6 Chapter 6

Multiferroic Properties in BiFeO$_3$-CoFe$_2$O$_4$
Heterostructures Thin Films Deposited On (111) SrTiO$_3$
Substrate$^3$

6.1 Introduction

Recently the artificially engineered nanostructured composite materials attracted a lot of attention because of its novel physical properties [14, 103-105]. One of particular interest is the multilayer heterostructures thin films of functional oxides, such as, ferroelectric (FE), ferromagnetic (FM), antiferromagnetic (AFM) and multiferroics (MF), colossal magneto resistance (CMR) and other different order materials [14, 103, 104, 106]. Heterostructures multilayer thin films are consist of thin layers of two or more different nanostructures that are piled in a well-defined arrangement, which may reveal remarkable properties that do not exist in either of their parent forms [6, 7].

In this chapter, the synthesis and characterization of highly textured BiFeO$_3$-CoFe$_2$O$_4$ (BFO/CFO) thin films deposited on SrTiO$_3$ (111) substrates are systematically investigated. The samples were prepared using pulsed laser deposition (PLD). The X–ray diffraction analysis reveals the existence of BFO and CFO in two separate phases without any intermediate phase. The ferromagnetic properties of BFO/CFO grown on STO (111) substrate

$^3$ Some part of the work has been published in AIP Conf. Proceeding 1731, 080043 (2016).
is found to be enhanced as compare to pure BFO. The coercive field in BFO/CFO heterostructures thin films increases as compare to BFO/STO (111) films.

6.2 Experiments

BiFeO$_3$ and CoFe$_2$O$_4$ powder was synthesized by using solid state reaction method. The details about the growth of the materials can be found elsewhere [52, 121, 123]. The Bi$_2$O$_3$ (99.99%) and Fe$_2$O$_3$ (99.99%) powder was mixed by mechanical ball milling process for 24 hours and then the resultant powder was calcined at 820°C for 24 h. Similarly we prepared the CoFe$_2$O$_4$ target materials for which the starting materials were Fe$_2$O$_3$ (99.99%) and Co$_2$O$_3$ (99.99%) and in this case the calcined temperature was kept constant at 900°C. The both mixture were separately grinded to obtain homogeneous powder and afterwards the powder was pressed into a disc-shaped pellet. After that the pellet was sintered slightly above the calcine temperature.

The BiFeO$_3$-CoFe$_2$O$_4$ (BFO/CFO) bilayer films deposited at different temperature was grown using pulsed laser deposition (PLD) technique which has a KrF excimer laser with wavelength, $\lambda=240$ nm. The BFO thin films were grown under an oxygen pressure of 100 mTorr at 620 °C, using a laser energy density of (3.0 J -cm$^2$) and repetition rate of 3 Hz. The CFO layer was then deposited on top of the BFO layer under an oxygen pressure of 100 mTorr at 400 °C, using similar laser energy density as BFO and repetition rate of 5 Hz. After deposition the heterostructures was annealed at 650 °C for 30 min in oxygen at a pressure of 300 Torr. Note that the lattice-constant mismatch between the BFO film and the STO layer is very small (~1.4%), resulting in a slightly tensile in-plane stress (111)-oriented BFO/CFO heterostructures thin films in volume fraction (1:1). The thickness of these films was estimated to be 200±30 nm using field-emission scanning electron microscopy. Room-temperature magnetic measurements for all the samples was carried out using LAKE SHORE’S VIBRATING SAMPLE MAGNETOMETER (VSM) with the magnetic field applied parallel
to the film plane. The ferroelectric and dielectric properties were measured by RT6000HVS (Radiant) and impedance-phase analyzer (HP4294A).

6.3 Results and discussions

6.3.1 Structural properties

Figure 6.1 shows the room temperature (0-20) X-ray diffraction (XRD) pattern for BFO/CFO multilayers thin films deposited on STO (111) buffered by a conducting SrRuO$_3$ (SRO) conducting layer. XRD pattern of the films showed very clear peaks of two separate phases of BFO and CFO. It also reveals that heterostructures thin films were highly textured along the substrate orientation. No secondary phase is observed which indicates good crystalline quality of the materials. The high intense BFO peak also suggests that BFO/CFO heterostructures are oriented along (111) of STO substrate. The XRD pattern reveals that both BFO with rhombohedral structure and CFO with spinel structure present in the heterostructures thin films.
Figure 6-1: XRD pattern BFO/CFO heterostructures on a SrTiO3 (111) substrate.

6.3.2 Dielectric Properties

Figure 6.2 shows the frequency dispersion of (a) dielectric constant (ε) and (b) tangent loss (tanδ) of BFO/CFO/STO (111) heterostructures thin films as a function of frequencies at different selected temperatures (i.e. from 100K to 450K), respectively. These measurements reveal that the dielectric constant decreases rapidly with increasing frequencies from 100Hz to 1MHz indicating the dispersive nature at low frequency region. The dispersion occurring in low frequency region can be explained in terms of Maxwell Wagner polarization model [123, 295, 336]. In addition, the capacitance arising from grain boundaries and interface between the layers as a consequence of the contribution of two different ferrimagnetic (CFO) and multiferroic (BFO) materials. Further, a substantial increase in dielectric constant (ε) in the low frequency range may additionally be contributed by dipolar polarization [31, 123, 294, 368]. The observed dispersion behavior of dielectric constant (or
dielectric loss) with frequency can be explained on the basis of dipolar relaxation phenomenon, in which dipoles are able to follow the applied field at low frequencies, this leads to high dielectric values at low frequency [31, 124, 286, 293, 294, 369, 370]. But at higher frequencies the dielectric constant decreases because the dipoles are unable to follow an applied electric field [31, 124, 286, 293, 294, 369, 370]. Therefore, the dielectric constant remains constant at higher frequencies [31, 124, 286, 293, 294, 369, 370].

Figure 6.3 shows the temperature dependence of (a) dielectric constant ($\varepsilon$) and (b) tangent loss $\tan(\delta)$ of BFO/CFO heterostructures thin films at different frequencies (100Hz, 1 K Hz, 10KHz, 100KHz and 1MHz ), respectively. The value of dielectric constant ($\varepsilon$) increases as temperature increases. This increment perhaps associated with the thermally activated dipoles as the more and more dipoles participated towards the polarization with increasing the temperature.
Figure 6-2: (a) Frequency dependent dielectric constant ($\varepsilon$) of BFO/CFO/STO (111) heterostructures at different temperature. (b) Frequency dependent tangent loss Tan ($\delta$) of BFO/CFO/STO (111) heterostructures at different temperature.

The dielectric anomaly start appears as temperature increases above 300K to 600K. The monotonic increase of the dielectric constant ($\varepsilon$) and tan ($\delta$) with the temperature is probably an indication of dielectric anomaly at much higher temperature. In the case of the heterostructures of BFO/CFO, at low temperature dipoles freezes due to space charge relaxation process at the interface which causes decrement in polarization, as a result a smaller value of dielectric constant at low temperature the gradually increment in the dielectric constant as the temperature increases could be due to thermally activated charges carriers [31, 129, 293-295, 337, 368].
Figure 6-3: Temperature dependent (100 K to 600K) (a) dielectric constant ($\varepsilon$) of BFO/CFO/STO (111) heterostructures at different frequencies. (b) Temperature dependent (100K to 600K) (b) Tangent loss [Tan ($\delta$)] of BFO/CFO--STO (111) heterostructures at different frequencies.

The dielectric property is attributed to the interfacial effect across the presence of CFO as separate phase embedded in the BFO matrix. The variation of dielectric constant and dielectric loss for BFO/CFO thin suggests Maxwell-Wagner polarization modal [123].
6.3.3 Magnetic Properties

Figure 6-4: Magnetization of (a) BiFeO3 and, (b) BiFeO3–CoFe2O4 multilayer thin film deposited on STO (111) as a function of applied magnetic field at Room temperature.

Figure 6.4 shows the M–H hysteresis loops at 300K of single layer (a) BFO and heterostructures of (b) BFO/CFO thin films on STO (111), respectively. The BFO thin films do not give a perfect ferromagnetic loop. However, BFO/CFO/STO (111) thin film heterostructures show very well-shaped ferromagnetic magnetization hysteresis loops with saturated magnetization and high coercive field, which are significantly larger than pure BiFeO3 thin films deposited under the similar conditions. These results suggested the improvement of ferromagnetic properties in BFO/CFO heterostructures thin film due to the presence of CFO phase [117, 121-123]. The observed value the coercive field ($H_c$), remnant
magnetization ($M_s$) and saturation magnetization ($M_r$) from the M-H loop for BFO/STO (111) and BFO/CFO/STO (111) are given in Table 1.

Table 6-1: Ferromagnetic and ferroelectric parameter of BFO-STO (111) and BFO/CFO/STO (111) thin films at room temperature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Magnetic Parameters</th>
<th>Ferroelectric Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{Max}$ (emu/cm$^3$)</td>
<td>$M_r$ (emu/cm$^3$)</td>
</tr>
<tr>
<td>BFO/STO</td>
<td>74.4506</td>
<td>6.4085</td>
</tr>
<tr>
<td>BFO/CFO/STO</td>
<td>64.5010</td>
<td>17.5712</td>
</tr>
</tbody>
</table>

6.3.4 Ferroelectric Properties

Figure 6.5 (a) and 5(b) show the ferroelectric polarization loop (P-E) for pure BFO and BFO/CFO heterostructures thin films grown on substrate STO (111) buffered with a very thin conducting layer of SrRuO$_3$ at 100 Hz. The BFO-CFO thin film exhibits the unsaturated ferroelectric behavior with slightly lossy loop behavior at 300K. A little lossy behavior of the P-E hysteresis loop can be attributed to the leakage current where the anion vacancies or fluctuations of valance electron of metal ions lead to electronic conduction [175, 371].
Figure 6-5: Polarization versus applied electric field at room temperature for (a) BFO-STO (111) and (b) BFO/CFO/STO (111) films respectively.

Ferroelectric properties of heterostructures are found to be enhanced in compare with pure BFO thin films deposited in similar condition. The improvement of ferroelectric property for BFO/CFO thin film is attributed to the coupling between BFO and CFO layers[120, 123, 124, 126, 372]. The calculated value of spontaneous polarization ($P_s$), remnant polarization ($P_r$) and the coercive field ($E_c$) of thin films at room temperatures is shown in table 1.

6.4 Conclusions

In conclusion, multilayers of BFO and CFO heterostructures thin films were successfully grown on SrTiO3 (111) substrates using pulsed laser deposition technique. XRD pattern of the films clearly indicates the two separate phases of BFO and CFO and these films are found to be highly textured along the direction of substrate plane. The observed
ferromagnetic properties in BFO/CFO heterostructures thin films could be due to the presence of CFO as a separate phase embedded in BFO matrix. The coercive fields of BFO/CFO on STO (111) film is found to be very high as compared to BFO/STO (111) film. The BFO/CFO thin film exhibits the unsaturated ferroelectric behavior at room temperature. The frequency dependent dielectric constant and dielectric loss at different temperature are systematically investigated. The temperature dependent dielectric constant and dielectric loss for BFO/CFO/STO (111) thin films at various frequencies is also studied. The room temperature multiferroic properties of BFO/CFO/STO (111) thin films are found be enhanced as compare to pure BFO/STO (111) thin film.