</sub>	MgO	96	77	-75	2.45	-1.99	44.4	0.27
$PZT_{SL}$	STO	68	34	-45	1.99	-1.58	35.7	0.43
$PZT_{DL}$	STO	108	91	-92	2.65	-1.67	43.2	0.20

From the listed values in Table 3.5 it can be seen that the  $P_{max}$  values at 9 V for the  $PZT_{DL}$  films have increased about 50% from their values for the  $PZT_{SL}$  films. The  $P_r$ values have also almost doubled for  $PZT_{DL}$  films. The  $P_r$  values for  $PZT_{SL}$  (Table 3.5) are consistent with earlier reports for LSMO/PZT/LSMO capacitors grown by PLD [133, 134]. For the PZT<sub>DL</sub>-STO film, a P<sub>r</sub> value of 91  $\mu$ C/cm<sup>2</sup> was observed. This is the first observation of such high value for remnant polarization in in-situ grown PZT films. Reported P<sub>r</sub> values vary from 15 to 54  $\mu$ C/cm<sup>2</sup> [42, 135] for PLD grown PZT films with one of the highest P<sub>r</sub> values reported as  $\approx$ 70  $\mu$ C/cm<sup>2</sup> for PLD grown PZT films, but required ex-situ post annealing at 750 °C in air by rapid thermal annealing (RTA) technique [136].



Figure 3.2.32. P-E hysteresis loops measured with 9V driving voltage for  $PZT_{DL}$  and  $PZT_{SL}$  films on MgO substrates. The inset shows a schematic illustration of the capacitors with the thicknesses of LSMO and PZT layers being 100 nm and 500 nm, respectively.

The P-E loop for  $PZT_{SL}$ -STO in Figure 3.2.33 shows a slight shift towards positive voltages as a consequence of high built-in field [133]. However, the P-E curve for  $PZT_{DL}$  did not show any such asymmetric behavior which could result in imprint failures.



Figure 3.2.33. P-E hysteresis loops measured with 9V driving for  $PZT_{DL}$  and  $PZT_{SL}$  films on STO substrates. The inset shows a schematic illustration of the capacitors with the thicknesses of LSMO and PZT layers being 100 nm and 500 nm, respectively.

Leakage currents in ferroelectric thin film capacitors are measured by applying a DC voltage until the current level stabilizes [86]. High leakage currents are unacceptable as they create anomalous effects such as distortion in hysteresis loops [86]. Leakage current density ( $J_L$ ) implies current per unit area of the electrode. Leakage current densities ( $J_L$ ) in all PZT<sub>DL</sub> and PZT<sub>SL</sub> capacitors were measured by applying a stress voltage of 9 V for a period of 1 s (soak time). The values have been shown in Table 3.5. Figure 3.2.34 shows a comparison of the leakage current densities ( $J_L$ ) for PZT<sub>DL</sub> and PZT<sub>SL</sub> capacitors are measured earlier. The PZT<sub>DL</sub> capacitors have lower leakage current densities compared to PZT<sub>SL</sub> capacitors.



Figure 3.2.34. Capacitor leakage current densities  $(J_L)$  measured using a stress voltage of 9 V for a soak time of 1000 ms for  $PZT_{DL}$  and  $PZT_{SL}$  films grown on (a) MgO and (b) STO substrates under same conditions, respectively.

### 3.2.2.3.1. Fatigue Characterization

The fatigue measurements were performed using standard positive-up negativedown (PUND) testing mode to simulate ferroelectric memory operation. During the PUND test, a series of stress measurement periods is applied to the capacitor. The stress is in the form of a 10 kHz switching pulse waveform of 0.01 ms pulse width. The pulse waveform is similar to a square wave except that the maximum positive and negative voltages are applied for only a fraction of the period of the waveform. During the remaining portion of the waveform, the sample is held at zero volts. The waveform is applied for a specified period, and then the PUND measurement is made. In each subsequent stress period, the duration (and therefore the number of switching cycles) of the stress waveform is doubled. The PUND characterization for the films was performed using peak voltages +9 V and –9 V which simulate the read and write voltages of the memory device. The final polarization of the device after PUND test is the difference between the (+/-) switching polarization ( $P_{sw}$ ) and linear non-switching polarization ( $P_{ns}$ ) values when a (+/-) read voltage (9 V/-9V) was applied to the capacitors. For device application the value of ( $P_{sw} - P_{ns}$ ) should be large enough for signal detection. Figures 3.2.35 (a, and b) show the fatigue (degradation) properties of  $PZT_{DL}$  and  $PZT_{SL}$  films on STO and MgO substrate, respectively.



Figure 3.2.35. Results of positive-up negative-down (PUND) fatigue tests at 10 kHz using +/- 9 V read voltages for LSMO/PZT/LSMO capacitors grown by dual-and single-laser ablation on (a) STO (b) MgO substrates.

From Figure 3.2.35 it is evident that there is no change in the polarization for  $PZT_{DL}$  films even after 10<sup>9</sup> switching cycles. However there are small variations in the polarization for  $PZT_{SL}$  films. From the PUND test it is clear that  $PZT_{DL}$  films exhibited a better fatigue response compared to  $PZT_{SL}$ . Possible explanation could be associated with a reduced number of oxygen vacancies at electrode-film interface for  $PZT_{DL}$ .

## **3.2.3.** Conclusions

In summary, using the dual-laser ablation process, PZT films have been successfully grown with the proper stoichiometry and particulate-free smooth surfaces. The films have the desired perovskite structure and no impurity phases. These films have superior ferroelectric properties as compared to films grown by single laser ablation. This technique could be generalized to all multi-component thin film growth with a high volatility element which would lead to non-stoichiometric transfer of materials in other processes.

#### **3.3. CFO-PZT Bilayer Thin Films**

#### **3.3.1. Experimental Details**

CFO-PZT bilayer thin films were grown on 1cm x 0.5 cm single crystalline MgO (100) and SrTiO3 (STO) (100) substrates from compressed powder targets of CFO and Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub>. Henceforth, the nomenclature CFO/MgO and CFO/STO for CFO single layer thin films on MgO and STO substrates, respectively, will be used in the text. Similarly, the CFO-PZT bilayer thin films grown on MgO and STO substrates will be referred as, PZT/CFO/MgO and PZT/CFO/STO, respectively. A schematic diagram of the structure is shown in Figure 3.3.1.



Figure 3.3.1. Schematic diagram of CFO-PZT bilayer films deposited on MgO or STO substrates.

CFO/MgO and CFO/STO films of similar thicknesses were prepared under the same experimental conditions for comparison. For the PZT/CFO/MgO and PZT/CFO/STO thin films, the CFO layer was deposited at 450 °C and 10 mTorr  $O_2$  pressure for a 200 nm layer thickness. The subsequent PZT layer of same thickness was deposited at 550 °C, 300 mTorr  $O_2$  pressure. Table 3.6 summarizes the deposition conditions for the individual CFO and PZT layers.

Layers in	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Thickness
CFO-PZT bilayer	$(J/cm^2)$	$T_{s}(^{\circ}C)$	$pO_2(mT)$	(nm)
CFO	2	450	10	200
PZT	2	550	300	200

Table 3.6. Deposition conditions of the layers in the CFO-PZT bilayer films that were grown on MgO and STO substrates.

For the polarization measurements, CFO-PZT bilayer capacitors were fabricated using conducting LSMO top and bottom electrodes. Figure 3.3.2 shows the schematic diagram of the LSMO/CFO/PZT/LSMO capacitor grown on MgO (100) and STO (100) substrates.



Figure 3.3.2. Schematic diagram of the CFO-PZT bilayer capacitor fabricated using LSMO top and bottom electrodes.

Table 3.7 summarizes the deposition conditions for the individual layers. The PZT layer was deposited using dual laser ablation. In Section 3.2 it was illustrated how the ferroelectric properties of PZT could be improved using dual laser ablation. The top LSMO electrodes were deposited in-situ using a shadow mask that produced 100  $\mu$ m diameter contacts.

Layers in	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Thickness
CFO-PZT capacitor	$(J/cm^2)$	$T_{s}(^{\circ}C)$	$pO_2(mT)$	(nm)
LSMO (bottom electrode)	2	600	10	100
CFO	2	450	10	200
PZT	UV:3, IR:2	550	500	500
LSMO (top electrodes)	2	600	10	100

Table 3.7. Deposition conditions of the layers in the CFO-PZT capacitor using LSMO top and bottom electrodes.

# **3.3.2. Results and Discussions**

# **3.3.2.1. Structural Properties**

Figure 3.3.3 shows SEM images of the PZT top layer in PZT/CFO/Si film. The surface is dense and shows distinct grain coalescing (at higher magnification) due to the high growth temperature.



Figure 3.3.3. SEM images of the PZT surface in CFO-PZT bilayer film grown on Si substrate.

Figure 3.3.4 (right panel) shows the cross-section of a PZT/CFO/MgO film. The image is obtained by first milling a wedge pattern (left panel) on the film surface using Focussed Ion Beam (FIB) and then looking at the exposed layers using SEM.



Figure 3.3.4. SEM images of CFO-PZT bilayer film grown on MgO substrate (cross-sectional view).

The small lattice mismatch (0.04 %) between PZT (tetragonal perovskite, lattice parameters, a=b=4.036 Å, c=4.146 Å) and CFO (face-centered cubic, lattice parameter, a = 8.391 Å) as well as between CFO and the substrates allows for the growth of the epitaxial films. Figures 3.3.5 (a, and b) show the XRD  $\theta$ -2 $\theta$  spectra for PZT/CFO/MgO and CFO/MgO, respectively. XRD spectra for PZT/CFO/STO and CFO/STO are shown in Figures 3.3.5 (c, and d), respectively. In all the samples the single phase nature and epitaxial relationship with the substrates are observed. The XRD peak in CFO is assigned to the (400) plane, corresponding to the face-centered cubic (fcc) phase of CFO with space group Fd-3m (227). For PZT/CFO/MgO and PZT/CFO/STO films, the PZT peak is indexed to the (100) plane of tetragonal PZT with space group P4mm (99) (Figures 3.3.5 a, and c). Due to the small lattice mismatch between MgO (face-centered-cubic, 2 x

lattice parameter = 8.42 Å) and CFO, the MgO (200) and CFO (400) peaks are in close occurrence to each other in the  $\theta$ -2 $\theta$  spectra. Insets to the Figures 3.3.5 (a, and b) visibly show the MgO and CFO peaks in the samples.



Figure 3.3.5. XRD  $\theta$ -2 $\theta$  scans for single layer CFO and bilayer CFO-PZT films grown on MgO (a, and b) and STO (c, and d) substrates, respectively. The insets to (a) and (b) show the details of the MgO (200), CFO (400) and PZT (200) peaks around 43° (2 $\theta$ ).

However, due to the larger lattice mismatch between STO (primitive cubic, 2 x lattice parameter = 7.81 Å) and CFO, the (400) peaks of CFO are shifted significantly (Figures 3.3.5 c and d) as compared to the peaks of polycrystalline CFO [17]. The out-of-

plane lattice parameter ( $a_{\perp}$ ) for CFO was calculated from the XRD  $\theta$ -2 $\theta$  scans (Table 3.8).

In order to verify the in-plane epitaxial relationship and cubic symmetry for the CFO and PZT layers,  $\varphi$  scans were performed. Figures 3.3.6 (a, and b) show the  $\varphi$  scan spectra from the PZT (101) plane for PZT/CFO/STO and PZT/CFO/MgO, respectively. Figures 3.3.6 (c, and d) show the  $\varphi$  scan spectra from the CFO (311) plane for PZT/CFO/STO and PZT/CFO/MgO, respectively. Figures 3.3.6 (e) and (f) show the  $\varphi$ scan spectra from the CFO (311) plane for CFO/STO and CFO/MgO, respectively. In all cases, the peaks in the  $\varphi$  spectra occur at intervals of 90° suggesting the four-fold cubic symmetry and cube-on-cube growth. Figures 3.3.6 (g, and h) show the rocking curves ( $\omega$ scans) about the CFO (400) planes for PZT/CFO/STO and CFO/STO, and PZT/CFO/MgO and CFO/MgO, respectively. The small full-width at half maximum (FWHM) values ( $< 1^{\circ}$ ) of the rocking curves confirm a good degree of in-plane orientation for CFO in all the samples (see Table 3.8 for FWHM values). However the (400) texture is sharper in the films grown on MgO which may be attributed to the smaller lattice mismatch between CFO and MgO. In addition, the degree of (400) texturing of CFO weakens slightly in PZT/CFO/STO and PZT/CFO/MgO compared to PZT/STO and PZT/MgO, respectively. Figures 3.3.6 (i, and j) show the asymmetric scans of (511) and (440) planes of CFO for CFO/STO and CFO/MgO, respectively. Figures 3.3.6 (k, and l) show the similar asymmetric scans for PZT/CFO/STO and PZT/CFO/MgO, respectively. For Figures 3.3.6 (i - l) the left peaks are from CFO (511) plane and the right peaks are from CFO (440) planes. The average in-plane lattice

parameters  $(a_{II})$  for CFO in the samples were calculated from the asymmetric scans shown in Figures 3.3.6 (i - 1) (Table 3.8).



Figure 3.3.6. Left and right columns represent the films grown on STO and MgO substrates respectively. (a and b) are  $\varphi$  scan spectra from PZT (101) reflection in CFO-PZT bilayer film. (c and d) and (e and f) are  $\varphi$  scan spectra from (311) CFO reflection in CFO-PZT bilayer and single layer CFO films respectively. (g and h) are rocking curves of CFO (400) peaks. (i and j) and (k and l) are asymmetric scans of (511) and (440) CFO planes for single layer CFO films and bilayer layer CFO-PZT films respectively. (i – l) Left peaks are from CFO (511) plane and the right peaks are from CFO (440) planes.

The strain ( $\epsilon$ ) in the CFO layer was calculated by using the formula  $\epsilon = (a - a_o)/a_o$ , where a is out-of-plane  $(a_{\perp})$  or in-plane  $(a_{\parallel})$  lattice parameter and  $a_o$  is the bulk unstressed lattice parameter of CFO ( $a_o = 8.39$  Å) [17]. The in-plane stress ( $\sigma_{\mu}$ ) in the film was calculated using the relation  $\sigma_{II} = Y \epsilon_{II}$  where  $\epsilon_{II}$  is the in-plane strain ( $\epsilon$ ) and the Young's modulus value for CFO (Y =  $1.5 \times 10^{12}$  dyne/cm<sup>2</sup>) [98]. Table 3.8 summarizes the lattice parameters and strains calculated for the out-of-plane and in-plane configurations. From the strain values listed in Table 3.8 it is seen that the CFO/MgO films grows with slight in-plane tensile ( $\varepsilon_{\parallel} = 0.0015$ ) and out-of plane compressive ( $\varepsilon_{\perp} =$ -0.0005) strains. On the other hand, the CFO/STO film grows with larger in-plane compressive ( $\epsilon_{II}$  = -0.0116) and out-of plane tensile ( $\epsilon_{\perp}$  = 0.0124) strains. This can be attributed to the different lattice mismatches of CFO with MgO and STO substrates. The lattice mismatch at room temperature was calculated using the relation  $(a_s$  –  $a_o)/a_s$  (%) where as is the lattice parameter of the substrate. The calculated values for CFO/MgO and CFO/STO are 0.36 % and 7.8 %, respectively. It is also observed that the in-plane lattice parameter ( $a_{II}$ ) of CFO for the PZT/CFO/MgO film ( $a_{II} = 8.294$  Å) is smaller than that of the CFO/MgO film ( $a_{II} = 8.403$  Å). This suggests that possibly with the deposition of the PZT layer on top, the CFO layer experiences an in-plane compression that compels it to match its  $a_{\parallel}$  to the smaller lattice parameter of PZT (a = b = 4.036 Å, c = 4.146 Å).

As a consequence the in-plane strain and consequently the stress is amplified in PZT/CFO/MgO. However, an opposite trend is observed for the films grown on STO substrates. The CFO/STO film is already highly strained due to the large mismatch between the STO substrate and CFO. With PZT layer on top of it the PZT/CFO/STO film is slightly relaxed to a lower strain state.
	FWHM of		Out-of-plane		In-plane	In-plane
Sample	Rocking curve	$a_{\perp}$	strain	a <sub>II</sub>	strain	stress
	(°)	(Å)	$\epsilon_{\perp}$	(Å)	ε <sub>II</sub>	$x 10^9 (dyne/cm^2)$
CFO/MgO	0.076	8.386	-0.0005	$8.403\pm0.004$	$0.0015 \pm 0.0005$	$2.3 \pm 0.6$
PZT/CFO/MgO	0.321	8.338	-0.0062	$8.294 \pm 0.007$	$-0.0114 \pm 0.0008$	$-17.1 \pm 0.1$
CFO/STO	0.915	8.494	0.0124	$8.292 \pm 0.005$	$-0.0116 \pm 0.0006$	$-17.5 \pm 0.09$
PZT/CFO/STO	0.986	8.479	0.0106	$8.330\pm0.002$	$-0.0071 \pm 0.0002$	$-10.7 \pm 0.03$

Table 3.8. FWHM of rocking curves about CFO (400) plane, in-plane ( $a_{II}$ ) and out-of-plane ( $a_{\perp}$ ) lattice parameters obtained from XRD peaks, in-plane ( $\epsilon_{II}$ ) and out-of-plane ( $\epsilon_{\perp}$ ) strains for CFO and CFO-PZT films on MgO and STO substrates.

In order to analyze the surface morphologies of the thin films and predict their mechanisms of growth, AFM was employed. Figure 3.3.7 (a) illustrates an AFM image of the CFO top layer for CFO/MgO film. The image reveals a very smooth and compact surface with a root mean square roughness (R<sub>rms</sub>) value of 2.084 nm and small grain size with relatively uniform size distribution. As reported earlier such a flattened surface could be indicative of a layer-by-layer growth mechanism [110]. Figure 3.3.7 (b) shows an AFM image of the PZT top layer for PZT/CFO/MgO film. The PZT layer is relatively less smooth with R<sub>rms</sub> value of 11.456 nm and larger grain size as compared to CFO/MgO. Uniform grain size distribution is also observed for PZT. The surface exhibited a texturing which is probably reminiscent of the epitaxial growth. Additionally, the grains appear to be preferentially elongated in one in-plane orientation. This effect can be correlated to the larger difference in the  $a_{\parallel}$  (8.294 Å) and  $a_{\perp}$  (8.338 Å) values of the CFO layer in PZT/CFO/MgO (Table 3.8). From Figure 3.3.7 (c), which is a 3 dimensional projection of the PZT top layer shown in Figure 3.3.7 (b), distinct cusp (or valleys) and dome features are observed on the film surface. It has been reported earlier that such cusps are associated with high stress concentration regions [137] which increase

of the surface energy and gets compensated by the decrease of strain energy via elastic strain relaxation in the films. This strain relaxation of the top PZT layer suggests that probably the bottom CFO layer is more strained. The films grown on STO substrates showed distinctly different surface morphologies. Figure 3.3.7 (d) shows the surface of CFO/STO film. The surface appears rougher than CFO/MgO with  $R_{rms}$  value of 7.502 nm. It also consists of grains with various shapes and sizes. This could be attributed to the island growth mode [110, 113]. Figure 3.3.7 (e) shows the PZT top surface for PZT/CFO/STO film. The various grain sizes with larger grain growth and  $R_{rms}$  value of 22.683 nm still conform to the island growth mechanism.



Figure 3.3.7. AFM images of (a) CFO surface of CFO/MgO film, (b) top PZT surface of PZT/CFO/MgO film, (c) 3D rendition of part (b), (d) CFO surface of CFO/STO film and (e) top PZT surface of PZT/CFO/STO films. Scan areas are  $1x1 \mu m$  with z-height of 100 nm.

The following paragraphs discuss the structural properties of CFO-PZT bilayer films (see schematic in Figure 3.3.2) using LSMO bottom electrodes grown on MgO and STO substrates (LSMO/MgO and LSMO/STO) used for the ferroelectric measurements. The small lattice mismatches (8 % for LSMO-MgO and 0.009 % for LSMO-STO) between LSMO (pseudo-cubic, a = 0.387 nm), MgO (cubic, a = 0.421 nm) and STO (cubic, a = 0.3905 nm) allowed for the growth of epitaxial LSMO bottom electrodes on MgO and STO substrates. Figure 3.3.8 shows the XRD  $\theta$ -2 $\theta$  scan for the LSMO/PZT/CFO/LSMO film grown on MgO substrate. [138].



Figure 3.3.8. XRD  $\theta$ -2 $\theta$  scans for the CFO-PZT bilayer grown on single crystal MgO (100) substrate with a conducting LSMO top and bottom electrode layers. The PZT (*l*00) where *l* = 1, 2, and 3 peaks are denoted by \*. The LSMO (*l*00) where *l* = 1, and 2 peaks are denoted by  $\gamma$ . The inset shows the details of MgO (200) and CFO (400) peaks.

Only the CFO (400) peak and the PZT (l00) where l = 1, 2, and 3 peaks are observed. No impurity or additional orientations of CFO or PZT are observed. This

confirms that the film is single phase and epitaxial in nature. The MgO (200) peak and CFO (400) peak have been shown in detail in the inset to Figure 3.3.8.

Figure 3.3.9 shows the XRD  $\theta$ -2 $\theta$  scan for the CFO-PZT bilayer grown on LSMO/STO substrate (see schematic diagram in Figure 3.3.2). It is again evident that the structure is highly epitaxial in nature with only (*l*00) where *l* = 1, 2, and 3 orientations from the constituent layers. Due to the small lattice mismatch between STO, LSMO, PZT and CFO, the (200) peaks of STO, PZT and LSMO, and the (400) peak of CFO have been shown in detail in the inset to Figure 3.3.9.



Figure 3.3.9. XRD  $\theta$ -2 $\theta$  scans for the CFO-PZT bilayer grown on single crystal STO (100) substrate with a conducting LSMO top and bottom electrode layers. The PZT (*l*00) where *l* = 1, 2, and 3 peaks are denoted by \*. The LSMO (*l*00) where *l* = 1, 2, and 3 peaks are denoted by  $\gamma$ . The inset shows the details of LSMO (200), STO (200), PZT (200) and CFO (400) peaks.

## **3.3.2.2. Magnetic Properties**

Figure 3.3.10 shows the magnetization (M) - magnetic field (H) hysteresis loops for PZT/CFO/MgO and CFO/MgO, respectively. Similarly, Figure 3.3.11 shows the M-H loops for PZT/CFO/STO and CFO/STO, respectively. The in-plane and out-of-plane configurations symbolized by II and  $\perp$ , respectively, represent the application of the magnetic fields parallel and perpendicular to the film planes. The hysteresis loops were acquired after the removal of the diamagnetic contribution from the substrates. In addition since the thickness of CFO layer was kept constant in all the films, the magnetization values were only normalized to the volume of the CFO layer assuming no magnetic contribution from the PZT layer. Table 3.9 summarizes the saturation magnetization ( $M_s$ ), ratio of remnant magnetization ( $M_r$ ) to  $M_s$  and the coercivity ( $H_c$ ) for all the samples at 300 K and 10 K. The  $M_r/M_s$  ratio provides an estimate of the degree of squareness of the loops. The magnetic measurements were performed both at 300 K and 10 K to emphasize the consistency of the underlying mechanisms. The M<sub>s</sub> values for CFO films on STO substrates are larger than those on MgO substrates [28]. The M<sub>s</sub> value for the PZT/CFO/STO film is about 5.8  $\mu_B$  per  $\text{Co}^{2+}$  site which is much higher than the theoretical bulk value of 3  $\mu_B$  per Co<sup>2+</sup> site [17].

From Figure 3.3.10 it is observed that the magnetization of CFO reduces in PZT/CFO/MgO film as compared to that in CFO/MgO film both at 300 K and 10 K. Around 25 % decrease in the M<sub>s</sub> values is observed for CFO/MgO film with the deposition of the PZT top layer top both in the in-plane and out-of-plane directions at 300 K (Table 3.9). However the H<sub>c</sub> values still remain about the same. The out-of-plane anisotropy exhibited by the CFO/MgO film is clearly seen in the M-H loops measured at

10 K (Figures 3.3.10 a, and c). The in-plane magnetization does not show any saturation even at 50 kOe while on the other hand the out-plane magnetization shows well behaved saturation. This behavior is preserved in the M-H loops of PZT/CFO/MgO films. This suggests that the easy axis of magnetization of CFO/MgO film does not change with deposition of the PZT top layer. In short, the net effect of addition of the PZT layer on top of CFO/MgO film is an observed decrease in magnetization with nominal change in coercivity and squareness.

Table 3.9. Summary of saturation magnetization ( $M_s$ ), ratio of remnant magnetization ( $M_r$ ) to  $M_s$  and the coercivity ( $H_c$ ) for CFO/PZT bilayer and CFO single layer films measured at 300 K and 10 K. The in-plane and out-of-plane directions have been denoted by the symbols II and  $\perp$ , respectively.

				300 K				
Sample	$M_{s}\parallel$	$M_{s}\parallel$	$M_r\!/M_s \parallel$	H <sub>c</sub> ∥	$M_{s}\bot$	$M_{s}\bot$	$M_{r}\!/M_{s}\!\perp$	$\mathrm{H_{c}} \bot$
	(emu/cm <sup>3</sup> )	$(\mu_{\rm B}/{\rm Co}^{2^+})$	(%)	(kOe)	(emu/cm <sup>3</sup> )	$(\mu_{\rm B}/{\rm Co}^{2^+})$	(%)	(kOe)
CFO/MgO	$305 \pm 4$	2.4	37.6	3.8	$310 \pm 6$	2.5	<13.9	< 0.03
PZT/CFO/MgO	$228\pm2$	1.8	25.8	1	$234 \pm 5$	1.8	<5.9	< 0.03
CFO/STO	$478 \pm 5$	3.8	53.9	3.5	> 164	> 1.3	>21.6	3.0
PZT/CFO/STO	$592 \pm 5$	4.7	53.6	3.4	190	1.5	41.5	0.1
				10 K				
Sample	$\mathbf{M_s} \parallel$	$\mathbf{M_s} \parallel$	$M_r\!/M_s\parallel$	$H_c \parallel$	$M_s \perp$	$M_s \perp$	$M_r\!/M_s\!\perp$	$H_c \perp$
	(emu/cm <sup>3</sup> )	$(\mu_{\rm B}/{\rm Co}^{2^+})$	(%)	(kOe)	(emu/cm <sup>3</sup> )	$(\mu_{\rm B}/{\rm Co}^{2^+})$	(%)	(kOe)
CFO/MgO	>497	>3.9	>41.3	10	$441 \pm 12$	3.5	30.9	0.3
PZT/CFO/MgO	>400	>3.2	>39.6	4	$353 \pm 3$	2.8	18.1	0.3
CFO/STO	$541\pm9$	4.3	63.1	11	> 164	> 1.3	>14.6	0.7
PZT/CFO/STO	$728\pm9$	5.8	65.6	11	206	1.6	28.8	0.5



Figure 3.3.10. M-H loops measured at (a, and c) 10 K and (b and d) 300 K for the CFO-MgO and PZT-CFO-MgO films, respectively. The in plane and out of plane denote directions for the magnetic field applied parallel or perpendicular to the film plane, respectively.

In contrary, magnetization of CFO/STO film increases with the addition of PZT on top as shown in Figure 3.3.11. Around 25% and 34% increase in the in-plane  $M_s$  can be estimated for PZT/CFO/STO at 300 K and 10 K, respectively (Table 3.9). The out-of-plane  $M_s$  also increases by 25% at 10 K in the PZT/CFO/STO film as compared to CFO/STO film. The CFO/STO film exhibits strong in-plane anisotropy with well

saturated loops in the in-plane direction (Figures 3.3.11 a, and b) and almost no saturation in the out-of-plane direction (Figures 3.3.11 c, and d). However from Figure 3.3.11 (d) it is evident that the out-of-plane magnetization at 300 K for PZT/CFO/STO shows well saturated behavior with an almost double  $M_r/M_s$  ratio (Table 3.9) compared to CFO SL film on STO. A similar trend is observed at 10 K (Figure 3.3.11 c).



Figure 3.3.11. M-H loops measured at (a, and c) 10 K and (b and d) 300 K for the CFO-STO and PZT-CFO-STO films, respectively. The in plane and out of plane denote directions for the magnetic field applied parallel or perpendicular to the film plane, respectively.

This possibly indicates a reorientation in the direction of the easy axis of magnetization for CFO/STO film with the deposition of the PZT top layer. Thus the net effect on the magnetic properties of CFO/STO film with PZT top layer is an increase in magnetization and possible change in direction of magnetic anisotropy.

The effect of stress ( $\sigma$ ) on the magnetization of a magnetostrictive material can be understood from the following thermodynamic relation [38, 139]:

$$\frac{1}{l}\frac{\partial l}{\partial H} = \frac{1}{4\pi}\frac{\partial B}{\partial\sigma}$$
(3.1)

where *B* is the magnetic induction,  $\sigma$  is the stress, *l* is the length of the material and *H* is the external applied magnetic field. From equation (3.1) it can be assumed that the magnetization is decreased (increased) by tension (compression) if the magnetostriction  $(\Delta l/l)$  is negative (positive) when  $\partial \sigma$  is positive (negative). Since CFO is a negative magnetostrictive material the magnetization would be reduced by stress (tensile).

The CFO/MgO film is under in-plane tensile stress (Table 3.8), due to the lateral stretching along the film plane which results in the  $a_{II}$  (8.403 Å) being larger than  $a_{\perp}$  (8.386 Å). With the addition of a top PZT layer the in-plane residual stress may be increased which results in reduced magnetization in PZT/CFO/MgO. On the contrary, the CFO/STO film is under large in-plane compressive stress with  $a_{\perp}$  (8.494 Å) larger than  $a_{II}$  (8.292 Å). With the deposition of the PZT layer, the stress is released making the  $a_{II}$  (8.330 Å) in PZT/CFO/STO larger than that in CFO/STO. Thus strain relaxation enhanced the magnetization in PZT/CFO/STO film. The results matched well with the negative magnetostriction of CFO.

An increase in the residual stress due to the top PZT layer on the CFO layer and its effect on magnetization has been reported earlier on the polycrystalline films grown on silicon [89]. Sim et. al. had suggested that the residual stress in the CFO films on Si could be intrinsic and associated with the orientation change or defect incorporation or non-equilibrium phase formation. However the stress mechanisms were complicated and difficult to quantify [89]. In this work the residual stress could be estimated due to epitaxial growth.

The suppression of the  $M_s$  with higher stress ( $\sigma$ ) can also be understood qualitatively in terms of magnetic strain energy density, which is given by  $E_{\sigma} = 3/2$  $\lambda_s \sigma \sin^2 \theta$ , where  $\lambda_s$  is the magnetostrictive coefficient at saturation, and  $\theta$  is the angle between the stress ( $\sigma$ ) and the saturation magnetization  $M_s$ . When  $\lambda_s \sigma$  is negative (as in the case for CFO in tension), the domains tend to align perpendicular to the axis of tension. This maximizes the energy since  $\theta$  is 90°, which in turn makes the domains unstable. Thus the magnetization will be decreased as observed in our experiment. In addition, since the out-of-plane  $M_s$  in all the films follows the same trend as in-plane  $M_s$ , there is no change in magnetic anisotropy in bilayers as compared to single layers.

#### **3.3.2.3.** Ferroelectric Properties

Figure 3.3.12 shows the ferroelectric (FE) hysteresis loops for CFO-PZT bilayer films on LSMO/MgO substrates. All the data was measured using a driving voltage of 9 V that was required for the proper saturation of the loops but changing the frequency in the range 1Hz to 10 Hz. The best FE response is observed at 10 Hz with a well saturated and square shaped loop with  $P_{max} = 127 \ \mu C/cm^2$ ,  $P_r = + 121 \ \mu C/cm^2$  and  $-120 \ \mu C/cm^2$ , and nominal voltages required for switching,  $V_c = + 4.72 \ V$  and  $- 4.53 \ V$ , respectively.



Figure 3.3.12. Ferroelectric hysteresis loops for CFO-PZT bilayer film on MgO substrate at 9V driving voltage in the frequency range 1 Hz to 10 Hz.

The hysteresis loops at lower frequencies in the range 1 Hz to 2 Hz loops are tilted with  $P_{max} < P_r$ . This is due to the presence the intermediate CFO dielectric layer along with the ferroelectric PZT layer. Such behavior was not observed for the PZT-MgO films (see Section 3.2). The intermediate CFO layer has a lower dielectric constant than PZT and separates the bound charges that are due to polarization from compensating the charges on the bottom LSMO electrode. Due to the incomplete compensation a depolarizing field (E<sub>d</sub>) develops across the PZT layer during measurement. The depolarizing field is given by  $E_d = - Pd/(\epsilon_d t)$  where d and  $\epsilon_d$  are the thickness and the complex permittivity of the dielectric layer, and P and t are the polarization and thickness of the ferroelectric layer [140]. The complex permittivity ( $\epsilon_d$ ) is dependent on the frequency of the applied field ( $\omega$ ) by the relation  $\epsilon_d = \epsilon + i$  ( $\sigma/\omega$ ) where  $\sigma$  and  $\epsilon$  are the conductivity and real part of permittivity of the medium, respectively. At low frequencies the contribution from the complex part of  $\varepsilon_d$  is enhanced and effects the  $E_d$ . This is manifested as the tilting of hysteresis loops at low frequencies.

Figure 3.3.13 shows the frequency dependence of  $P_r$  and  $V_c$  at 9 V driving voltage. The similar values of +  $P_r$  and -  $P_r$  are associated with the symmetric electrode configuration. Further, in the range 1 Hz to 1 kHz, the  $P_r$  values decrease monotonically indicating typical ferroelectric behavior.



Figure 3.3.13. Frequency dependence of remnant polarization  $(P_r)$  and nominal voltage for switching  $(V_c)$  for CFO-PZT bilayer on MgO substrate.

The V<sub>c</sub> values increase almost linearly in the frequency range 1 Hz to 100 Hz with a slight drop at 1 kHz. Such linear behavior has recently been reported for PZT films grown on different substrates [141]. The linear dependence of coercive field ( $E_c$ ) with switching field frequency ( $\omega$ ) is associated with the viscous motion of domain boundaries given by  $E_c = V_c/d = (P_o\Gamma h/\delta) \omega$  where  $P_o$  is the spontaneous polarization,  $\Gamma$  is the viscosity of domain wall motion, d and h/2 are the half widths of domain wall and crystallite, respectively.

Figure 3.3.14 shows the ferroelectric hysteresis loops for CFO-PZT bilayer film on STO substrates measured at 9 V driving voltage but changing the frequency from 1 Hz to 10 Hz. Well saturated and square shaped hysteresis loops are observed at 1 Hz with  $P_{max} = 185 \ \mu C/cm^2$ ,  $P_r = +182 \ \mu C/cm^2$  and  $-180 \ \mu C/cm^2$ , and  $V_c = +5.85 \ V$  and  $-4.95 \ V$ , respectively.



Figure 3.3.14. Ferroelectric hysteresis loops for CFO-PZT bilayer film on STO substrate at 9V driving voltage in the frequency range 1 Hz to 10 Hz.

Figure 3.3.15 shows the frequency dependence of  $P_r$  and  $V_c$  at 9 V driving voltage. The monotonically decreasing  $P_r$  values and linearly increasing Vc values with increasing frequency again indicate typical ferroelectric behavior.



Figure 3.3.15. Frequency dependence of remnant polarization ( $P_r$ ) and nominal voltage for switching ( $V_c$ ) for CFO-PZT bilayer on MgO substrate.

Figure 3.3.16 shows the P-E loops for the CFO-PZT bilayer (BL) and PZT single layer (SL) films grown on LSMO/MgO substrates. Similarly, Figure 3.3.17 shows the P-E loops for the CFO-PZT bilayer (BL) and PZT single layer (SL) films grown on STO substrates. All the presented loops were measured using triangular pulses at 1000 ms hysteresis period (i.e. 1 Hz frequency) at 9 V driving voltage. The thickness (d) of the PZT layer was kept constant at 500 nm both in the BL and SL films.



Figure 3.3.16. Ferroelectric hysteresis loops for CFO-PZT bilayer and PZT single layer films grown on MgO substrates under same conditions. Data measured at 9V driving voltage.

The polarization hysteresis values for the bilayer (BL) and single layer (SL) on different substrates have been summarized in Table 3.10. The coercive field ( $E_c$ ) has been calculated using  $E_c = |(V_c(+)+V_c(-))|/2d$ . The leakage current density ( $J_L$ ) has been measured at 9 V for 1000 ms soak time. It is clear from Figures 3.3.16 and 3.3.17 that there is a huge enhancement in the polarization values for the BLs as compared to the SLs.



Figure 3.3.17. Ferroelectric hysteresis loops for CFO-PZT bilayer and PZT single layer films grown on STO substrates under same conditions. Data measured at 9V driving voltage.

Table 3.10. Summary of maximum polarization ( $P_{max}$ ), remnant polarization ( $P_r$ ), nominal switching voltage ( $V_c$ ), coercive field ( $E_c$ ) and leakage current density  $J_L$  (A/cm<sup>2</sup>) for CFO-PZT bilayer and PZT single layer films grown on MgO and STO substrates. Data measured at 9 V driving voltage at 1 Hz.

Sample	Substrate	P <sub>max</sub>	Pr		Vc		E <sub>c</sub>	$J_L$
		$(\mu C/cm^2)$	$(\mu C/cm^2)$		(V)	)	(kV/cm)	$(A/cm^2)$
			(+)	(-)	(+)	(-)		x 10 <sup>-9</sup>
CFO-PZT	MgO	127	121	-120	4.72	-4.53	92.5	1.99
PZT	MgO	93	75	-72	2.64	-1.99	46.3	0.27
CFO-PZT	STO	185	182	-180	5.85	-4.95	108.0	8.61
PZT	STO	108	91	-92	2.62	-1.69	43.1	0.20

The  $P_{max}$  values for CFO-PZT BL on MgO and STO increased by almost 37 % and 70 % respectively as compared to the SL PZT films. The  $E_c$  values also increased in the BLs which is attributed to the larger depolarizing fields in the BLs due to the presence of the intermediate CFO layer.

Figure 3.3.18 shows a comparison of the leakage current densities  $(J_L)$  for CFO-PZT BL and PZT SL capacitors on STO substrates measured under constant voltage stress of 9V applied for a soak time of 1000 ms (Table 3.10). Although the BL films exhibited higher polarization values compared to the SL films, the leakage current densities in the BLs were higher than in the SLs.



Figure 3.3.18. Leakage current density in CFO-PZT bilayer and PZT single layer thin film capacitors grown on STO substrates under same conditions. Inset shows a schematic diagram of CFO-PZT bilayer during the leakage current density measurement.

One possible explanation for the observed enhancement of polarization in BLs could be due to the difference in stress in the PZT layer grown on CFO in BL and on LSMO on SL. The lattice mismatches of the substrates and electrodes with PZT are summarized in Table 3.11. Due to the smaller lattice mismatch between PZT and CFO (0.04 %) as compared to PZT and LSMO (4.1 %), the PZT layer in CFO-PZT BL film is less strained which lead to higher polarization values.

Table 3.11. Summary of crystal structure of substrates and electrodes used for growth of bilayers and single layers and lattice mismatches with respect to PZT.

Material	Crystal structure	Lattice parameters (Å) (a, b, c)	Lattice mismatch (%) with respect to PZT	
PbZr <sub>0.52</sub> Ti <sub>0.42</sub> O <sub>3</sub> (PZT) La <sub>0.7</sub> Sr <sub>0.3</sub> MnO <sub>3</sub> (LSMO) CoFe <sub>2</sub> O <sub>4</sub> (CFO) MgO SrTiO3 (STO)	tetragonal perovskite pseudocubic perovskite face centered cubic cubic rock salt cubic perovskite	a=b=4.036,c=4.146 a=b=c=3.876 a=b=c=8.391 a=b=c=4.216 a=b=c=3.905	-4.1 0.04 4.3 -3.4	

From the above ferroelectric measurements there is a clear evidence of ferroelastic coupling in these CFO-PZT BL films. The change in polarization in the CFO-PZT BLs with respect to the SL PZT film could be attributed to the interfacial stress between the layers. The change in the ferroelectric property due to the introduction of a CFO layer shows a possibility of magnetoelectric (ME) coupling in CFO-PZT bilayer.

## **3.3.3.** Conclusions

To summarize, the epitaxial bilayer films of CFO and PZT were grown on single crystalline MgO and STO substrates. The films grown on MgO (100) showed better inplane epitaxy compared to the films grown on STO (100). In-plane strain on the film grown on MgO increased with the PZT layer on top of the CFO layer. This increase in stress in the bilayer resulted in lowered saturation magnetization compared to the single layer CFO-MgO film. In the case of the film grown on STO (100), the strain was already high even in the single-layer CFO film. With the bilayer CFO-PZT film on STO, the inplane strain reduced slightly, which in turn resulted in higher saturation magnetization. The strain-modulated magnetism in these bilayers leads to the possibility of magnetoelectric coupling sought in multiferroics. The ferroelectric properties of the bilayers showed huge enhancements in the polarization as compared to the single layer. This could be attributed to stress mediated ferroelastic coupling which could again lead to a possible magnetoelectric (ME) coupling in these structures.

# 3.4. Chapter Summary

In conclusion, this chapter described the ferromagnetic and ferroelectric properties of epitaxial CFO and PZT thin films, respectively. In case of CFO films it was observed that the epitaxial strain played an important role in governing the magnetic anisotropies. The growth of high quality PZT films required a through investigation of the problem of Pb depletion. Using the dual laser process, finally enhanced ferroelectric properties were observed. After the successful optimization of the growth parameters of the single layers, the horizontal composite CFO-PZT bilayered structures were fabricated. Simultaneous observation of ferromagnetism and ferroelectricity confirmed the multiferroic nature of the structure. X-analysis of interfacial stress and their correlation to the observed properties showed a clear evidence of magneto-elastic coupling in the heterostructures. This indicated a possibility of ME effect in these multiferroic structures. However in order to prove ME effect the magnetic properties have to be studied under an applied electric field and vice versa.

### CHAPTER 4:

### **DOPED ZINC OXIDE HETEROSTRUCTURES**

This chapter describes the growth and properties of doped Zinc oxide (ZnO) thin films. ZnO is a direct wide band gap (3.4 eV) semiconductor that has sustained research interest for quite some time because of its multifunctionality like room temperature (RT) ferromagnetism (FM) [142], and piezoelectricity [143]. ZnO has found applications in optoelectronics [144], gas sensing [145, 146], photocatalysis [147 - 149], and UVphotoelectronics [150 - 152]. It has also been used as a transparent conducting oxide [153], and as electrodes for photoelectrochemical cells [154 - 156]. The most important feature for this wide scale research in ZnO is the simplicity of its growth in different forms using diverse physical and chemical methods. PLD technique has been very successful for growing ZnO thin films with defined dopant concentrations and complex morphologies for various applications [157]. ZnO thin films have preferred grow with a c-axis orientation irrespective of the type of substrate used [158]. As long as the same hexagonal symmetry is present in the surface-unit cell of the substrate compared to the cplane of ZnO, i.e. the (0001) crystallographic plane, the epitaxial relationship between substrate and the film is maintained. This allows for the growth of epitaxial ZnO films on c-cut sapphire  $(Al_2O_3)$  substrates although the lattice mismatch between sapphire and ZnO is as large as 26 %. This large misfit hinders a pseudomorphic growth and consequently results in defects and film imperfections that affect their properties.

In recent times, it has been reported that the ferromagnetic properties of ZnO can be enhanced by 3d transition metal doping producing RT dilute magnetic semiconductors (DMS) [159]. Among the transition metals that have been doped, Manganese (Mn) has attracted more attention due its complete solid solubility in ZnO and the ability to introduce a strong magnetic moment when doped in ZnO [160]. On the other hand, it was also reported that the piezoelectric properties of ZnO can be greatly enhanced by doping it with vanadium (V) [161, 162]. From the viewpoint of material constituents, multiferroic materials in single phase have always attracted more attention than composites due to the direct ME coupling between the two order parameters and less interfacial defects [14]. In this viewpoint, the single phase structure and the observation of simultaneous RT ferromagnetic and ferroelectric properties make the Mn and V doped ZnO thin films an attractive candidate for a potential multiferroic device. In this work, the doped ZnO heterostructures have been grown for the first time to test the magnetoelastic coupling.

The following sections describe the growth and ferromagnetic and ferroelectric characterization of Mn doped and V doped ZnO thin films respectively. The final section describes the fabrication and properties of the Mn and V doped ZnO heterostructure. Evidence of possible magneto-electric coupling in these structures is shown.

## 4.1. Mn doped ZnO Thin Films

Almost a decade ago Dietl et al. [163] had first made the theoretical predictions about RT FM in Mn doped ZnO (ZMO) and the potential applications as spintronic devices. This had started an extensive research effort in ZMO thin films. However diverse experimental results ranging from paramagnetism [144], spin glass [165], anti-FM [166], low temperature FM [167] to even RT FM [168 - 170] have been reported over the years. Sharma et al. [168] who were the first to report the RT FM had shown that Mn when doped nominally in ZnO was in Mn<sup>2+</sup> valence state and the FM was carrier induced. In contrast Kundaliya et al. [169] later suggested that the FM was due to an oxygen-vacancy-stabilized  $Mn_{2-x}Zn_xO_{3-\delta}$  phase rather than carrier induced interaction among separate Mn atoms in ZnO matrix. Subsequently, Garcia et al. [170] showed that the RT FM in the ZMO was associated with the coexistence of  $Mn^{3+}$  and  $Mn^{4+}$  via a double-exchange mechanism. Such conflicting arguments produced no consensus on the origins of FM in ZMO systems. A fundamental understanding of the mechanism of magnetism in these materials is essential in order to achieve desired properties for use in device applications. Further experimental reports on the effects of growth conditions such as substrate temperature ( $T_s$ ) and oxygen pressure (pO<sub>2</sub>) in controlling the magnetic properties of ZMO films grown by pulsed laser deposition (PLD) suggested that higher saturation magnetization ( $M_s$ ) was observed in the conducting films grown at a  $T_s$  of 500-600 °C under low pO<sub>2</sub> [171 - 173]. These reports indicated that the observed FM was very sensitive to sample preparation, crystalline quality, residual defects and resulting carrier concentrations. In 2005, Coey et al. [174] proposed a defect mediated bound magnetic polaron (BMP) model to explain the FM in ZMO. In recent years such defect

mediated FM was experimentally observed [173, 175]. More recently, Calderon et al. [176 - 178] proposed a model based on two complementary magnetic mechanisms – the BMP percolation at low temperatures in insulating samples and the indirect RKKY exchange mechanism in more conducting samples at temperatures where substantial thermally activated carriers were present in the impurity band. However, there have been no direct observations that have validated this model. In this work both experimental and theoretical investigations suggested that the dual FM model [176] may finally resolve some of the controversies associated with the origins of FM in ZMO systems.

### **4.1.1. Experimental Details**

The ZMO target was fabricated by conventional solid state reaction technique. Stoichiometric amounts of high purity ZnO and MnO<sub>2</sub> powders (both 99.99% pure) were mixed, calcined at 400 °C for 12 h followed by uniaxial isostatic cold pressing at 200 MPa and finally was sintered for 12h at 1000 °C in air in order to make a hard ceramic target. Care was taken so that no impurities were introduced during the mixing and sintering process. EDS analysis on different regions of the target surface was performed to estimate the atomic % of Mn and also to check the uniform distribution of Mn in the target. The average atomic % Mn in the target was determined to be  $2.0 \pm 0.4$  %.

ZMO films were grown on 10 x 5 mm<sup>2</sup> c-cut sapphire (Al<sub>2</sub>O<sub>3</sub>) (001) substrates by varying the substrate temperatures ( $T_s$ ) and background O<sub>2</sub> pressures (pO<sub>2</sub>). Table 4.1 shows the deposition conditions for the samples. For ZMO films grown by varying  $T_s$ , the pO<sub>2</sub> was kept constant at 10 mT. The best crystalline sample was achieved at 600 °C. In order to optimize the deposition conditions ZMO films were also grown by varying pO<sub>2</sub>, with  $T_s$  at 600°C. Corresponding to each ZMO film, an undoped ZnO film was

deposited under the same conditions for comparison. The film thicknesses were measured

using a profilometer also shown in Table 4.1.

Sample	Substrate	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Film Thickness
		$(J/cm^2)$	$T_{s}(^{\circ}C)$	$pO_2(mT)$	(nm)
ZMO(RT)	$Al_2O_3$	2	RT	10	453±16
ZMO(200)	$Al_2O_3$	2	200	10	454±25
ZMO(400)	$Al_2O_3$	2	400	10	458±13
ZMO(600)	$Al_2O_3$	2	600	10	403±60*
ZMO(0mT)	$Al_2O_3$	2	600	0 (~10-3)	1210±24
ZMO(10mT)	$Al_2O_3$	2	600	10	403±60*
ZMO(50mT)	$Al_2O_3$	2	600	50	1182±42
ZMO(300mT)	$Al_2O_3$	2	600	300	1179±16

Table 4.1. Deposition parameters for ZMO thin films. \* ZMO(600) and ZMO(10mT) are the same samples.

## 4.1.2. Results and Discussion

### **4.1.2.1. Structural Properties**

The prepared ZMO target was observed under SEM to reveal the microstructure. Figure 4.1.1 shows the ZMO target surface under different magnifications. The target constituted of hexagonal crystals of about 5  $\mu$ m size in average. Presence of hexagonal crystals suggests absence of secondary phases. XRD was performed to confirm the crystallinity of the ZMO target, and the undoped ZnO and MnO<sub>2</sub> powders that were mixed to prepare the target. Figures 4.1.2 (a, b, and c) show the XRD  $\theta$ -2 $\theta$  scans of the ZMO target, MnO<sub>2</sub> powder, and undoped ZnO powder, respectively. The XRD patterns for both the ZMO target (Figure 4.1.2. a) and the undoped ZnO powder (Figure 4.1.2. c) match with the hexagonal lattice structure with space group P63mc (186) and lattice parameters a = 3.253 Å, and c = 5.213 Å, respectively.



Figure 4.1.1. SEM images of the Mn doped ZnO target surface.



Figure 4.1.2. XRD patterns of (a) Mn doped ZnO target (b)  $MnO_2$  powder and (c) undoped ZnO powder, respectively.

In order to rule out the presence of other impurity phases of Mn in the ZMO thin films a careful XRD analysis was conducted. Figure 4.1.3 shows the  $\theta$ -2 $\theta$  XRD scans of

ZMO films deposited at increasing growth temperatures ( $T_s$ ) of RT, 200 °C, 400 °C and 600 °C, labeled as ZMO(RT), ZMO(200), ZMO(400) and ZMO(600) respectively.



Figure 4.1.3. XRD patterns of  $(Zn_{0.98}Mn_{0.02})O$  films on sapphire substrates grown at room temperature, 200 °C, 400 °C and 600 °C with a background oxygen pressure of 10 mT named as ZMO(RT), ZMO(200), ZMO(400) and ZMO(600) respectively. The sapphire substrate peaks have been denoted by \*.

The films are highly textured with no observed peaks (within the resolution limits of XRD) from secondary phase formation of oxides of Mn or ZnMnO alloys which could lead to anti-ferromagnetic cluster formation. The log-scale for intensity has been used to

magnify the low intensity. Table 4.2 shows the observed peak shifts to lower angles in the doped samples which can possibly indicate Mn incorporation into Zn lattice sites. However since the ionic radii for  $Mn^{2+}$  (0.91 Å) and  $Zn^{2+}$  (0.83 Å) are fairly close to each other, the peak shift due to Mn substitution in ZnO lattice is extremely small for low % of doping. It can be calculated that for 2 atomic % Mn doping into ZnO there is ~ 0.01Å increase in lattice parameter if  $Mn^{2+}$  substitutes the Zn sites. The increase in the peak intensities in Figure 4.1.3 for ZMO films of similar thicknesses suggest that the crystallinity improved with higher T<sub>s</sub>.

Table 4.2. FWHM of rocking curve about (002) plane of ZnO, FWHM of (002) peak of ZnO from  $\theta$ -2 $\theta$  scan and average crystallite size from Scherrer formula for ZMO films at various growth temperatures.

Sample	Growth temperatures $T_s$ (°C)	2θ (°)	FWHM (°) of Rocking curve	FWHM (°) of θ-2θ curve	Crystallite size D (nm)
ZMO(RT)	RT	34.35	n.a	0.280	41
ZMO(200)	200 °C	34.55	2.307	0.217	54
ZMO(400)	400 °C	34.50	1.399	0.214	54
ZMO(600)	600 °C	34.50	0.417	0.211	56
UndopedZnO	600 °C	34.55	0.404	0.232	50

To confirm the improved crystallinity, rocking curves were performed about the ZnO (002) peak for the samples. Due to the poor crystallinity of ZMO(RT), no rocking curve spectrum was obtained. Figure 4.1.4 shows the narrowing of the rocking curves for samples deposited at higher  $T_s$ . From Table 4.2 a slight increase (by ~0.01°) in FWHM from rocking curves for ZMO(600) film is observed as compared to the undoped ZnO film grown under same conditions. This is presumably due to the strain induced from the occupation of Mn ions at Zn ion sites.

The average crystallite size in the films assuming spherical grains (D=4/3L) were calculated using the Scherrer formula,  $L = 0.94\lambda/B\cos\theta$  where L is the coherence length, B is the FWHM of (002) peak of ZnO in this case,  $\lambda = 1.54439$  Å wavelength of CuK $\alpha$  X-rays used and  $\theta$  is the angle of diffraction. The average grain size increased with higher T<sub>s</sub> and better crystallinity (Table 4.2).



Figure 4.1.4. Rocking curves about the (002) plane of ZnO for ZnO:Mn films grown at 200 °C, 400 °C and 600 °C with a pO<sub>2</sub> of 10 mT named as ZMO(200), ZMO(400), and ZMO(600), respectively.

The surface microstructures of the ZMO films were studied using SEM. Figure 4.1.5 shows SEM images of (a) undoped ZnO film grown at 600  $^{\circ}$ C, (b) ZMO(600), (c) ZMO(400), and (d) ZMO(200), respectively. The improved crystallinity and grain agglomeration are observed with higher growth temperatures.



Figure 4.1.5 SEM images of (a) undoped ZnO film grown at 600°C, (b) ZMO(600), (c) ZMO(400) and (d) ZMO(200), Mn doped ZnO films on c-cut sapphire substrates.

AFM was used to analyze the surface morphologies of the films. Figures 4.1.6 (a, and b) show AFM images of the ZMO(600) and ZMO(RT) surfaces, respectively. Clear evidence of grain agglomeration at higher temperatures is observed. The average grain size calculated for ZMO(600) is  $\approx$  228 nm whereas that for ZMO (RT) is  $\approx$  54 was nm. Figures 4.1.6 (c, and d) show 3D projections of (a) and (b) respectively. ZMO(600) exhibits a rougher surface with the root mean square roughness (R<sub>rms</sub>) value of 14.69 nm while that for ZMO(RT) is 4.01 nm. The surface features on ZMO(RT) (z-height 10 nm) are much smaller than those for ZMO(600) (z-height 100 nm). The AFM analysis again confirmed the improved crystallinity and surface morphology with higher T<sub>s</sub>. Similar structural features have been reported earlier for ZMO films [167–171].



Figure 4.1.6. AFM images of Mn doped ZnO thin films grown at (a) 600 °C and (b) room temperature under  $pO_2$  of 10mT. Scan areas are 1  $\mu$ m x 1  $\mu$ m. (c) and (d) are 3D projections for (a) and (b), respectively.

The crystallinity of ZMO films deposited at varying background oxygen pressures was analyzed. Figure 4.1.7 shows the XRD patterns for the ZMO films deposited at 600  $^{\circ}$ C but varying the pO<sub>2</sub> from 0 mT to 300 mT. The XRD patterns indicate that the films are single phase and c-axis preferred oriented with no impurity Mn-oxide phases. However since the film thicknesses were larger (> 1 µm) than the critical thicknesses

required for maintaining the epitaxial relationship, at higher deposition pressures (100 mT, 300 mT), the films show polycrystalline nature.



Figure 4.1.7. XRD patterns for Mn doped ZnO thin films on c-cut sapphire substrates deposited at 600 °C with varying oxygen background pressure.

Surface microstructure of epitaxial ZnO films grown under different  $pO_2$  were compared with polycrystalline ZnO films deposited on Si (100) substrates under the same conditions. Figure 4.1.8 shows SEM images of undoped ZnO films deposited on sapphire (a, b) and Si (100) (c, d) substrates. The left panel images (a, c) represent films grown at low  $pO_2$  of 10 mT while the right panel images (b, d) represent those at 300 mT. It is clear that the grain size increases with higher  $pO_2$  on both substrates and the hexagonal faceting is lost due to large grain agglomeration. However the epitaxial ZnO films (a, b) have more compact and flattened surface as compared to the polycrystalline films (c, d) which appear to be porous. The growth morphologies of ZnO films on different substrates have been studied in details elsewhere [179].



Figure 4.1.8. SEM images of undoped ZnO films grown on (a, b) c-cut sapphire substrates and (c, d) Si (100) substrates. Inset to (c) shows the details on one of the hexagonal facets of ZnO on the film.

### 4.1.2.2. Electrical Properties

The electrical properties of ZMO films were investigated using standard Van der Pauw configuration [82, 83]. Table 4.3 lists the resistivity ( $\rho$ ), carrier concentration ( $n_c$ ), and Hall mobility ( $\mu_H$ ) measured at room temperature for ZMO films deposited at various  $T_s$ , and constant  $pO_2$  of 10 mT.

Sample	Growth temperatures	$\rho(\Omega cm)$	$n_{\rm C}  ({\rm cm}^{-3})$	$\mu_{\rm H}(cm^2/Vs)$
ZMO(RT)	RT	1.36 x 10 <sup>4</sup>	7.78 x 10 <sup>12</sup>	58.81
ZMO(200)	200 °C	9.69	$2.89 \ge 10^{17}$	2.23
ZMO(400)	400 °C	8.33	$3.88 \ge 10^{17}$	1.93
ZMO(600)	600 °C	0.46	2.51 x 10 <sup>18</sup>	5.45
Undoped ZnO	600 °C	0.02	$1.04 \ge 10^{18}$	330.19

Table 4.3. Resistivity ( $\rho$ ), carrier concentration ( $n_c$ ) and Hall mobility ( $\mu_H$ ) measured at room temperature of ZnO:Mn thin films on c-cut sapphire substrates grown at various growth temperatures at constant background oxygen pressure.

All the measured films show n-type conduction. The films become more conducting with increasing growth temperatures. Conductivity in ZnO films is associated with donor-type defect sites such as intrinsic oxygen vacancies or Zn interstitials that are created during the deposition process [180]. These donor-type defects give the n-type carriers in the films. With higher T<sub>s</sub> and low pO<sub>2</sub> (10 mT), less O<sub>2</sub> is incorporated into the films giving rise to more O<sub>2</sub> vacancies and more free carriers and higher conductivity [180]. Generally in doped samples there is an overall increase of p because the charged dopants  $(Mn^{2+})$  act as scattering sites for electrons [181]. This explains the orders of magnitude increase in p for ZMO(RT), ZMO(200), ZMO(400) and ZMO(600) as compared to undoped ZnO thin film ( $\rho \sim 10^{-2} \ \Omega cm$ ). ZMO(RT) is highly insulating with very low density of free carriers (Table 4.3). This is probably associated with the poor crystalline nature of the film which makes the system strongly disordered. Table 4.4 shows the resistivity ( $\rho$ ), carrier concentration ( $n_c$ ) and Hall mobility ( $\mu_H$ ) measured at room temperature for ZMO and undoped ZnO films deposited at  $600^{\circ}$ C, and varying pO<sub>2</sub> from 0 mT to 50 mT. The films show n-type conduction decreases conductivity with higher background O<sub>2</sub> pressure. Increasing the background O<sub>2</sub> pressure during the

deposition facilitates the incorporating of  $O_2$  into the films and hence decreasing the number of  $O_2$  vacancies. Thus the free carrier density decreases making the films more insulating.

Table 4.4. Resistivity ( $\rho$ ), carrier concentration ( $n_c$ ) and Hall mobility ( $\mu_H$ ) measured at room temperature of ZnO:Mn thin films on c-cut sapphire substrates grown at 600°C with varying background O<sub>2</sub> pressure.

Sample	O <sub>2</sub> pressure (mT)	$\rho(\Omega cm)$	$n_{\rm C}$ (cm <sup>-3</sup> )	$\mu_{\rm H}(cm^2/Vs)$
ZMO(0mT)	0	0.32	$1.92 \times 10^{18}$	10.06
ZMO(10mT)	10	0.46	$2.51 \times 10^{18}$	5.49
ZMO(50mT)	50	84.8	$6.40 \ge 10^{16}$	1.15
Undoped ZnO	0	0.01	$9.56 \times 10^{17}$	653.76
Undoped ZnO	10	0.02	$1.04 \ge 10^{18}$	330.19
Undoped ZnO	50	17.50	$1.04 \ge 10^{16}$	34.27

Figure 4.1.9 shows the variation of  $\rho$  and  $n_c$  as a function of temperature for

ZMO(600). An increase in  $n_c$  with higher temperatures is observed.



Figure 4.1.9. Resistivity ( $\rho$ ) and carrier concentration ( $n_c$ ) versus temperature measured for ZMO(600).
## 4.1.2.3. Magnetic Properties

The magnetic properties of bulk ZMO powder were measured. Figure 4.1.10 shows the magnetization versus magnetic filed (M-H) hysteresis loop measured at 10 K for bulk ZMO powder. The straight line curve indicates a diamagnetic nature. This confirms that the observed FM in ZMO systems is manifested only in thin film form [182]. During the magnetic measurements, the samples were handled very carefully to avoid any trace magnetic contamination. They were always handled with gloves using non-magnetic tweezers and kept in closed dry containers. The substrates were cleaned by standard acetone-methanol ultrasonication. The samples were loaded in non-magnetic capsules using non-magnetic tape in the PPMS probe. The substrates were checked for magnetic contamination before deposition. The background diamagnetic contribution due to the sapphire substrates has been corrected consistently in all the presented curves.



Figure 4.1.10. Magnetization measurement at 10 K for ZMO powder that was prepared by grinding a piece cut from the corresponding target.

To investigate the role of Mn doping in enhancing the FM of ZMO films, M vs H loops were first measured for the film ZMO(600) and the undoped ZnO film grown under

the same conditions ( $T_s = 600$  °C,  $pO_2 = 10$  mT). The saturation magnetization ( $M_s$ ) for ZMO(600) is four times higher than undoped ZnO film, both showing RT FM as shown in Figure 4.1.11. FM in undoped ZnO films has been associated with defects that are mostly located at the film surface and interface between the substrate and the film [182]. However Mn doping into ZnO plays a very important role in improving the magnetic properties of these ZMO systems.



Figure 4.1.11. M-H loops measured at (a) 10 K and (b) 300 K for undoped ZnO and ZMO films on c-cut sapphire substrates both grown under same conditions.

The magnetic anisotropy in ZMO films was studied by measuring M versus H loops at 10 K and 300 K by applying the magnetic field both parallel (in-plane) and perpendicular (out-of-plane) to the film plane. However such measurements for ZMO(600) showed no noticeable variation in the  $M_s$  and  $H_c$  at 10K as shown in Figure 4.1.12(a). Absence of anisotropic ferromagnetism suggests a weak contribution from magnetic point defects which was very large for Co doped ZnO thin films as reported by Venkatesan et al. [174, 183]. FM in ZMO systems at low temperatures (10 K) is intrinsic and not governed by defects. However, the different  $M_s$  values at 300 K (Figure 4.1.12.

b) for the in-plane and out-of plane configurations indicates that defects play a role in governing the magnetic behavior at higher temperatures.



Figure 4.1.12. M-H loops measured at (a) 10 K and (b) 300 K for ZMO(600) when the magnetic field was applied parallel (in-plane) and perpendicular (out-of-plane) to the film surface.

Figure 4.1.13 show M-H loops measured in-plane at (a) 10 K and (b) 300 K for ZMO(RT) and ZMO(600), respectively. Table 4.5 lists the M<sub>s</sub> and H<sub>c</sub> values for all the samples. An increase in the 300 K, M<sub>s</sub> from 1.09  $\pm$  0.02 to 1.67  $\pm$  0.02 emu/cm<sup>3</sup> and H<sub>c</sub> from ~120 Oe to ~250 Oe is observed as the  $T_s$  is increased from RT to 600 °C.

Samples on		10 K		300 K	
c-cut Al <sub>2</sub> O <sub>3</sub>	Growth temperatures	M <sub>s</sub>	H <sub>c</sub>	$M_s$	H <sub>c</sub>
substrates	$T_s(^{\circ}C)$	(emu/cm <sup>3</sup> )	(Oe)	(emu/cm <sup>3</sup> )	(Oe)
ZMO(RT)	ВТ	$217 \pm 0.03$	110	$1.09 \pm 0.02$	120
ZMO(200)	200	$2.51 \pm 0.05$ $2.51 \pm 0.05$	120	$1.09 \pm 0.02$ $1.12 \pm 0.01$	120
ZMO(400)	400	$2.93\pm0.02$	120	$2.02\pm0.01$	130
ZMO(600)	600	$3.08\pm0.12$	180	$1.67\pm0.02$	250
Undoped ZnO	600	$0.94 \pm 0.02$	120	$1.36 \pm 0.02$	305

Table 4.5. Magnetic properties at 10 K and 300 K for ZMO(RT), ZMO(200), ZMO(400) and ZMO(600) films, respectively.

The increase in  $H_c$  from ZMO(RT) to ZMO(600) most likely is related to the increase in grain size with higher  $T_s$  shown earlier [167-171]. The  $H_c$  and  $M_s$  for films ZMO(200) and ZMO(400) also follow the same trend.



Figure 4.1.13. M-H loops measured at (a) 10 K and (b) 300 K for ZMO films deposited on c-cut sapphire substrates at RT and 600 °C with a constant  $pO_2$  of 10 mT named as ZMO(RT) and ZMO(600) respectively.

Figure 4.1.14 shows M-H loops measured in-plane at (a) 10 K and (b) 300 K for samples ZMO(0mT) ZMO(10mT) ZMO(50mT) and ZMO(300mT), respectively. The magnetization is reduced with increasing  $pO_2$ . The magnetic properties have been summarized in Table 4.6.

Table 4.6. Magnetic properties at 10 K and 300 K for ZMO(0mT), ZMO(10mT), ZMO(50mT) and ZMO(300mT) films, respectively.

-				
Samples on	Background	10 K		300 K
c-cut Al <sub>2</sub> O <sub>3</sub>	O <sub>2</sub> pressure	M <sub>s</sub>	H <sub>c</sub>	M <sub>s</sub> H <sub>c</sub>
substrates	(mT)	(emu/cm <sup>3</sup> )	(Oe)	(emu/cm <sup>3</sup> ) (Oe)
ZMO(0mT)	0	$2.75 \pm 0.04$	800	$1.47 \pm 0.03 \ 203$
ZMO(10mT)	10	$3.08\pm0.12$	180	$1.67 \pm 0.02$ 250
ZMO(50mT)	50	$2.45\pm0.03$	1010	$0.47 \pm 0.02$ 265
ZMO(300mT)	300	$1.16\pm0.02$	105	$0.33 \pm 0.03$ 120



Figure 4.1.14. M-H loops measured at (a) 10 K and (b) 300 K for ZMO films deposited on c-cut sapphire substrates at 600 °C by varying the  $pO_2$  from 0 mT to 300 mT.

## 4.1.3. Theoretical Modeling

This section describes the "dual mechanism of FM" in ZMO thin films. The dual model is a combination of percolation of bound magnetic polarons (BMPs) at lower temperature and Ruderman–Kittel–Kasuya–Yosida (RKKY) FM at higher temperature. The analysis is based on the experimental data on ZMO films grown at different temperatures named as ZMO(RT), ZMO(200), ZMO(400) and ZMO(600). The most probable mechanism for the observed magnetism at low temperatures (10 K) in the highly insulating sample ZMO(RT) is due to the percolation of BMPs. In contrast, films deposited at 200 °C, 400 °C and 600 °C, which are more conducting, it is the indirect RKKY mechanism which dominates the magnetic behavior [176].

Since both mechanisms depend on thermally generated carriers, the activation energies ( $\Delta E$ ) for ZMO(RT) and ZMO(600) were estimated by fitting the resistivity ( $\rho$ ) curves to the expression,  $\rho = \rho_0 \exp(\Delta E/k_BT)$ . Figure 4.1.15 shows the ln( $\rho$ ) versus 1000/T curves for ZMO(RT) and ZMO(600). The  $\Delta E$  was calculated from the slopes of the linear fits of ln( $\rho$ ) versus 1000/T data points. The value of  $\Delta E$  for ZMO(RT) and ZMO(600) are ~6.4 meV and ~42.4 meV respectively. The smaller value of  $\Delta E$  in ZMO(RT) indicates that it has a shallower donor level than in ZMO(600). Since Mn doping into ZnO does not create additional donors, the available donors are associated with defect sites. The larger density of defects associated with the poor crystalline quality of ZMO(RT) contributed to intermediate impurity bands which effectively reduced the  $\Delta E$ .



Figure 4.1.15. Resistivity ( $\rho$ ) versus temperature dependence of (a) ZMO(RT) and (b) ZMO(600).

# 4.1.3.1. RKKY exchange interaction

The RKKY potential energy is given by  $U_{RKKY}(\mathbf{r}) = -J_{RKKY}(\mathbf{r}) \mathbf{S}_{1.}\mathbf{S}_{2}$  where  $J_{RKKY}$  is the exchange integral and  $\mathbf{S}_{1}$  and  $\mathbf{S}_{2}$  are the interacting magnetic spins [45]. The RKKY exchange integral  $J_{RKKY}$  has the form,  $J_{RKKY}(\mathbf{r}) = (V_{o} \cos 2k_{f} \mathbf{r})/r^{3}$  where  $V_{o}$  is the strength of RKKY interaction,  $k_{f}$  is the Fermi wave vector and r is the separation between the magnetic spins For FM, when  $U_{RKKY} < 0$  i.e. energy minimum,  $J_{RKKY} > 0$ , since  $\mathbf{S}_{1.}\mathbf{S}_{2} = 1$  [45]. The range of the average separation (r) between randomly oriented magnetic dopant spins that interact via FM RKKY mechanism can be estimated by plotting the exchange

integral J<sub>RKKY</sub> as a function of r for V<sub>o</sub> = 1 and assuming the intrinsic Fermi energy E<sub>f</sub> = 1.65 eV to be half the band gap for ZnO (E<sub>g</sub> = 3.3 eV). This assumption is valid because the carrier concentration (n<sub>c</sub>) does not much alter in ZMO(600) (n<sub>c</sub> = 2.51 x 10<sup>18</sup>) due to Mn doping as compared to undoped ZnO (n<sub>c</sub> = 1.04 x 10<sup>18</sup>) (Table 4.3). The Fermi wave vector (k<sub>f</sub>) was calculated from the relation  $E_f = (h^2/8 \pi^2 m) k_f^2$  which came out to be 6.57 x 10<sup>9</sup> (nm<sup>-1</sup>). Figure 4.1.16 shows the variation of J<sub>RKKY</sub>(r) as a function of r.



Figure 4.1.16. Plot of RKKY exchange integral  $J_{RKKY}(r)$  as a function of the average separation between magnetic spins (r). The inset shows the range of r when  $J_{RKKY} > 0$ .

From the plot it is observed that  $J_{RKKY} > 0$  in the ranges r < 0.11 nm and 0.36 nm < r < 0.59 nm and 0.84 nm < r < 1.07 nm. For 2 atomic % doping of Mn in ZnO the average separation between Mn<sup>2+</sup> spins was found to be  $r \sim 1.05$  nm, which is based on the relation  $r = (1/n_i)^{1/3}$  where  $n_i = 8.438 \times 10^{20}$  cm<sup>-3</sup> (i.e. density of Mn<sup>2+</sup> spins). Thus r

falls within the range of FM RKKY interaction. This implies that at such dilute doping levels RKKY interaction would give FM.

F. W. Smith [184] in his work on the magnetization of dilute magnetic alloys showed that the measured magnetization in ZnMn or CuMn alloys is dominated by impurity-impurity interaction via RKKY potential. In a high magnetic field (H) such that  $g\mu_BH \gg k_BT$  and  $n_iV_o$  the approach to saturation of the magnetization (M) follows the relation:

$$M = g\mu_B Sn_i [1 - 2(2S + 1)n_i V_o/3g\mu_B H]$$
(4.1)

where  $n_i$  is the concentration of the active magnetic impurities (Mn<sup>2+</sup>) interacting via RKKY,  $V_o$  is the strength of RKKY interaction and S = 5/2 is the spin of magnetic impurity [168]. However, in this case  $g\mu_BH \sim k_BT$  but is >>  $n_iV_o$ . Figure 4.1.17 shows the approach to saturation of M as H is increased from 0 to 50 kOe. The inset and also shown as the black solid line in Figure 4.1.17 show the free-spin magnetization described by paramagnetic moments given by the expression [45]:

$$M = n_i g \mu_B SB_S(x) \text{ with } x = g \mu_B SH/k_B T$$
(4.2)

where the magnetic impurity density  $n_i = 8.438 \times 10^{20} \text{ cm}^{-3}$  for 2 atomic % Mn doping,  $B_S(x)$  is the Brillouin function with spin S = 5/2, the Lander factor g = 2 as expected for  $Mn^{2+}$ ,  $\mu_B$  is the Bohr magneton, and  $k_B$  is the Bohtzmann constant. The experimental curves show ferromagnetic behavior by reaching saturation more rapidly as a function of applied field as compared to free-spins. This indicates that the  $Mn^{2+}$  spins are not free and interact via a carrier mediated mechanism.



Figure 4.1.17. Initial magnetization curves at 10 K for  $(Zn_{0.98}Mn_{0.02})O$  films deposited at various growth temperatures with constant background O<sub>2</sub> pressure. The inset shows the free-spin Brillouin function B<sub>s</sub> (10K) for S=5/2 at 10 K.

Figure 4.1.18 shows the linear fits of M versus 1/H data for 20 kOe < H < 50 kOe. From the slopes and intercepts of the linear fits of M versus 1/H data points at saturation measured at 10 K, for ZMO(RT), ZMO(200), ZMO(400) and ZMO(600),  $n_i$  and  $V_o$  were calculated using Equation 4.1. The calculated values have been summarized in Table 4.7. From Figure 4.1.18 and the values in Table 4.7 it is observed that the intercepts and slopes increase slightly from ZMO(200) to ZMO(600). This shows that the number of magnetic impurities interacting via RKKY mechanism increases with higher  $T_s$  and better crystallinity.



Figure 4.1.18. M versus 1/H (kOe<sup>-1</sup>) plots at 10 K for (Zn<sub>0.98</sub>Mn<sub>0.02</sub>)O films deposited at various growth temperatures with constant pO<sub>2</sub>. (b) The solid lines are the linear fits for the data points for films named ZMO(RT), ZMO(200), ZMO(400) and ZMO(600).

Table 4.7. Summary of RKKY parameters for ZMO films, deposited at various temperatures.

Sample	Intercept	Slope	n <sub>i</sub>	Vo	n <sub>i</sub> Vo (meV)
			$(10^{19} \mathrm{cm}^{-3})$	$(10^{-37}  \text{ergcm}^3)$	
ZMO(RT)	2.3741	10314	5.12	6.75	0.0216
ZMO(200)	2.8173	14166	6.08	6.58	0.0250
ZMO(400)	3.1209	14782	6.73	5.59	0.0235
ZMO(600)	3.3896	15399	7.31	4.94	0.0226

However the slope of the linear fit for ZMO(RT) is different than the others showing a smaller value for  $n_i$ . The calculated value of  $n_i$  for ZMO(600) is  $n_i \sim 7.31 \times 10^{19}$  cm<sup>-3</sup>. It is much lower than the magnetic impurity density for 2 atomic % doping of Mn in

ZnO which is 8.438 x  $10^{20}$  cm<sup>-3</sup>. In other words only ~8 % of the total number of Mn<sup>2+</sup> ions in the system are involved in RKKY mediated FM.

From Figure 4.1.13 (a) for ZMO(600) the  $M_s$  is ~3.1 emu/cm<sup>3</sup> which corresponds to an average magnetic moment of 0.4  $\mu_B/Mn^{2+}$  assuming a uniform Mn ion distribution. This is again 8 % of the theoretical value which is 5  $\mu_B/Mn^{2+}$  when all the Mn spins are aligned [168]. Thus only about 8 % of the incorporated Mn atoms at substitutional Zn sites contribute to FM via RKKY mechanism. The remaining Mn atoms possibly occupy interstitial defect sites or get accumulated at the grain boundaries. However, the contribution of interstitial Mn ion to FM via a defect mediated mechanisms such as BMP has been shown to be very small [174], and therefore does not account for the observed magnetism in our highly crystalline ZMO (600) films. Further, the carrier density  $(n_c)$  at 10 K for ZMO(600) estimated using  $n_c(T) = n_{co}exp(\Delta E/k_BT)$  for the measured values of  $n_c$  (300K) and  $\Delta E$  is  $n_c \sim 2.01~x~10^{16}~cm^{-3}.$  Since  $n_c << n_i$  or in other words the mean distance between the carriers is greater than that between the spins, RKKY interaction would give FM as also predicted by Priour et al. [185]. The average value of  $V_0 \approx (5.96)$ +/- 0.85) x  $10^{-37}$  ergcm<sup>3</sup> is consistent with those observed by Smith. Moreover, the average value of  $n_i V_o \approx 0.02$  meV (<  $k_B T$ ), the spin-spin interaction energy for RKKY, is smaller than the thermal energy at 10 K (0.863 meV) ensuring the availability of enough carriers to mediate RKKY FM even at such low temperatures.

The above analysis has been also extended to ZMO films grown at 600 °C but varying the pO<sub>2</sub>. Figure 4.1.19 shows the magnetization curves for samples ZMO(0mT), ZMO(10mT), ZMO(50mT), and ZMO(300mT).



Figure 4.1.19. Initial magnetization curves at 10 K for  $(Zn_{0.98}Mn_{0.02})O$  films deposited at 600 °C but varying the background O<sub>2</sub> pressure.

Figure 4.1.20 shows the linear fits of M versus 1/H data for 20 kOe < H < 50 kOe. From the slopes and intercepts of the linear fits of M versus 1/H data points at saturation measured at 10 K, for ZMO(0mT), ZMO(10mT), ZMO(50mT) and ZMO(300mT),  $n_i$  and  $V_o$  were calculated using Equation 4.1. The calculated values have been summarized in Table 4.8.



Figure 4.1.20. M versus 1/H (kOe<sup>-1</sup>) plots at 10 K for (Zn<sub>0.98</sub>Mn<sub>0.02</sub>)O films deposited at 600 °C but varying the background O<sub>2</sub> pressure. The solid lines are the linear fits for the data points for films named ZMO(0mT), ZMO(10mT), ZMO(50mT) and ZMO(300mT).

Table 4.8. Summary of RKKY parameters for ZMO films under varying background pressures.

Sample	Intercept	Slope	n <sub>i</sub>	Vo	n <sub>i</sub> Vo (meV)
			$(10^{19} \mathrm{cm}^{-3})$	$(10^{-37}  \text{ergcm}^3)$	
ZMO(0mT)	2.9276	10648	6.31	4.58	0.0181
ZMO(10mT)	2.3933	11115	5.16	7.15	0.0231
ZMO(50mT)	1.6335	6865.6	3.52	9.48	0.0209
ZMO(300mT)	1.3181	7678.9	2.84	10.6	0.0289

# 4.1.3.2. Percolation of Bound Magnetic Polarons (BMPs)

BMPs are formed in ZMO thin films by the alignment of the spins of  $Mn^{2+}$  with that of localized electrons. The electrons are localized to some point defects (i.e. the

magnetic impurity  $Mn^{2+}$ , and the oxygen vacancies created during deposition) by electrostatic interaction within an electron confinement radius ( $a_B$ ). Within this radius of influence the electron interacts anti-ferromagnetically with the  $Mn^{2+}$  forming a BMP. The size of the BMP increases as the temperature decreases eventually overlapping with neighboring BMPs. This overlap aligns the  $Mn^{2+}$  spins forming ferromagnetic clusters. The FM emerges when an "infinite cluster" (of the size of the system) is formed, i.e. when percolation of BMPs occur [176].

In order to explain the FM in ZMO(RT) by the BMP model, the electron confinement radius ( $a_B$ ) was calculated using  $a_B = \epsilon (m_o/m_e^*)a$  where  $\epsilon$  is the static dielectric constant,  $m_e^* = 0.28m_o$  is the electron effective mass and a = 0.52 Å is the Bohr radius [176]. First, the value of  $\epsilon$  was computed from the capacitance measurements of the films using a Hewlett Packard 4192A High Frequency Impedance Analyzer at 1 MHz and 1 V rms oscillation voltage. The value of  $\epsilon$  for ZMO(600) was 1.95  $\pm$  0.36 but for ZMO(RT) the value was higher than the impedance limit of the instrument. Secondly,  $\epsilon$ for ZMO(RT) and ZMO(600) were computed using the Brus equation (Equation 4.3) [186, 187] where the change in band gap was equated to the activation energy ( $\Delta E$ ) measured earlier and the crystal radius was calculated from Scherrer formula as in Table 4.2. The Brus equation is given by:

$$\Delta E = \frac{h^2}{8R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4\pi\varepsilon_o \varepsilon R}$$
(4.3)

where  $\Delta E$  is the carrier activation energy which is same as the change (decrease) in the band gap of the material due to doping, R is the crystal radius,  $m_e^* = 0.28 m_o$  and  $m_h^* = 0.59 m_o$  are the effective masses of the electron in the conduction band and the hole in the valence band (considered independent of Mn content) respectively,  $\varepsilon_o$  is the permittivity

of free space, e and h are the electronic charge and Planck's constant, respectively,  $m_o$  is the free electron mass and  $\varepsilon$  is the static dielectric constant of the material. The calculated  $\varepsilon$  values for ZMO(RT) and ZMO(600) are 11.3 and 2.06 respectively. The electron confinement radii for ZMO(RT) and ZMO(600) are ~ 20 Å and ~ 4 Å respectively. The radius value for ZMO(RT) is larger owing to the shallower defect level ( $\Delta E \sim 6.4 \text{ meV}$ ) [176]. The BMP model is valid only in the low carrier density regime where  $n_c a_B^3 \ll 1$ and when  $n_i \gg n_c$ . This is true for both ZMO(RT) and ZMO(600). Following Calderon et al. [176] the temperature dependence of the radius of the polaron ( $R_P$ ) was plotted using the following equation

$$R_{\rm P}(T) \equiv (a_{\rm B}/2) \ln (sS|J| (a_0/a_{\rm B})^3/k_{\rm B}T)$$
(4.4)

where  $s = \frac{1}{2}$  the spin of carriers (electrons),  $S = \frac{5}{2}$  the spin of magnetic dopant (Mn<sup>2+</sup>), using J  $\approx$  1 eV the local exchange coupling between carrier spin and the magnetic Mn moments [176] and  $a_0^3 = 47.77$  Å<sup>3</sup> the unit cell volume for ZnO.

Figure 4.1.21 show the curves for the ZMO(RT) and ZMO(600). For ZMO(RT), polarons only start forming at a temperature of  $T_{initiation} \sim sS|J| (a_0/a_B)^3/k_B \sim 75$  K above which there are no polarons in the system. However in ZMO(600) polarons are always present even at room temperature. The size of the BMPs in ZMO(RT) increases drastically from ~0.7 Å at 70 K to ~20 Å at 10 K whereas for ZMO(600) the increase in size is gradual from ~7 Å at 300 K to ~13 Å at 10 K. The magnetic dopant spins at a distance r < R<sub>P</sub> tend to align with the localized carrier spin. The average separation between randomly oriented magnetic dopant spins is found to be ~ 10 Å, which is based on the relation r =  $(1/n_i)^{1/3}$  where  $n_i = 8.438 \times 10^{20}$  cm<sup>-3</sup> for 2 atomic % doping of Mn in ZnO. With lowering of temperature, polarons start overlapping with neighboring BMPs

forming FM clusters which keep growing in size to form an infinite cluster (of the size of the system) i.e. when the BMP percolation occurs.



Figure 4.1.21. Variation of the radius of polarons  $R_p$  in angstroms at different temperatures for ZMO(RT) and ZMO(600), (Zn<sub>0.98</sub>Mn<sub>0.02</sub>)O films deposited at RT and 600 °C respectively.

The percolation radius ( $r_{perc}$ ) for ZMO(RT) at 10 K is ~ 5 µm calculated from  $r_{perc} \approx 0.86/n_c^{-1/3}$  [18] where  $n_c$  (10K) was estimated using  $n_c(T) = n_{co} \exp(\Delta E/k_BT)$  from  $n_c(RT)$  and  $\Delta E$  values measured earlier. The  $r_{perc}$  in ZMO(RT) is larger than the thickness of the film and implied long range FM at 10 K. The  $r_{perc}$  for ZMO(600) at 10 K is 0.03 µm which is much smaller than the film thickness to mediate large FM via BMP percolation throughout the sample. From Figure 4.1.21 it was observed that for ZMO(600),  $R_p \approx r$ , in the range 10 K – 300 K. This implies that the BMPs are always

overlapping with their spins aligned with the carriers. If there are substantial thermally activated carriers, the BMP scenario extrapolates to RKKY FM.

# 4.1.4. Conclusions

To summarize, Mn doped ZnO films have been grown using PLD. The ferromagnetic properties have been investigated. The observed FM in  $Zn_{0.98}Mn_{0.02}O$  films shows characteristics of both intrinsic and carrier mediated mechanisms. The experimental results show a strong correlation between effective carrier densities due to different growth conditions and the FM in the samples. The data is consistent with the dual ferromagnetic theoretical model proposed for dilute magnetic semiconductors (DMS). Although these results are encouraging for a fundamental understanding of the origins of the observed ferromagnetic phases in DMS, higher values of M<sub>s</sub> at RT would be required for any potential device application.

#### 4.2. V doped ZnO Thin Films

ZnO has the strongest piezoelectric response among the tetrahedrally bonded semiconductors [143] which makes it a suitable material for technological applications that require strong electromechanical coupling such as sensors and actuators [188]. Recently, Yang et al. [161, 162] has reported an electromechanical coefficient  $(d_{33})$  in 2.5 atomic % V-doped ZnO to be as high as 110 pC/N. This value is an order higher compared to the  $d_{33}$  coefficient of bulk ZnO [189] which is 9.9 pC/N. Another significant property due to V doping is reported to be the switchable P<sub>s</sub> indicated by a butterfly like displacement (D) versus electric field (E) graph [161]. Yang et. al. proposed a microscopic explanation for the enhancement of piezoresponse in ZVO systems. The dominant effect of applying electric field on the wurtzite structure of ZnO is the rotation of the bonds that are non-collinear with the polar c-axis, (i.e., Zn<sub>2</sub>-O<sub>1</sub> bonds as shown schematically in Figure 4.2.1) towards the direction of applied field and thus producing strain. The V ions which replace the Zn sites are in  $5^+$  valence state [162]. When  $V^{5+}$ substitutes  $Zn^{2+}$  sites, due to their higher positive charge, they make the V-O<sub>1</sub> (Figure 4.2.1) bonds more polar than  $Zn_2-O_1$  bonds. Hence V-O<sub>1</sub> bonds rotate more easily in applied field enhancing the piezoresponse. In short, doping  $Zn^{2+}$  sites by  $V^{5+}$  creates a mixed valency as well as strain in the original ZnO hexagonal structure because of the reduced ionic size of  $V^{5+}$  and higher positive charge. The mixed valency creates charge polarity between Zn-O and V-O bonds. The charge polarity and rotation of the nonlinear V-O bonds with respect to the Zn-O bonds under electric field gives enhanced ferroelectricity [161].



Figure 4.2.1. Schematic diagram of the unit cell and neighboring atoms in V doped ZnO crystal structure.

Ferroelectricity (FE) is exhibited in insulating films. As described earlier in Section 4.1, ZnO films grow with intrinsic oxygen deficiencies when deposited under low background  $O_2$  pressure (pO<sub>2</sub>). However the films grown under high pO<sub>2</sub> (> 100 mT) are more insulating and ideal for exhibiting P<sub>s</sub>. Thus the effect of pO<sub>2</sub> in the growth and properties of ZVO films were studied.

## **4.2.1. Experimental Details**

The ZVO target was prepared by standard solid state reaction method. Highly pure (99.99%) powders of ZnO and V<sub>2</sub>O<sub>5</sub> were mixed in stoichiometric proportion and well ground before being calcined in air for 6 hrs at 600°C. The calcined mixture was ground again and cold pressed under a pressure of 90 MPa into a 1 inch diameter and 0.25 inch thick target. The pressed target was sintered at 1000 °C in air for 12 h EDS analysis on different regions of the target surface confirmed the uniform distribution of V in the target. The average atomic % of V in the target was  $2.0 \pm 0.6$  %.

A series of ZVO films were grown on c-cut sapphire (Al<sub>2</sub>O<sub>3</sub>) (001) substrates at 600°C by varying the background O<sub>2</sub> pressure from the  $Zn_{0.98}V_{0.02}O$  ceramic target. Table 4.9 shows the deposition parameters used in this study.

Sample	Substrate	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Film Thickness
		$(J/cm^2)$	$T_{s}(^{\circ}C)$	$pO_2(mT)$	(nm)
		× ,			
ZVO(100mT)	$Al_2O_3$	2	600	100	1033±10
ZVO(300mT)	$Al_2O_3$	2	600	300	971±25
ZVO(500mT)	$Al_2O_3$	2	600	500	953±24
ZVO(500mT)	LSMO/Si	2	600	500	1300±20

Table 4.9. Deposition parameters for ZVO thin films.

#### 4.2.2. Results and Discussions

## 4.2.2.1. Laser-target interactions and Plume Diagnostics

The ZVO target surface was irradiated by 1000 KrF laser pulses for a range of laser fluences from 1 J/cm<sup>2</sup> to 5 J/cm<sup>2</sup> under 500 mT pO<sub>2</sub>. After ablation, the surface morphologies and the compositions of the laser-target interaction sites were examined by SEM and EDS. Figures 4.2.2 (a, b, c, and d) show SEM images of the ZVO target surface before ablation (KrF 0 J/cm<sup>2</sup>), after ablation at 2 J/cm<sup>2</sup> (KrF 2 J/cm<sup>2</sup>), after ablation at 3 J/cm<sup>2</sup> (KrF 3 J/cm<sup>2</sup>), and after ablation at 5 J/cm<sup>2</sup> (KrF 5 J/cm<sup>2</sup>), respectively. From Figure 4.2.2 (b) it is observed that the ablated target surface at 2 J/cm<sup>2</sup> has melted exposing some voids and cracks. On the other hand, from Figure 4.2.2 (c) shows that at 5 J/cm<sup>2</sup> the ablated target surface exhibits distinct large circular cavities possibly formed by the release of gas (vapor) from the target surface due to subsurface boiling. Consequently, films deposited at 5 J/cm<sup>2</sup> showed increased particulate density on the surface.



Figure 4.2.2. SEM images of (a) unablated ZVO target surface (b) ablated surface at 2  $J/cm^2$  and (c) ablated surface at 5  $J/cm^2$ .

Figure 4.2.3 shows the variation of atomic % of Zn, V and O in the ablated target for different laser fluences, obtained from EDS analysis. It is evident that the stoichiometry remains almost constant for all the different fluences, that implies that congruent evaporation of the elements occur above the ablation threshold.



Figure 4.2.3. Atomic % obtained from EDS analysis for the ZVO target under various laser fluences. On x-axis 0 J/cm<sup>2</sup> implies the unablated target.

Figure 4.2.4 shows the ICCD images of the total visible light emitted from the plasma plumes for different laser fluences (F) under  $pO_2$  of 0 mT and 500 mT. In order to capture the complete visible emission, the camera was set at 20 µs exposure time and 25 frames were integrated each having a 200 ns step size to get the final image. From Figure 4.2.4 it is clear that the plume expansion profiles along the axial direction increased with higher laser fluence both at 0 mT and 500 mT. However due to the high background gas pressure the transverse expansion profiles at 500 mT are restricted as compared to those at 0 mT. This indicates that the kinetic energies of the ablated species are probably larger along the axial direction at 500 mT compared to those at 0 mT.



Figure 4.2.4. ICCD images of total visible emission spectra of single laser plumes varying the excimer fluences (F) from 1 to 4 J/cm<sup>2</sup> under different gas pressures ( $pO_2$ ).

The plume profiles were also studied for different background oxygen pressure and at constant laser fluence. Figure 4.2.5 show ICCD images of the ablated plumes at 2  $J/cm^2$  under varying pO2 of 100 mT, 300 mT, and 500 mT.



Figure 4.2.5. ICCD images of total visible emission spectra of laser ablated plumes under different gas pressures ( $pO_2$ ) and constant fluence of 2 J/cm<sup>2</sup>.

The images show transverse plume confinement and represent the deposition conditions for the as-grown ZVO films (Table 4.9). The relative intensities for the plumes under 100 mT, 300 mT and 500 mT are 100 %, 62 % and 45 % respectively. The

FWHMs of the plume intensity profiles at 2 cm from the target were 1.10 cm for 100 mT, 0.71 cm for 300 mT and 0.54 cm for 500 mT respectively.

# 4.2.2.2. Structural Properties

Figure 4.2.6 shows the XRD  $\theta$ -2 $\theta$  scans of ZVO films, named as ZVO(100mT), ZVO(300mT), and ZVO(500mT), respectively. The films are highly textured with only (002) orientation. There are no observed peaks from secondary phase formation of oxides of V or other impurities within the resolution limits of XRD.The in plane epitaxial relationship was verified by rocking scans about the (002) plane of ZnO as shown in Figure 4.2.7. The narrow FWHM (< 1°) confirms the high degree of texturing in all the samples. However, the slightly larger FWHMs for ZVO(300mT) and ZVO(500mT) as compared to ZVO(100mT) implies a less preferential orientation.



Figure 4.2.6. XRD  $\theta$ -2 $\theta$  scans (a) ZVO(500mT), (b) ZVO(300mT), and (c) ZVO(100mT) films, respectively. The substrate peak is denoted by \*.



Figure 4.2.7. XRD rocking curves about (002) plane of ZnO for (a) ZVO(500mT), (b) ZVO(300mT), and (c) ZVO(100mT) films, respectively.

Figures 4.2.8 (a, b, and c) show AFM images of ZVO(100 mT), ZVO(300 mT), and ZVO(500 mT) films, respectively. It is observed that the particulate density on the film surface increases with higher pO<sub>2</sub>. From Figure 4.2.8 (c) it is apparent that the large number of micron size droplets visible on the ZVO(500mT) film surface possibly came from the target during ablation. To confirm that the particles are not any foreign object, EDS was performed on top of the droplets. The EDS spectra showed the presence of only Zn and O confirming that they came from the target. The root mean square surface roughnesses (R<sub>rms</sub>) for ZVO(100mT), ZVO(300mT), and ZVO(500mT) were 17.5 nm, 33.5 nm and 55.8 nm, respectively. The R<sub>rms</sub> increased by three times as the pO<sub>2</sub> increased from 100 mT to 500 mT.



Figure 4.2.8. AFM images V-doped ZnO thin films grown at  $600^{\circ}$ C but varying the background O<sub>2</sub> pressure from (a) 100 mT, (b) 300 mT, and (c) 500 mT, named as ZVO(100mT), ZVO(300mT), and ZVO(500mT) respectively.

# 4.2.2.3. Electrical properties

The electrical properties were measured using the Van der Pauw technique. Table 4.10 summarizes the room temperature resistivities ( $\rho$ ) and carrier concentrations ( $n_c$ ) for ZVO films. As observed earlier for ZMO films, in this case also the  $\rho$  increases and the  $n_c$  decreases with higher pO<sub>2</sub>. The  $\rho$  for ZVO(500mT) was higher than the instrumental limits. For this reason, the  $\rho$  and  $n_c$  for a ZVO film grown at 200 mT named ZVO (200mT) has been included in Table 4.10. It emphasized the trend in the electrical properties in ZVO films as a function of pO<sub>2</sub>.

Sample	O <sub>2</sub> Pressure	Sheet resistance	Resistivity	Carrier Conc.	Mobility
	$pO_2(mT)$	$R_{S}(\Omega)$	$\rho(\Omega cm)$	$n_{\rm C}$ (cm <sup>-3</sup> )	$\mu_{\rm H}  (cm^2/Vs)$
ZVO(100mT)	100	$2.76 \times 10^2$	8.82 x 10 <sup>-3</sup>	$2.66 \ge 10^{19}$	26.51
ZVO(200mT)	200	$2.38 \times 10^5$	7.61	$3.08 \ge 10^{17}$	2.67
ZVO(300mT)	300	$1.19 \ge 10^7$	$4.53 \times 10^2$	$3.76 \ge 10^{15}$	3.65
ZVO(500mT)	500	$> 10^{8}$	$> 10^{4}$	-	-

Table 4.10. Resistivity ( $\rho$ ), carrier concentration ( $n_c$ ) and Hall mobility ( $\mu_H$ ) measured at room temperature of ZnO:V thin films on c-cut sapphire substrates grown at 600 °C with varying background O<sub>2</sub> pressure.

#### **4.2.2.4.** Ferroelectric properties

The ferroelectric properties for the ZVO films on insulating  $Al_2O_3$  substrates were tested using a co-planar electrode configuration. A schematic diagram of the capacitor has been shown in the inset to Figure 4.2.9. Gold palladium (Au - Pd) electrodes were sputter coated on top of the film using a shadow mask with 500 µm holes.

Figure 4.2 9 shows the polarization (P) loops for ZVO(100mT), ZVO(300mT), and ZVO(500mT) capacitors, respectively measured at 1 kHz. Table 4.11 summarizes the P values for the ZVO films. The remnant polarization (P<sub>r</sub>) for ZVO(500mT) (0.25  $\mu$ C/cm<sup>2</sup>) is consistent with the reported value (0.2  $\mu$ C/cm<sup>2</sup>) for ZVO films deposited on Si (111) substrates [161, 162].



Figure 4.2.9. P-V loops for ZVO(100mT), ZVO(300mT), and ZVO(500mT) films, respectively. Inset shows a schematic diagram of ZVO capacitor.

Table 4.11. Summary of polarization data for ZnO:V thin films on c-cut sapphire substrates grown at 600  $^{\circ}$ C with varying background O<sub>2</sub> pressure.

Sample	Maximum Polarization $P_{max} (\mu C/cm^2)$	Remnant Polarization $P_r (\mu C/cm^2)$	Coercive Field E <sub>C</sub> (kV/cm)
ZVO(100mT)	0.01	0.0045	2.05
ZVO(300mT)	0.48	0.1	4.4
ZVO(500mT)	0.83	0.24	4.9

The high polarization value for ZVO(500mT) can be associated the reduction in donor type defects like  $O_2$  vacancies created during deposition at high pO<sub>2</sub>. Less number of defects within the film can inhibit the current percolation paths and consequently

reduce the leakage current across the capacitor. This allows the measurement of P by applying higher driving voltages without causing a dielectric break down in the capacitor.

The ferroelectric properties of ZVO films deposited on Si (100) substrates were also investigated using LSMO top and bottom electrodes (inset Figure 4.2.10). The LSMO electrodes were deposited in-situ using PLD at 600 °C and 10 mT pO<sub>2</sub>. Figure 4.2.10 shows the polarization loops of LSMO/ZVO(500mT)/LSMO capacitors measured at 1 kHz. Compared to the co-planer Au-Pd electrodes, the LSMO top-bottom electrodes allow applying higher driving voltages and consequently measuring higher polarization.



Figure 4.2.10. Polarization loops for ZVO (500mT) film. The inset shows a schematic diagram of LSMO/ZVO(500mT)/LSMO capacitor.

Figure 4.2.11 (a) shows the frequency dependence of polarization at a driving voltage of 5 V for the LSMO/ZVO(500mT)/LSMO capacitor. The nominal switching field ( $V_c$ ) increased with lower frequency consistent with typical ferroelectric behavior.

Lower frequency allows more time for the dipoles to align with the applied field and thus increases the polarization. Figure 4.2.11 (b) shows the capacitance vs voltage loops for the ZVO(500mT) capacitor.



Figure 4.2.11. (a)Polarization and (b) capacitance versus driving voltage for V-doped ZnO thin film grown pO<sub>2</sub> of 500mT, named as ZVO(500mT), respectively.

The behavior is characteristic of a leaky capacitor which is possibly due to the defects in the film which produce percolation paths for the current. Table 4.12 summarizes the polarization data obtained for the ZVO(500mT) films using LSMO electrodes.

Driving Voltage	Frequency	P <sub>max</sub>	P <sub>r</sub> (+)	P <sub>r</sub> (-)	V <sub>c</sub> (+)	V <sub>c</sub> (-)
(V)	(Hz)	$(\mu C/cm^2)$	$(\mu C/cm^2)$	$(\mu C/cm^2)$	(V)	(V)
2	1000	0.488	0.109	-0.118	0.384	-0.396
4	1000	0.911	0.254	-0.227	0.701	-1.017
5	1000	1.129	0.349	-0.292	0.773	-1.42
5	100	1.849	0.848	-0.765	1.366	-1.885
5	10	3.694	3.313	-3.447	2.602	-3.107
6	1000	1.357	0.456	-0.364	0.736	-1.856
9	1000	2.055	0.838	-0.572	0.447	-3.382
9	100	3.476	1.95	-1.72	2.174	-4.035

Table 4.12. Summary of polarization values for ZVO(500mT) film using LSMO electrodes.

# 4.2.3. Conclusions

To summarize, V doped ZnO films have been grown using PLD. The ferroelectric properties have been measured. Ferroelectric switching is observed at around 4 V driving voltage. Higher saturation polarization is achieved for films grown at higher oxygen pressure. This is related to the more insulating nature of the films at high pressures. However larger polarization needs to be achieved for potential device application.

## 4.3. ZnO:Mn-ZnO:V Heterostructure

A schematic diagram of the ZnO:Mn/ZnO:V heterostructure has been shown in Figure 4.3.1. It consists of three layers. First, a 300 nm thick conductive ZnO layer was deposited on c-cut sapphire substrate to serve both as a bottom electrode during polarization measurement and a buffer layer for the epitaxial growth. Second, a 1.2  $\mu$ m ZnO:Mn layer was deposited at the conditions that gave the highest magnetization in ZMO films. Third, a 1.1  $\mu$ m ZnO:V layer was deposited at the conditions that gave the highest polarization in ZVO films. Finally, 0.5 mm diameter Au electrodes were sputter coated to serve as top electrodes during polarization measurements.



Figure 4.3.1. Schematic diagram of ZnO:Mn-ZnO:V heterostructure.

#### **4.3.1. Experimental Details**

The individual layers were grown under the conditions which gave the highest ferromagnetic and ferroelectric response during the growth of the single layers as discussed in section 4.1 and 4.2. The deposition conditions for the in-situ grown individual layers have been summarized in Table 4.13.

Layers in	Laser Fluence	Growth Temperatures	O <sub>2</sub> Pressure	Film Thickness
heterostructure	$(J/cm^2)$	$T_{s}(^{\circ}C)$	$pO_2(mT)$	(nm)
ZnO	2	600	10	300
ZnO:Mn	2	600	10	1200
ZnO:V	2	600	500	1100

Table 4.13. Deposition conditions of the layers in the ZnO:Mn-ZnO:V heterostructure on c-cut sapphire substrate.

#### 4.3.2. Results and discussions

#### **4.3.2.1.** Structural properties

Figure 4.3.2 shows the XRD  $\theta$ -2 $\theta$  scan of ZnO:Mn-ZnO:V heterostructure. The high counts from the peak intensities confirm the good crystalline quality. The heterostructure is highly textured since the major peaks are only from the [002] planes of ZnO. Some low intensity peaks from other orientations of ZnO are also observed. This is associated to the large thickness (approximately 2.6 µm) of the whole structure where the epitaxial relationship among the individual layers is difficult to maintain throughout the structure. On the other hand, no impurity peaks from secondary phase segregation are observed even in the logarithmic scale. This implies that the structure is single phase. The degree of in-plane orientation in the heterostructure was measured by rocking curves performed about the (002) plane of ZnO. Figure 4.3.2 shows the rocking curves about the ZnO:Mn-ZnO:V heterostructure and the ZnO:Mn single layer film. The small FWHM (1.158°) for the heterostructure confirms the high degree of in-plane texturing.



Figure 4.3.2. XRD  $\theta$ -2 $\theta$  scan of ZnO:Mn-ZnO:V heterostructure. The c-cut sapphire substrate peak is denoted by \*.



Figure 4.3.4. Rocking curves about the (002) plane of ZnO for the ZnO:Mn-ZnO:V heterostructure and the ZnO:Mn single layer film.

The slight relaxation of the preferential orientation in the heterostructure as compared to single ZnO:Mn film (FWHM =  $0.962^{\circ}$ ) is again due to the large thickness and different growth conditions of the individual layers.

# 4.3.2.2. Magnetic Properties

The magnetic properties were for both the heterostructure and the individual layers. Figure 4.3.5 shows the in-plane M-H loops measured at 10 K and 300 K for the ZnO:Mn-ZnO:V heterostructure, ZnO:Mn single layer, and ZnO:V single layer, respectively. Room temperature (RT) FM is observed in the heterostructure which is important for device application purpose. The magnetization in ZnO:V layer is similar to the undoped ZnO film which implies that V doping does not contribute to the observed FM in ZnO films. The ZnO:Mn single layer film exhibits the highest magnetization which is related higher carrier concentration in the film. The magnetization in the heterostructure is lower than that in ZnO:Mn single layer. One of the possible explanations is that carrier concentration in the heterostructure is lower. During the growth of the heterostructure, the ZnO:V layer is deposited at high  $pO_2$  (500 mT) which possibly allows more  $O_2$  incorporation into the ZnO:Mn layer and reduces the carriers.

The electric field control of magnetization was investigated by measuring the magnetization before and after poling the ZnO:Mn - ZnO:V heterostructure. The ferroelectric ZnO:V top layer was poled by applying 4 V of d.c. bias voltage across the coplanar Au electrodes (Figure 4.3.1). Figure 4.3.6 shows the M versus H loops at 300 K for the heterostructure before and after poling. A large drop in the magnetization after poling indicates a possible magnetoelectric coupling at room temperature. This decrease
in magnetization by applying electric field can be attributed to a probable interaction between the magnetic moments in ZnO:Mn layer and the electric dipoles in ZnO:V layer.



Figure 4.3.5. M-H loops measured at (a) 10 K and (b) 300 K for the individual layers, ZnO:Mn and ZnO:V, and the ZnO:Mn-ZnO:V heterostructure, all grown on c-cut sapphire subtrates. The magnetic field was applied parallel to the film plane.



Figure 4.3.6. Magnetization loops at 300 K before and after poling the ZnO:Mn/ZnO:V epitaxial heterostructure.

# 4.3.3. Conclusions

To summarize, multiferroic layered ZnO:Mn-ZnO:V heterostructure has been fabricated using PLD. The heterostructure exhibited simultaneous magnetic and ferroelectric properties. Possibility of magneto-elastic coupling through a cross interaction between the layers has been observed. It is probable that such a coupling mechanism could arise from the difference in carrier concentration across the interface of the two phases. Further research in this direction is required to enhance the saturation values for practical device application.

## 4.4. Chapter Summary

In conclusion, this chapter described that the magnetic and ferroelectric properties of ZnO thin films may be enhanced by proper doping. It was observed that both the ferromagnetism in Mn doped ZnO films and the ferroelectricity in V doped ZnO films depended strongly on the carrier concentration in the films. Finally the single phase multiferroic heterostructure was fabricated and characterized. Possibility of magnetoelastic coupling was confirmed in the heterostructure. Since such structures have been grown for the first time, lack of theoretical background inhibited the progress. The exact mechanism of magnetoelastic coupling in not clearly understood. The difference of carrier concentration across the interface probably played an important role. Further research is needed to enhance magnetization and polarization values for a potential device application.

#### CHAPTER 5:

#### **CONCLUSIONS AND FUTURE DIRECTIONS**

In this thesis the horizontal heterostructures were studied for two systems namely the CFO/PZT bilayer films and the ZnO:Mn/ZnO:V structures. On one hand, it was shown that the interfacial strain played an important part in the observed magnetic and ferroelectric properties of the CFO/PZT films. On the other, it was probably the difference of carrier concentration across the interface in ZnO:Mn/ZnO:V films that lead to the possible magnetoelastic coupling. Both systems showed great potential as a composite multiferroic material.

Fabrication of epitaxial CFO/PZT multilayers was also attempted during the thesis. However in order to maintain the epitaxial relationships between the layers, the individual layer thickness had to be limited to tens of nm. At such small thicknesses the PZT layers could not be polarized due to substrate clamping effects. Increasing the layer thickness destroyed the epitaxy. Growth of CFO/PZT multilayers can be been possible using techniques like molecular beam epitaxy (MBE) where deposition of layers at an atomistic scale is possible.

In order to increase the magnetism in Mn doped ZnO thin films, higher doping percentages were also attempted. However, higher doping of Mn into ZnO (6 at. % Mn in ZnO) proved to be futile due to the precipitation of anti-ferromagnetic Mn oxide phases

in the films. Consequently, the saturated magnetization in the higher doped ZnO films was lower than in  $Zn_{0.98}Mn_{0.02}O$  films.

An important feature that was shown during the course of this thesis was the growth ZnO nanorods on different substrates using PLD (see Appendix D: Publications). The nanorods allow more surface area for better interfacial interaction of the different phases. Since ZnO can be doped with Mn or V to enhance their magnetic and ferroelectric behavior and studying the coupling effects in such doped nano-structures could be a future direction of work.

Another future direction for composite multiferroic heterostructures could be the ferrimagnetic nano-pillars of CFO embedded in a ferroelectric matrix of PZT as described in Chapter 1 (Section 1.2.2.2). Although there have been some reports of vertical nanostructured films in which CFO nanopillars were embedded in a BiFeO<sub>3</sub> film [60, 61], such structures have not been studied in details. In order to grow the CFO nanopillars the oblique angle deposition can be used [190 – 192]. The following section will give a brief account of the preliminary experiments done in this direction.

#### 5.1. Oblique Angle Deposition of CFO Thin Films

Oblique angle deposition using laser ablation has been reported to be successful in the growth of nano-columnar structures through the shadowing effect and the low adatom mobility [190 - 192]. During oblique angle deposition the substrate is tilted so that the angle formed between the surface normal of the target and the surface normal of the substrate is oblique. A schematic diagram of the set up is shown in Figure 5.1.1. The angle  $\alpha$  shown in the Figure 5.1.1 is the oblique angle.



Figure 5.1.1. Schematic diagram of the oblique angle deposition and the shadowing effect (Adapted from Ref. [190]).

As shown schematically in Figure 5.1.2, for normal incidence deposition, nucleation sites or island of materials deposited on the substrates, grow faster in the lateral direction in the substrate plane and eventually cover up the surface of the substrate leading to a polycrystalline film with no preferred orientation. However, for oblique angle deposition, due to the strong shadowing effect [193] the islands grow taller in the vertical direction; due to preferred orientation of the material concerned. The initial

islands shadow a considerable amount of surface area in the film (Figure 5.1.2). This results in the enhancement of the preferred growth direction and possible columnar growth in the initial deposited layer [194].



Figure 5.1.2. Schematic diagram of the growth of columnar structures by oblique angle deposition (Adapted from Ref. [194]).

Due to the increased surface of such columnar ferromagnetic layer, with the ferroelectric material deposited on top would lead to strain magnification in the interfaces of the two phases for better coupling between the magnetic and ferroelectric phases. The height and orientations of the columns could be manipulated by changing the oblique angle.

A series of CFO films were deposited on Si (100) substrates using an oblique angle ( $\alpha$ ) of 120° between the substrate and target normal directions. The substrate temperature and ambient O<sub>2</sub> pressure were kept at 450 °C and 10 mT respectively. Figure

5.1.3 shows the XRD patterns of oblique angle deposited CFO film with the thicknesses varying as 100 nm, 200 nm, 400 nm, and 600 nm, respectively.



Figure 5.1.3. XRD patterns of CFO thin films deposited on Si (100) substrates at an oblique incident angle of 60  $^{\circ}$  with different thicknesses as (a) 600 nm, (b) 400 nm, (c) 200 nm and (d) 100 nm, respectively. The substrate peak is denoted by \*.

It is observed that there is preferred growth in the (111) direction for 100 nm and 200 nm films (Figures 5.1.3 c, and d). However with increasing thicknesses the preferred growth is lost, resulting in polycrystalline bulk like XRD pattern.

Figures 5.1.4 (a, and b) show XRD patterns of CFO films both deposited under the same conditions as mentioned above but using oblique and normal incidence deposition respectively. The film thickness was 200 nm.



Figure 5.1.4. XRD patterns of CFO thin films deposited on Si under same conditions using (a) oblique and (b) normal incidence deposition, respectively.

On one hand when a normal incident CFO film of thickness about 200 nm shows no preferred orientation, on the other, the film deposited at oblique incidence still shows preferred growth in the (111) plane. This proves that preferred direction of growth is enhanced by oblique incidence. Figure 5.1.5 shows AFM images of the surface of the CFO films deposited on Si substrates at oblique incidence for variuos thicknesses. As the films thicknesses increase the grain boundaries get less distinct and eventually gets all smeared up after 600 nm. Comparing this with the XRD data in Figure 5.1.2 it can be inferred that there is initial preferred growth which gets destroyed as the film thickness increases.

Figure 5.1.6 shows in-plane M-H loops for CFO deposited under the same conditions but using oblique and normal incidence deposition respectively. The film thickness was 200 nm. It can be seen that the in-plane magnetization is reduced in the oblique angle deposited film. This could indicate that the moments are aligned perpendicular to the film plane for the oblique angle deposited film. However, further investigations are required to confirm the results.

It can be concluded that oblique angle deposition facilitates preferred growth and probable columnar structures. The enhancement of preferred growth by oblique angle of deposition has been demonstrated for the first time for CFO. This is promising because the ferroelectric layer could be deposited on top of the oblique angle deposited film. The deposition of the ferroelectric layer should be done using normal incidence deposition. This would make the top layer flat for polarization measurements. This oblique angle deposition technique could be used in future to grow new composite multiferroic structures.



Figure 5.1.5. AFM images of CFO films with different thicknesses as (a) 200 nm using normal, and (b) 100 nm, (c) 200 nm, (d) 300 nm, (e) 400 nm, and (f) 600 nm using oblique incidence deposition, respectively.



Figure 5.1.6. M-H loops for CFO films on Si substrates measured at (a) 300 K and (b) 10 K grown using normal and oblique incidence depositions. The magnetic field has been applied in-plane.

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**APPENDIX A:** 

POLYCRYSTALLINE CFO THIN FILMS

### **Appendix A: Polycrystalline CFO thin films**

Polycrystalline CFO thin films were grown on Si and c-cut sapphire substrates. Figures A.1 (a, b, c, and d) show SEM images of CFO-Si films deposited at 450 °C varying the background  $O_2$  pressure (pO<sub>2</sub>) as 0 mT, 10 mT, 40 mT and 60 mT, respectively. The surface appears to be smooth and relatively clean with very few particulates in the film deposited at 10 mT (Figure A.1. b) which was chosen as pO<sub>2</sub> during deposition. The film thicknesses were 200 nm.



Figure A.1. SEM images of CFO films on Si (100) substrates deposited at 450  $^{\circ}$ C varying the background O<sub>2</sub> pressure as (a) 0 mT, (b) 10 mT, (c) 40 mT, and (d) 60 mT, respectively.

Figures A.2 (a, b, and c) show the XRD  $\theta$ -2 $\theta$  scans of CFO-Si films grown under the same conditions for different thicknesses of 200 nm, 100 nm and 50 nm, respectively. The XRD pattern of the 200 nm thick film (Figure A.2 a) demonstrates a bulk-like polycrystalline nature (see Figure 3.1.6 for powder XRD).





Figure A.2. XRD patterns for (a) 200 nm, (b) 100 nm and (c) 50 nm thick films of CFO grown on Si (100) substrate, respectively.

However, the XRD pattern of the 100 nm thick film (Figure A.2 b) shows a (111) crystallographic texture as indicated by the high relative intensity of the series of [111] peaks compared to the (311) peak (highest peak in the bulk XRD pattern). The XRD pattern of the 50 nm thick film (Figure A.2 c) shows only a strong (111) texture. It has been reported earlier that below a critical film thickness, the (111) orientation is the preferred growth direction for CFO-Si thin films [1, 2].

Figure A.3 shows the XRD  $\theta$ -2 $\theta$  scan of CFO film grown on c-cut sapphire (Al<sub>2</sub>O<sub>3</sub>) (0001) substrate. The pattern shows only a strong (111) texture with no addition orientations of CFO although the film thickness is 200 nm.



Figure A.3. XRD  $\theta$ -2 $\theta$  scan of CFO film grown on c-cut sapphire substrate.

It has been reported that spinel-type ferrite thin films grow with a strong (111) orientation on  $Al_2O_3$  substrates [3, 4]. The hexagonal surface unit cells of  $Al_2O_3$  substrate provide triangular lattice nucleation sites for the CFO (111) plane. This gives a small lattice mismatch of 2.8 % between CFO and  $Al_2O_3$  along the (111) direction.

The average crystallite sizes (D) in CFO films were calculated from the broadening of the XRD  $\theta$ -2 $\theta$  peaks using the Scherrer formula [5, 6].

The Scherrer formula estimates the crystallite diameter D assuming spherical crystallites as D = 4/3L where L is given by

$$L = \frac{\kappa \lambda}{B\cos\theta}$$
(A.1)

Here L is the coherence length of reflected X-rays,  $\kappa$  is the particle shape factor (for spherical particles,  $\kappa = 0.94$ ),  $\lambda$  is the wavelength of X-rays (for CuK $\alpha$ ,  $\lambda = 1.54439$  Å), B is the FWHM of  $\theta$ -2 $\theta$  peak and  $\theta$  is the angle of diffraction. Table A.1 summarizes the crystallite sizes (D) calculated using Equation A.1. The lattice parameters (a) were also calculated from the XRD  $\theta$ -2 $\theta$  peaks and listed in Table A.1.

Table A.1. Lattice parameter (a) and crystallite size (D) calculated using Scherrer formula from the XRD patterns for CFO target and the deposited films on Si and sapphire substrates.

Sample	Film Thickness (nm)	Lattice parameter a (Å)	Crystallite size D (nm)	
CFO target CFO-Si CFO-Si CFO-Si CFO-Al <sub>2</sub> O <sub>3</sub>	200 100 50 200	$\begin{array}{l} 8.391 \pm 0.004 \\ 8.402 \pm 0.014 \\ 8.391 \pm 0.05 \\ 8.423 \pm 0.003 \\ 8.429 \pm 0.009 \end{array}$	$62 \pm 9$ $35 \pm 7$ $35 \pm 10$ $28 \pm 5$ $43 \pm 17$	

The lattice parameters for the 200 nm and 100 nm thick CFO-Si films (Table A.1) are very close to that for the CFO target (or bulk powder). The unchangeable lattice parameters suggest that there are no detectable stresses related to lattice distortions in these films. However the lattice parameter in the 50 nm thick CFO-Si film is larger than the CFO powder (Table A.1) which implies that the film is under a tensile stress.

Further, in all the samples the crystallite sizes are in the range 28-40 nm which is smaller than the critical single domain size for CFO ( $\approx$ 40 nm) [7].

Figure A.4 shows the in-plane and out-of-plane M-H loops at 300 K and 10 K for the (111) textured 100 nm thick CFO-Si films.



Figure A.4. M-H loops measured at (a) 300K and (b) 10 K for 100 nm thick textured polycrystalline CFO film grown on Si (100) for in plane and out of plane configuration.

The magnetic properties have been summarized in Table A.2. The magnetic behavior of CFO-Si(100nm) film is almost isotropic with similar  $M_s \perp$  and  $M_s \parallel$  values.

At 300 K, the values are about 4 and 4.5  $\mu_B$  per Co site (Table A.2), respectively,

which is higher with the bulk value (4  $\mu_B$  per Co site) [8]. This could be related to the

textured growth and unstressed state of the film as confirmed by XRD (Table A.2). The

higher Ms in CFO-Si film compared to the bulk CFO is possibly due to the smaller grain

size as also confirmed by XRD crystallite size calculation (Table A.2).

Table A.2. Saturation magnetization  $(M_s)$ , ratio of remnant magnetization  $(M_r)$  to  $M_s$  (squareness), and coercive field  $(H_c)$  measured at 300 K and 10 K for in-plane and out-of-plane configurations for 100 nm and 50 nm thick CFO films on Si substrates and 200 nm thick film of CFO on sapphire substrates. The symbols  $\parallel$  and  $\perp$  denote the in-plane and out-of-plane configurations respectively.

				300 K				
Sample	$\mathbf{M_s} \parallel$	$\mathbf{M_s} \parallel$	$M_r\!/M_s \parallel$	$\mathbf{H_c} \parallel$	$M_{s}\bot$	$M_s \bot$	$M_r\!/M_s\!\perp$	$H_{c}\bot$
	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)
CFO-Si (100nm)	$502 \pm 12$	4.0	30.1	0.5	$564 \pm 6$	4.5	15.8	0.4
CFO-Si (50nm)	$616 \pm 14$	4.9	13.8	0.2	>631	>5.3	>13.7	0.3
CFO-Al <sub>2</sub> O <sub>3</sub> (200nm)	$342 \pm 5$	2.7	12.2	0.3	>325	>2.6	>7.6	0.1
				10 K				
Sample	$M_s \parallel$	$\mathbf{M_s} \parallel$	$M_r\!/M_s \parallel$	$\mathbf{H_c} \parallel$	$M_{s}\bot$	$M_s \bot$	$M_r\!/M_s\!\perp$	$\mathrm{H_{c}}\bot$
	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)	(emu/cm <sup>3</sup> )	$(\mu_B/Co^{2^+})$	(%)	(kOe)
CFO-Si (100nm)	$632 \pm 3$	5.0	47.2	2	$441 \pm 12$	2.5	30.9	0.3
CFO-Si (50nm)	$570 \pm 5$	4.5	15.3	0.2	>240	1.9	>25.4	0.3
CFO-Al <sub>2</sub> O <sub>3</sub> (200nm)	$473 \pm 5$	3.8	44.3	5	>225	1.8	>14.2	0.2
,								

Figure A.5 shows the M-H loops at 300 K and 10 K for the highly (111) textured 50 nm thick CFO-Si film. The M-H loop shows strong in-plane anisotropy.

This behavior is consistent with earlier reports which suggest that below a critical film thickness, the shape anisotropy in CFO overcomes the magnetocrystalline anisotropy [9].

This aligns the magnetic moments along the film plane i.e (111) crystallographic plane for CFO-Si(50 nm) film. The magnetic properties have been summarized in Table A.2.



Figure A.5. M-H loops measured at (a) 300K and (b) 10 K for 50 nm thick highly (111) textured CFO film grown on Si (100) for in plane and out of plane configuration.

Figure A.6 shows the M-H loops 200 nm thick CFO-Al<sub>2</sub>O<sub>3</sub> film. The M-H loops show strong in-plane anisotropy.

The magnetic properties have been summarized in Table A.2. The magnetization in CFO-Al<sub>2</sub>O<sub>3</sub>(200nm) film is similar to CFO-Si(50nm) film except for the higher  $H_c$  and  $M_r/M_s$  ratio at 10 K.



Figure A.6. M-H loops measured at (a) 300K and (b) 10 K for 200 nm thick highly (111) textured CFO film grown on c-cut sapphire substrate for in plane and out of plane configurations.

The thickness dependence of magnetization for CFO-Si films is shown in Figure A.7. Table A.3 lists the in-plane magnetic properties for all the samples.
The M<sub>s</sub> increased and H<sub>c</sub> decreased with decreasing film thickness. The results are

consistent with earlier reports [10].

Table A.3. Saturation magnetization  $(M_s)$ , ratio of remnant magnetization  $(M_r)$  to  $M_s$  (squareness), and coercive field  $(H_c)$  measured at 300 K and 10 K for in-plane configurations for 200nm, 100 nm and 50 nm thick CFO films on Si substrates. The symbol  $\parallel$  denotes the in-plane configurations.

		300 K		
Sample	$\mathbf{M}_{\mathbf{s}} \parallel$	$\mathbf{M_s} \parallel$	$M_r\!/M_s \parallel$	$\mathbf{H_c} \parallel$
	(emu/cm <sup>3</sup> )	$(\mu_{\rm B}/{\rm Co}^{2^+})$	(%)	(kOe)
CFO-Si (200nm)	$416 \pm 2$	3.3	27.6	1.2
CFO-Si (100nm)	$502\pm12$	4.0	30.1	0.5
CFO-Si (50nm)	$616\pm14$	4.9	13.8	0.2
		10 K		
Sample	$M_{s}\parallel$	10 K M <sub>s</sub> ∥	$M_r\!/M_s\parallel$	$\mathbf{H_c} \parallel$
Sample	$M_s \parallel$ (emu/cm <sup>3</sup> )	$\begin{array}{c} 10 \text{ K} \\ M_{s} \parallel \\ (\mu_{B}/\text{Co}^{2^{+}}) \end{array}$	M <sub>r</sub> /M <sub>s</sub> ∥ (%)	H <sub>c</sub> ∥ (kOe)
Sample	$M_s \parallel$ (emu/cm <sup>3</sup> )	$\begin{array}{c} 10 \text{ K} \\ M_{s} \parallel \\ (\mu_{B}/Co^{2^{+}}) \end{array}$	M <sub>r</sub> /M <sub>s</sub> ∥ (%)	H <sub>c</sub> ∥ (kOe)
Sample CFO-Si (200nm)	$M_{s} \parallel (emu/cm^{3})$ $368 \pm 9$	$   \begin{array}{c}     10 \text{ K} \\     M_{s} \parallel \\     (\mu_{B}/\text{Co}^{2^{+}})   \end{array} $ 2.9	M <sub>r</sub> /M <sub>s</sub> ∥ (%) 59.2	H <sub>c</sub> ∥ (kOe) 10
Sample CFO-Si (200nm) CFO-Si (100nm)	$M_{s} \parallel$ $(emu/cm^{3})$ $368 \pm 9$ $632 \pm 3$	$\begin{array}{c} 10 \text{ K} \\ M_{s} \parallel \\ (\mu_{B}/\text{Co}^{2^{+}}) \\ 2.9 \\ 5.0 \end{array}$	M <sub>r</sub> /M <sub>s</sub> ∥ (%) 59.2 47.2	H <sub>c</sub> ∥ (kOe) 10 2
Sample CFO-Si (200nm) CFO-Si (100nm) CFO-Si (50nm)	$M_{s} \parallel (emu/cm^{3})$ $368 \pm 9$ $632 \pm 3$ $>570$	$\begin{array}{c} 10 \text{ K} \\ M_{s} \parallel \\ (\mu_{B}/\text{Co}^{2^{+}}) \\ 2.9 \\ 5.0 \\ 4.5 \end{array}$	M <sub>r</sub> /M <sub>s</sub>    (%) 59.2 47.2 >15.3	H <sub>c</sub> ∥ (kOe) 10 2 0.2

## Low field switching in Hysteresis loops

An interesting feature seen in the low temperature M-H loops of the CFO films is the low magnetic field switching (Figure A.7)). Step-like features due to such switching occur symmetrically on both sides of the zero field line. The steps seen in the M-H loops are similar to those observed in composite thin films [11] and in bilayers composed of hard and soft magnetic materials [12]. There could be several explanations for the low field switching such as the effect of substrate-film interface [11] or the characteristic of a preferred orientation.



Figure A.7. M-H loops measured at (a) 300K and (b) 10 K for CFO films grown on Si (100) for different thicknesses. The magnetic field was parallel to film plane.

In order to investigate this, the temperature dependence of magnetization was measured. Figures A.8 (a, b, and c) show the in-plane M-H loops for the 200 nm thick CFO film on Si substrate measured at different temperatures from 10 K to 300 K. The low field switching is clearly visible at low temperatures (10 K) due to the increase in coercivity ( $H_c$ ) resulting from the reduced thermal influence on the alignment of magnetic moments. Although the M-H loop at 300K (Figure A.8 c) is narrower it still

shows the step like switching when is magnified in the vicinity of the zero field regions. This confirms that low field switching is independent of temperature. The temperature dependence of coercivity ( $H_c$ ) is shown in Figure A.8 (d). In the case of a thin film with uniaxial symmetry, the temperature dependence of  $H_c$  can be fit to the following relation [13]:



Figure A.8. M-H loops measured at (a) 10 K, (b) 150 K and (c) 300 K for a 200 nm thick CFO film grown on Si (100) substrate. (d) The coercivity ( $H_c$ ) as a function of temperature.

From the slope of the fit shown in Figure A.8 (d), the blocking temperature ( $T_B$ ) is deduced to be about 355 K, which is consistent with earlier reports for CFO (~390K) [13]. The increase of coercivity with lowering temperature was also observed for the case of the 100 nm thick film, which has both (111) and (311) dominant peaks.

However, the switching behavior is not observed in the M-H loops for the highly (111) textured 50 nm thick CFO-Si film, even when magnified in the vicinity of the zero fields at 300 K and 10 K, as shown in Figure A.9. This implies that the low field switching probably arises only in thicker films from an interfacial layer at the film-substrate interface as reported earlier [14, 15].



Figure A.9. In-plane M-H loops measured at 300K and 10 K for 50 nm thick CFO film grown on Si (100) substrate. Steps seen in thicker films (100 nm and above) due to low field switching are not present in this case.

To affirm this, the in-plane M-H loops at 10 K for both the 50 nm and 200 nm films are overlapped as shown in Figure A.10. The M-H loop for the CFO-Si(50 nm) film lies exactly on the onset of the magnetic switching for the CFO-Si(200 nm) film, on both sides of the field sweep (Figure A.10).



Figure A.10. In plane M-H loops for CFO-Si 50 nm and 200 nm films measured at 10K. The y-axis is normalized with the saturation magnetic field. The M-H loop of the (111) oriented film overlaps on the first step of the magnetic reversal seen on the 200 nm film.

From Figure A.6 (b) it is observed that the in-plane magnetization for the 200 nm thick (111) textured CFO-Al<sub>2</sub>O<sub>3</sub> film also exhibits a step-like switching feature. This eliminates the possibility that the low field switching is associated with the (111) orientation. Thus the low field switching could arise mainly from the interface between the substrate and the film.

Growth of interfacial layer at the substrate-film interface is common in magnetic thin films [16]. The magnetic moments within the interfacial layer are probably aligned parallel to the film plane and are magnetically decoupled from the rest of the film. The degree of the alignment of the magnetization at the interface possibly depends on the interfacial stress and the thickness of the interfacial layer. The in-plane anisotropy of the interfacial layer facilitates the magnetic reversal when the applied field is parallel to the film plane. This explains why the low field switching is observed only in the in plane M-H loops but not in the out of plane configurations.

The low field step like features discussed above are different from the narrowing feature of the M-H hysteresis loops at low fields for CFO-Si(100nm) film. This behavior has also been observed for CFO nano-particles and can be attributed to the small grain size in the films [17].

## Probing magnetic switching using RF transverse susceptibility

A quantitative analysis of the field strength required to align the moments in the interfacial layer is discussed in the following paragraphs.

While the low field switching feature is clearly observed in the M-H loops, it is difficult to determine precisely magnetic switching field and particularly its dependence on measuring temperature. Thus a very sensitive and precise RF transverse susceptibility (TS) technique was utilized to probe magnetic switching and its temperature dependence in CFO films. The RF transverse susceptibility technique developed by Srikanth [18] et al., is based on a sensitive, self-resonant tunnel diode oscillator (TDO) incorporated into the PPMS.

It has been validated over the years to be an excellent technique for probing effective magnetic anisotropy and switching in a wide range of magnetic materials ranging from thin films [19], nanoparticles [20] to single crystals [21]. In TS experiments, a small perturbing AC or RF field (< 10 Oe) is applied to the sample in addition to the swept dc magnetic field. Since the sample is placed in an inductive RF coil that is part of a self-resonant circuit, the shift in the resonant frequency with varying dc magnetic field and/or temperature give a direct measure of the change in inductance and hence the sample susceptibility. The change in transverse susceptibility with dc magnetic field has been expressed by:

$$\left(\frac{\Delta \chi_T}{\chi_T}\right)\% = \left[\frac{\chi(H) - \chi(H_{\max})}{\chi(H_{\max})}\right] \times 100\%$$
(A.3)

where  $H_{max}$  is the maximum applied d.c. magnetic field.

Theoretically, the transverse susceptibility spectrum in a unipolar field scan from positive to negative saturation should consist of three singularities of which two occur at the anisotropy fields ( $\pm$  H<sub>k</sub>) and one at the switching field ( $\pm$ H<sub>s</sub>) [22, 23]. However, it has been experimentally shown that depending upon the magnetic nature of the sample and the orientation in which the sample is introduced in the inductive coil, either anisotropy peaks or switching peaks could be prominently observed.

In the present study, RF transverse susceptibility measurements were conducted at different temperatures (T = 300K, 200K and 10K) for the CFO films grown on MgO and STO. The maximum dc field applied was 5 kOe. The results are displayed in Figure A.11 and its inset. It can be clearly seen from Figure A.11 that the TS curves show only switching peak, but no anisotropy peaks are detected.

The absence of anisotropy peaks can be understood due to the fact that the anisotropy fields of the films investigated were beyond the maximum applied dc magnetic field. However, it was possible to detect the low field switching present in the cobalt ferrite films. The change of TS peak position with temperature (see inset of Figure A.11) clearly reveals that for the CFO films investigated, the switching field increases as the temperature is decreased. For the film grown on MgO, the switching fields at 300K, 200K and 10 K were  $\pm$ 70Oe,  $\pm$ 80 Oe and  $\pm$ 115 Oe respectively. In case of the CFO film grown on STO, the switching fields obtained for 300K, 200K and 10K were  $\pm$ 80 Oe,  $\pm$ 90 Oe and  $\pm$ 135 Oe respectively.



Figure A.11. TDO measurement of CFO films on STO at 300K with the film plane perpendicular to the DC field. The line with solid square represent the field sweep from positive to negative, where as the solid circles represent the field sweep from negative to positive.

The larger values of switching field for the case of the film grown on STO may be reconciled with the fact that the lattice mismatch and thus the stress is larger in this sample. The stress due to lattice mismatch would be more significant at the interface. This indicates that the origin of the low field switching steps seen in the M-H loops of the CFO films is associated with the stress at the interface between the substrate and the film.

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**APPENDIX B:** 

## **LSMO ELECTRODES**

#### **Appendix B: LSMO electrodes**

PZT capacitors fabricated using noble metal electrodes like Pt or Au exhibit a significant loss of switching polarization with repeated switching cycles also know as 'ferroelectric fatigue in thin films' [1]. This loss of switchable polarization limits the lifetime of a ferroelectric device, such as ferroelectric nonvolatile memory, where the write and read cycles both rely on ferroelectric switching. [1].To overcome this problem metallic oxide electrodes such as RuO<sub>2</sub>, La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub>, YBBCu<sub>3</sub>O<sub>y</sub>, LaNiO<sub>3</sub>, IrO<sub>2</sub> and La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (LSMO) are often used [2 - 8]. Fatigue is caused by the defects due to oxygen vacancies in the PZT films. [1]. It has been suggested that the oxide electrodes act as a sink for oxygen vacancies so that they do not pile-up at the film-electrode interface [3] [9]. This reduces the fatigue [10]. LSMO is a metallic oxide that has attracted great interest recently due to its colossal magnetoresistance [11]. Epitaxial LSMO films are highly conducting with a room temperature resistivity of 300 μΩ-cm [12]. PZT capacitors with LSMO top and bottom electrodes (LSMO/PZT/LSMO) have shown better fatigue endurance compared to other oxide electrodes [8].

The LSMO bottom electrodes were first deposited as a thin layer on the MgO and STO substrates prior to the PZT layer deposition.  $PLD_{SL}$  was used with a KrF fluence of 2 J/cm<sup>2</sup>. The LSMO target was purchased from Kurt J. Leskar Company with a composition of La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>. The LSMO films were deposited at 600 °C by varying the ambient oxygen pressure pO<sub>2</sub> from 10 mT to 100 mT for 100 nm thickness.

The small lattice mismatch (8 %) between LSMO (pseudo-cubic, a = 0.387 nm) and MgO (cubic, a = 0.421 nm) allowed for the epitaxial growth of LSMO on MgO [13]. However, it was observed that the pO<sub>2</sub> influenced the epitaxial growth.

Figures B.1 (a, b, c, and d) show XRD patterns of LSMO powder, and LSMO films deposited at 100 mT, 50 mT, and 10 mT of  $pO_2$  on MgO substrates, respectively.



Figure B.1. XRD patterns of (a) LSMO powder, and LSMO films on MgO (100) substrates deposited using  $pO_2$  of (a) 100 mT (LSMO-MgO 100mT), (b) 50 mT (LSMO-MgO 50 mT), and (c) 10 mT (LSMO-MgO 10 mT), respectively. The small peak denoted by \* around 38° in (c) and (d) is an artifact from the MgO substrate.

The XRD pattern for the 100 mT deposited film (Figure B.1. b) exhibits a polycrystalline nature similar to that of the LSMO powder (Figure B.1 a).

The peaks are indexed with the rhombohedral LSMO structure with a space group R-3c (167) (a = 5.5 Å, c = 13.37 Å) [14]. However, the LSMO films deposited at 50 mT and 10 mT pO<sub>2</sub> (Figure B.1 c, and d) are highly textured in the (100) direction with no other orientations observed. There is a peak shift to lower angles as compared to Figure B.1 (a). The peaks are indexed to the LSMO pseudo-cubic perovskite structure (a = 3.87 Å). The results are consistent with previous reports [13]. From the above study, the pO<sub>2</sub> during deposition of LSMO-MgO films was fixed at 10 mT.

The similar crystal structure between LSMO (pseudo-cubic, a = 0.387 nm) and STO (cubic, a = 0.3905 nm) and the extremely small lattice mismatch (0.009 %) allow for the growth of almost perfectly epitaxial LSMO films on STO substrates [15, 16]. Figures B.2 (a, and b) show XRD patterns for LSMO-STO film and STO substrate. The XRD patterns are almost identical indicating the highly epitaxial nature of the film. The insets (I) and (II) to Figure B.2 (a) shows the details of the STO(200)/LSMO(200) and STO(300)/LSMO(300) peaks. The inset to Figure B.2 (b) shows the rocking curve performed about the STO (200) plane. The FWHM of the rocking curve is 0.268° which confirms the high degree of in orientation in STO.

Figure B.3 shows SEM image of LSMO-STO film (bottom electrode for PZT capacitors). The surface appears to be dense and compact indicative of a layer by layer growth mode as reported earlier [16]. The average grain size is less than 100 nm. Further, no particulates are observed which could degrade the growth of the subsequent PZT layer.



Figure B.2. XRD patterns of (a) LSMO film on STO substrate and (b) STO substrates, respectively. The insets (I) and (II) to (a) shows the details of the STO(200)/LSMO(200) and STO(300)/LSMO(300) peaks. The inset to (b) shows the rocking curve performed about the STO (200) plane.



Figure B.3. SEM image of the surface of LSMO film deposited on STO substrate.

After the deposition of the PZT layer, the top LSMO electrodes were deposited in-situ using a shadow mask that produced 100  $\mu$ m diameter contacts as shown in the SEM image in Figure B.4.



Figure B.4. SEM images of LSMO top electrodes on PZT film grown using a shadow mask that produced  $100 \ \mu m$  diameter contacts.

An interesting feature was observed in  $PZT_{DL}$  films deposited on STO substrates using a KrF fluence 1 J/cm<sup>2</sup> and CO<sub>2</sub> fluence of 2 J/cm<sup>2</sup> with an interpulse delay  $\Delta t = -50$ ns as described in Chapter 3, Section 3.2 (Figure 3.2.10 f). In this case, the initial CO<sub>2</sub> pulse melted the target surface, followed by the KrF pulse which ablated the materials from the molten pool. This condition was completely opposite to that required for particulate free films. In this condition, huge amount of particulates are expected to get ejected from the target surface and get deposited on the film surface.

Figures B.5 (a to d) show SEM images at increasing magnification of the surface of PZT<sub>DL</sub>-STO film deposited using  $\Delta t = -50$  ns.



Figure B.5. SEM images of PZT films on STO substrates deposited using dual laser ablation with a KrF fluence 1 J/cm<sup>2</sup> and CO<sub>2</sub> fluence of 2 J/cm<sup>2</sup> with an interpulse delay  $\Delta t = -50$  ns.

At lower magnification (Figure B.5 a) the surface appears particulate laden and rough. However at higher magnifications (Figure B.5 b and c) it appears that the particulates on the surface are uniformly distributed and have a distinct shape.

Unlike the 'splashed' molten droplets seen earlier (Figure B.5 d), these particulates appear to be cubic or tetragonal just like PZT crystals. This suggests that the particulates are a result of crystallization on the film surface. The mono-dispersed arrangement (Figure B.5 d) coupled with the epitaxial and pure phase nature revealed from XRD make these films interesting. This could imply that the dual laser ablation process can be used not only to remove particulates but also to deliberately deposit particulates for specific application. These film did not show any ferroelectric behavior and further research is required which is not under the premise of this work.

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**APPENDIX C:** 

PLUME IMAGES

### **Appendix C: Plume Images**

In order to study the visible laser ablated plume propagation towards the substrate as a function of time, ICCD images were captured after various time intervals with the respect to a reference zero time. Figure C.1 shows time gated ICCD images using 200 ns exposure time of single laser ablated plumes from PZT target using a laser fluence of 2  $J/cm^2$  under 500 mT ambient O<sub>2</sub> gas. The position of the target is denoted by the white dotted rectangular box on the left hand side of each image. It is clearly seen that the relative separation between the plume and the target increases with time and reaches a constant separation after 6 µs.



Figure C.1. Time gated ICCD images using 200 ns exposure time of single laser ablated plumes from PZT target using laser fluence of 2 J/cm<sup>2</sup> under 500 mT ambient  $O_2$  gas.

The highest intensities from the plume propagation images were plotted as a function of distance from the target and time as shown in Figure C.2.



It can be seen that the intensity decreases almost exponentially with time and distance from the target surface.

Figure C.2. Plot of the highest intensities of the visible plumes captured at various time intervals as a function of the distance from target surface and time.

Figure C.3. shows ICCD images (20  $\mu$ s exposure time, 200 ns step size) of total visible emission spectra of single laser plumes (a - d) varying the excimer (KrF) fluences from 1 to 4 J/cm<sup>2</sup> and dual laser plumes (e –f) varying excimer fluences keeping 2 J/cm<sup>2</sup> CO<sub>2</sub> (IR) fluence and 100 ns peak to peak inter-pulse delay under vacuum. The plumes using dual laser ablation show broader transverse cross-section similar to the ones discussed in Chapter 3 (Section 3.2). However, unlike the ones in Chapter 3 which were under high ambient, the most intense part is closer to the target surface.



Figure C.3. ICCD plume images using single and dual laser ablation under vacuum.

Figure C.4 shows ICCD images of  $CO_2$  laser ablated plumes captured at different time intervals using a  $CO_2$  fluence of 3 J/cm<sup>2</sup>. It can be seen that particulates are ejected from the target surface at 3 J/cm<sup>2</sup> and they become visible only after the intense plume disappears.



Figure C.4. ICCD images of  $CO_2$  laser ablated plumes captured at various time intervals showing the ejection of particulates for the target surface using 500 µs exposure times.

**APPENDIX D:** 

PUBLICATIONS

#### **Appendix D: Publications**

### **Journal Articles**

- D. Mukherjee, T. Dhakal, H. Srikanth, P. Mukherjee, and S. Witanachchi, "Evidence for carrier-mediated magnetism in Mn-doped ZnO thin films", Phys. Rev. B 81, 205202 (2010).
- [2] T. Dhakal\*, D. Mukherjee\*, P. Mukherjee, R. Hyde, M. H. Phan, H. Srikanth, and S. Witanachchi, "Magnetic anisotropy and field-switching in cobalt ferrite thin films deposited by pulsed laser ablation", J. Appl. Phys. 107, 053914 (2010). (\*These authors contributed equally)
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   "Comparative study of ZnO thin film and nano-pillar growth on YSZ(111) and sapphire (0001) substrates by pulsed laser deposition", J. Cryst. Growth 312, 2012 (2010).
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## **Referred Conference Proceedings**

[1] D. Mukherjee, R. Hyde, T. Dhakal, H. Srikanth, P. Mukherjee and S. Witanachchi, "Investigation of the Pb depletion in single and dual pulsed laser deposited epitaxial PZT thin films and their structural characterization", Mater. Res. Soc. Symp. Proc. 1199, 37 (2010).

- [2] T. Dhakal, D. Mukherjee, R. Hyde, H. Srikanth, P. Mukherjee, and S. Witanachchi, "Enhancement in ferroelectricity in V-doped ZnO thin film grown using laser ablation" Mater. Res. Soc. Symp. Proc. 1199, 44 (2010).
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- [6] S. Witanachchi, R. Hyde, M. Beekman, D. Mukherjee, P. Mukherjee, and G. S. Nolas, "Synthesis and Characterization of Bulk and Thin Film Clathrates for Solid State Power Conversion Applications", 25<sup>th</sup> International Conference on Thermoelectrics, IEEE Proceedings (2006).

#### **CONFERENCE PRESENTATIONS**

#### **Oral Presentations**

- [1] "Dual-laser Deposition of Stoichiometric PZT/CoFe<sub>2</sub>O<sub>4</sub> Epitaxial Heterostructures" D. Mukherjee, R. Hyde, T. Dhakal, H. Srikanth, P. Mukherjee, and S. Witanachchi (2010 MRS Spring Meeting, San Francisco)
- [2] "Growth of Epitaxial ZnO:Mn/ZnO:V Heterostructures and Ferroelectricferromagnetic Characterization," D. Mukherjee, T. Dhakal, H. Srikanth, P. Mukherjee, and S. Witanachchi (2009 MRS Spring Meeting, San Francisco).

## **Poster Presentations**

- [1] "Investigation of the Pb depletion in single and dual pulsed laser deposited epitaxial PZT thin films and their structural characterization", **D. Mukherjee**, R. Hyde, T. Dhakal, H. Srikanth, P. Mukherjee, and S. Witanachchi (2009 MRS Fall Meeting, Boston).
- "Enhancement in ferroelectricity in V-doped ZnO thin film grown using laser ablation" T. Dhakal, D. Mukherjee, R. Hyde, H. Srikanth, P. Mukherjee, and S. Witanachchi (2009 MRS Fall Meeting, Boston).
- [3] "Growth of epitaxial CoFe<sub>2</sub>O<sub>4</sub>/PZT heterostructures and ferroelectric-ferromagnetic characterization" **D. Mukherjee**, T. Dhakal, R. Hyde, P. Mukherjee, H. Srikanth, and S. Witanachchi (2008 MRS Fall Meeting, Boston).

[4] "Growth of epitaxial CoFe<sub>2</sub>O<sub>4</sub>/PZT heterostructures and ferromagnetic characterization" **D. Mukherjee**, T. Dhakal, R. Hyde, P. Mukherjee, H. Srikanth, and S. Witanachchi (2008 Poster Symposium & Competition, "Global Challenges for the 21<sup>st</sup> Century, USF).

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Devajyoti Mukherjee earned his B.S. degree (1<sup>st</sup> class with distinction, silver medal) and M.S. degree (1<sup>st</sup> class) in Physics in 2002 and 2004, respectively, from Jadavpur University, Kolkata, India. In 2004, he was awarded a Junior Research Fellowship by the Council of Scientific and Industrial Research - University Grants Commission (CSIR-UGC), Govt. of India. In 2005, he came to USA and joined the Physics Department at the University of South Florida (USF). He was awarded the Duckwall Summer Fellowship by the Physics department, USF, two times during the course of his dissertation. He has published several peer-reviewed journal articles and scientific papers at conferences in the areas of material science, thin films and multiferroics.