CHAPTER 3

GROWTH OF BiMnO$_3$ THIN FILMS ON $n$-Si(100) AND $n$-Si(111) SUBSTRATES

3.1 INTRODUCTION

BMO is one of the few materials recently shown to be multiferroic and highly distorted perovskite structured material, which has been the focus of recent attention because of its potential for technological applications (Baettig et al 2007; Eerenstein et al 2005b; Moreira dos Santos et al 2002b). In BMO, FM arises from Mn$^{3+}$ ions while FE arises from Bi$^{3+}$ ions. The ferromagnetic and ferroelectric transition temperatures of BMO system are 105 K and 770-775K and their saturation magnetic moment and polarization are 3.6 $\mu_B$/Mn and 0.1 $\mu C$/cm$^2$ respectively (Yang et al 2009).

Recent structure determinations (Atou et al 1999; Moreira dos Santos et al 2002a) have found a noncentrosymmetric $C2$ space group, which permit the existence of ferroelectricity. However, bulk BMO can only be synthesized at high pressures and high temperatures (Moreira dos Santos et al 2004), making it a difficult material for research.

For device applications, maximization of the controllable multiferroic properties is necessary at and above RT. Especially ferromagnetic and ferroelectric properties of BMO films have rarely been reported as they have serious problems of low ferromagnetic $T_c$ and high leakage current at RT resulting in the impossibility of ferroelectric measurements (Belik et al 2007). It is well known that the properties of thin films can be widely tuned by varying the substrate material or substrate orientation. To establish the properties better, BMO thin films are grown on two different crystalline ($n$-
type Si(100) and n-type Si(111)) substrates. The Si substrate has been chosen because of its ease commercial availability and low cost. The optimization of growth conditions has led to room temperature FM and FE in the BMO system.

3.2 EXPERIMENTAL CONDITIONS

BMO thin films have been grown on n-type Si(100) and n-type Si(111) substrates by RF magnetron sputtering at an operating frequency of 13.56 MHz. The substrates are cleaned by successive rinses in ultrasonic baths of distilled water, acetone and ethanol and then blown with dry air before being loaded into the chamber. Ceramic (Bi-rich) targets are prepared by a solid-state reaction route from the stoichiometric mixture of Bi$_2$O$_3$ (99.99% of purity) and MnO$_2$ (99.98% of purity) powders. The prepared target and the substrate are loaded inside the chamber which is evacuated to the base pressure of 1×10$^{-6}$ mbar. The deposition process starts with pre-sputtering (about 20 minutes) to avoid chamber pollution and target poisoning. The sputtering is carried out for 45 minutes under Ar atmospheric pressure of 0.001 mbar. The substrate temperature, RF power and target-substrate distance have been maintained constantly at 600 ºC, 60W and 5cm respectively throughout the film growth.

The crystalline structure of the BMO films is examined using Rigaku (D/Max ultima III) X-ray diffractometer with CuK$_a$ radiation. Microstructures of the films are observed using SEM (JEOL, JSM – 6390LV) and AFM (Bruker Dimension scanasysts, ICON). The magnetic properties of the films have been obtained using Lakeshore 7404 VSM at RT. For the electrical measurements, the Au top electrodes with the typical area of 0.196 x 10$^{-2}$ cm$^2$ are deposited. The dielectric constant and dielectric loss of these films are measured by using precision LCR meter (Agilent 4284A). The P-E
hysteresis loops of the films are measured using ferroelectric test system (Radiant Technologies RT-66A).

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Phase Analysis

The phase purity and crystal structure of the grown films have been analyzed by XRD. Figure 3.1 shows the XRD pattern of BMO films grown on Si(100) and Si(111) substrates. The diffraction peaks have good agreement with standard JCPDS file (#894544). They reveal that the films possess monoclinic structure and are free from the formation of any other secondary phases. The sharp peaks with low full width at half maximum indicate the good crystallinity of the films with larger grains.

Further, the films grown on Si(100) substrate are highly crystalline due to the films lower lattice mismatch with the substrate. The result shows that the substrate surface plays a key role in determining the crystalline quality and crystallographic form of the films. The cell parameters of the films have been calculated and given in Table 3.1, which are closely comparable to the standard values: \(a = 9.532\,\text{Å}, \, b = 5.606\,\text{Å} \) and \(c = 9.853\,\text{Å}\). The crystallite size and strain of the films are calculated from Williamson and Hall (W-H) plot (Yogamalar et al 2009). W-H equation for Cauchy-Lorentzian is given by

\[
\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta
\]

where \(D\) is the crystallite size, \(\lambda\) is the X-ray wavelength (1.5406Å), \(\theta\) is the diffraction angle, \(k\) is the shape factor taken as 0.9 and \(\varepsilon\) is the strain induced in the film. \(\beta_{hkl}\cos\theta = \frac{c\lambda}{D} + 2\varepsilon\sin\theta\) W-H plot as shown in Figure 3.2 is drawn between 4sin\(\theta\) on x-axis and \(\beta_{hkl}\cos\theta\) on y-axis.
From the linear fit to the data, the average crystallite size and strain of the prepared films are extracted from the inverse of the intercept at the y-axis and slope respectively. These values also show that the films grown on Si(100) substrate have better crystalline nature than that of those developed on Si(111). The Texture Coefficient (TC) represents the texture of a particular plane, the deviation of which from unity implies the preferred growth
Quantitative information concerning the preferential crystallite orientation obtained from the $\text{TC}_{(hkl)}$ is expressed by

$$
\text{TC} \ (hkl) = \frac{I_{(hkl)} / I_{r(hkl)}}{[(1/n)\sum I_{(hkl)} / I_{r(hkl)}]}
$$

(3.2)

where $I_{(hkl)}$ indicates that the relative intensity of the peak corresponds to the (hkl) plane, $I_{r(hkl)}$ is the intensity of the reference diffraction pattern (JCPDS No. 894544) and $n$ is the reflection number. The higher value of the TC indicates the preferred orientation of the films along that diffraction plane. This means that the increase in the preferred orientation is associated with the increased number of grains along that plane.

**Table 3.1 Geometric parameters of BMO/Si(100) and BMO/Si(111) films**

<table>
<thead>
<tr>
<th>Film</th>
<th>Lattice constants (Å)</th>
<th>Cell volume ($\text{Å}^3$)</th>
<th>Crystallite size (nm)</th>
<th>(312)-Texture coefficient</th>
<th>(312)-Volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMO/ n-Si(100)</td>
<td>9.473</td>
<td>5.615</td>
<td>9.849</td>
<td>491.28</td>
<td>62</td>
</tr>
<tr>
<td>BMO/ n-Si(111)</td>
<td>9.422</td>
<td>5.622</td>
<td>9.807</td>
<td>488.30</td>
<td>38</td>
</tr>
</tbody>
</table>

The TC values for all the observed peaks have been calculated using the Equation 3.2. It is observed that the value of TC is higher for the peak of (312) which indicates the preferred orientation of the films along the (312) diffraction plane than that of the other planes. Further, it is observed that the film grown on Si(111) substrate has lower degree of preferential orientation along (312) plane when compared to the film grown on Si(100). The percentage of volume fraction of the BMO films is also calculated from Equation (3.3).
\[
V_i = \left[ \frac{\sum_{i=1}^{n} I^{(hkl)} / I^{r(hkl)}}{I^{(hkl)} / I^{r(hkl)}} \right]
\] (3.3)

The results reveal that the higher number of grains in BMO/Si(100) film is oriented along (312) direction than that of the BMO/Si(111) film due to the lower value of lattice mismatch.

### 3.3.2 Surface Analysis

The surface morphology of the BMO films has been examined by AFM analysis. 2-D and 3-D topographical images of the films are shown in Figure 3.3. The root mean square (rms) roughness (\(R_q\)) over a scan area (row x column: 256 x 256) of the BMO films deposited on Si(100) and Si(111) substrates are observed to be 3.55 nm and 0.8 nm respectively. It has been seen that the roughness value of the BMO/Si(100) film has higher value than that of the BMO/Si(111) film, which is due to the growth of crystallites. Moreover, it is inferred that the roughness increases with the increase in crystallite size (observed from XRD).

### 3.3.3 Elemental Analysis

Quantitative elemental composition of the films analyzed using EDAX indicates the formation of BiMnO\(_3\) phase on both the substrates with good stoichiometry as shown in Figure 3.4. The absence of the other elemental peaks in EDAX spectra implies that the prepared samples are in better quality. The result shows that the ratio of chemical elements Bi:Mn is approximately 1.4:1. This discrepancy in ratio of Bi and Mn elements is possibly due to the lesser desorption of Bi ions during the film growth process. The observed peaks at 2.42, 0.64, 5.90 and 0.52 keV are corresponding to the spectral lines of Bi-M\(_\alpha\), Mn-L\(_\alpha\), K\(_\alpha\) and O-K\(_\alpha\) respectively, confirming the presence of Bi,
Mn and O elements in the film and the absence of the impurity atoms. The atomic percentage of the elements present in the film has been given as insets of Figure 3.4.

Figure 3.3 AFM images of BMO/Si(100) [(a), (b)] and BMO/Si(111) [(c), (d)] films

Figure 3.4 EDAX spectra of (a) BMO/Si(100) and (b) BMO/Si(111) films
3.3.4 Magnetic Properties

Magnetic properties of the BMO films have been studied using VSM at RT. Figure 3.5 shows the magnetic field versus magnetization (M-H) curve for the BMO films grown on Si(100) and Si(111) substrates without subtracting the diamagnetic behaviour of the substrates. It is evident from the M-H curves that both the films exhibit ferromagnetic nature at RT. However, the BMO film grown on Si(100) substrate shows higher magnetization ($M_s = 395 \text{ emu/cc}$) than those developed on Si(111), which is possibly due to higher crystallinity of the film caused by less lattice misfit. These results have good agreement with the results obtained from XRD.

<table>
<thead>
<tr>
<th>Film</th>
<th>$M_s$ (emu/cm$^3$)</th>
<th>$M_r$ (emu/cm$^3$)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMO/$n$-Si(100)</td>
<td>395</td>
<td>208</td>
<td>305</td>
</tr>
<tr>
<td>BMO/$n$-Si(111)</td>
<td>204</td>
<td>87</td>
<td>157</td>
</tr>
</tbody>
</table>

Ferromagnetic properties of the films such as $M_s$, $M_r$ and $H_c$ are measured and given in Table 3.2. These results are similar to that of the results obtained by (Yang et al 2009). Moreover, the observed low magnetization behaviour of BMO/Si(111) film is due to the presence of $V_{Bi}$ that locally disturbs the complex orbital ordering essential for the long range ferromagnetic order in BMO (Moreira dos Santos et al 2002a).

3.3.5 Dielectric Properties

Variation of dielectric constant and dielectric loss as a function of frequency for BMO films measured at room temperature is shown in Figure 3.6. It is seen that the dielectric constant is very high at low frequency and it decreases with the increase in frequency.
Figure 3.5 M–H hysteresis loops of BMO/Si(100) and BMO/Si(111) films

Figure 3.6 Frequency dependent (a) dielectric constant and (b) dielectric loss of BMO/Si(100) and BMO/Si(111) films

Figure 3.7 Ferroelectric hysteresis loops of BMO/Si(100) and BMO/Si(111) films
At low frequency, the excitation of bound electrons, lattice vibration, dipole orientation and space charge polarization are active (Pan & Zhang 2006). These properties suggest that the dielectric constant strongly depends on the frequency of the applied field which is common in the ionic system (Rao & Smakula 1966). This very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and electro-optic devices.

The BMO film grown on Si(100) substrate has higher value of dielectric constant ($\varepsilon_r \sim 323$) than that of the film developed on Si(111) substrate ($\varepsilon_r \sim 289$) at 30 kHz, which is due to the decrease in the concentration of intrinsic defects ($V_{Bi}$), high crystallinity and less lattice misfit strain. This is very well affirmed by the present XRD and VSM results. Dielectric loss is the dissipation of energy through the movement of charges in an alternating electromagnetic field. The value of dielectric loss for both the BMO films is found to be $\sim 0.4$.

### 3.3.6 Ferroelectric Properties

The ferroelectric property of the materials depends on the chemical composition and orientation of the grains in the films. The typical polarization versus electric field (P-E) loops are measured for the BMO films grown on both the Si(100) and Si(111) substrates as depicted in Figure 3.7. The results clearly convey that the films have ferroelectric nature at RT. The $P_s$, $P_r$ and $E_c$ values are measured at 4V and listed in Table 3.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BMO/ $n$-Si(100)</th>
<th>BMO/ $n$-Si(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_s$ ($\mu$C/cm$^2$)</td>
<td>1.55</td>
<td>1.16</td>
</tr>
<tr>
<td>$P_r$ ($\mu$C/cm$^2$)</td>
<td>0.35</td>
<td>0.19</td>
</tr>
<tr>
<td>$E_c$ (kV/cm)</td>
<td>39</td>
<td>12</td>
</tr>
</tbody>
</table>
The small $P_r$ values are observed in both the BMO films due to the electrical leakage in the films which is possibly because of low thickness. This leakage current will be reduced during device fabrication by adding buffer layers on both side of the films as achieved by (Son et al 2010). The BMO/Si(100) film shows better ferroelectric property than that of BMO/Si(111) film due to increase in the preferential orientation along (312) plane indicating the growth of grains, i.e. increased crystallinity.

3.4 CONCLUSION

BMO thin films are deposited on n-type Si(100) and Si(111) substrates by RF magnetron sputtering. The effect of the substrate surface on the film properties such as structural, morphological, elemental, magnetic and electrical properties have been investigated. The XRD analysis shows that the BMO films are crystallized in monoclinic structure and the film grown on Si(100) substrate has better crystallinity. The atomic percentages of the elements present in the BMO films obtained from EDAX measurement show the sufficient stoichiometry of the compound. The surface roughness of the BMO films is calculated using AFM analysis.

The dielectric studies reveal that both the BMO films acquire higher value of permittivity at lower frequency and remain constant at higher frequencies. Further, they show that the BMO film grown on $n$-type Si(100) substrate has higher value of relative permittivity and low dielectric loss than that of the other film. The VSM and ferroelectric studies illustrate that the room temperature FM and FE of the films and the film grown on Si(100) substrate exhibits better properties than those grown on Si(111). All the studies clearly confirm that $n$-type Si(100) substrate is much suitable for the deposition of BMO films for achieving the good magnetic and electrical properties.