CHAPTER 6

GROWTH AND CHARACTERISATION OF SINGLE AND DOUBLE LAYER $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ THIN FILMS BY IBS TECHNIQUE

6.1 INTRODUCTION

There has been a renaissance of research after the discovery of colossal magneto resistance due to the astonishing magnetic and electrical properties in perovskite type manganese oxides. In the Ruddleson-popper series $(\text{A}_{1-x}\text{B}_x)\text{MnO}_3$ when part of trivalent ion (A=La, Pr, Nd, Sm, Gd) is substituted by bivalent alkaline earth ions (B=$\text{Sr}^{2+}$, $\text{Ba}^{2+}$, $\text{Ca}^{2+}$) it induces ferromagnetism due to double exchange mechanism. To explain this mechanism a theory of double exchange was developed by Zener (1951). Among the ferromagnetic series a great deal of attention has been focused on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ owing to its low resistivity and high Curie temperature ($T_c$) which provides a high potentiality in the application of magnetic devices such as magnetic recording, actuators and sensors (Prabhakaran et al 2002). It is well known that the physical properties of these materials depend on sample preparation methods. In the past several years variety of manganates have been fabricated and studied in the form of polycrystalline powders, thin films and single crystals (Bie et al 2003). There are some reports, which speculate that the magnetoresistance property appears in the samples, having large grain size. In order to realize the physical properties upon size reduction, it is essential to fabricate a good quality
thin films with low surface roughness. Hence most of the earlier works was focused on thin films rather than bulk forms (Attfield 2001).

There are wide number of methods to fabricate $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) thin films such as molecular beam epitaxy (MBE), chemical vapour deposition (CVD), pulse laser deposition (PLD), sol-gel and ion beam sputtering (IBS) techniques. Although there is no significant difference in the general features of crystalline forms manganite single crystals are highly useful for structural and morphological studies. There are some reports on the single crystal growth of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ by flux and floating zone methods. But there exists some difficulties in single crystal growth especially at higher temperatures (greater than 1000 °C). Hence in this study the thin film processing to grow good quality $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is opted. Among the different thin film fabrication methods, IBS technique offers higher versatility at low temperature fabrication of thin films to achieve smooth surface (Rauschenbach et al 2003). Moreover this technique, due to low temperature synthesis, yields smaller grains and also produces homogeneous thin films with high purity, precise composition control and homogeneous formation of thin film. To realize a good quality multilayer stacking thin films comprising of high temperature superconductors and CMR (colossal magneto-resistance) manganites to exploit tunable microwave filter devices, it is essential to fabricate thin films with smooth surface. The increase of roughness will increase the inter-diffusions between the substrate and film (Badica et al 2003), which in turn results in poor crystalline quality. To eliminate these problems low temperature processing is the promising technique. Due to the shortage of thermal energy it is difficult to grow good quality thin film at low temperature. The growth of crystal in thin film starts with layer by layer by the mobility of ions on the surface aided by their kinetic energy and the substrate temperature. It is noteworthy that strong
oxidants and excited energy are desirable for the perovskite thin film growth at lower temperatures and low ambient pressures (Tada et al 2001). Hence during the growth oxygen species such as oxygen molecules (ML) or oxygen plasma (PL) are supplied to the substrate.

It is well known that the substrate temperature ($T_s$) and oxygen partial pressure ($P_o$) are the essential parameters, which influence the orientation and structure of the films (Singh 2002). In the IBS grown films the surface roughness can easily be tuned by varying the $T_s$ and $P_o$. Experimentally it has been manifested that the magneto-resistance property can be tuned via changing the grain size and the CMR property exists only in the large grain samples. For example in the case of sol-gel technique the grain size can be tuned by varying the annealing temperature to explore the magneto-resistance behaviour. Hence in order to understand the effect of grain size on surface roughness, a detailed study is necessary. The knowledge of correlation between structure and $T_s$ and its oxygen molecules (ML) or oxygen plasma (PL) dependence allows to search for the more adequate composition in order to tailor their magnetic response. Understanding the growth mechanism at fixed substrate temperature ($T_s$) and oxygen partial pressure ($P_o$) for $La_{0.7}Sr_{0.3}MnO_3$ is important for possible application of this material. For this reason the present study was aimed at the preparation of series of samples with same composition for different oxygen partial pressures ($P_o$) and substrate temperature ($T_s$) in order to examine the systematic variation of growth mechanism as a function of oxygen molecules (ML) or oxygen plasma (PL).

For realizing tunable microwave filters ferrite garnets were used as substrates for the growth of HTS materials. However there are some drawbacks in using this substrates as they are not crystallographically compatible with high
\( T_c \) materials, and hence garnets substrates require high magnetic field to tune the device. Hence it was necessary to search for alternate material. It has been realized that CMR perovskites appear to be an excellent candidate for realizing tunable HTS filters owing to their crystalline compatibility with YBCO (Wosik et al 1999). Further it has been reported that heterostructures comprising of CMR/HTSC is highly useful for novel spin devices. Hence there has been a renewed interest on the fabrication of stacked multilayers encompassing high \( T_c \) superconductors and colossal magnetoresistance material. It is well known that in HTS material, the carriers are paired in the form of cooper pairs, whereas in the CMR material due to semi-metallic character it contains spin-polarized carriers. Therefore CMR/HTSC multi-stacked layer seems to be ideal for studying the interplay between superconductivity and magnetism. In this case the similarity in crystal structure and epitaxial compatibility leads to the interfacial structure unchanged during the fabrication processes of multi-stacked thin films (Bie et al 2003).

In order to optimise the growth condition of double layer \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_3 \), the growth was performed on \( \alpha \)-phase and mixed phase such as \( \alpha + \text{c} \) phase and \( \text{c} + 110 \) phase of YBCO. Initially YBCO layers were grown on MgO substrates and subsequently LSMO film was grown over the YBCO layer by IBS technique. Despite many successful efforts on fabrication of double layer thin film of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_3 \), there is no detailed report concerning the influence of growth parameters on surface roughness and crystalline quality. We have successfully evaluated the potential of plasma effect on the growth and surface roughness of single and double layer \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_3 \) grown over MgO/LAO substrates and YBCO layer by systematically varying the substrate temperature (\( T_s \)) and oxygen partial pressure (\( P_o \)) by supplying the oxidant species either oxygen molecules (ML) or oxygen plasma (PL). It has been
manifested that the crystal structure and morphology of the thin films which are determined not only by the method of fabrication, but also by the deposition parameters. In this chapter, the $P_0$ and $T_s$ dependence of crystallinity and surface roughness of molecule assisted and plasma assisted thin films grown on LAO/MgO substrates and double layer structure grown over YBCO has been reported.

6.1.1 Selection of substrate

Although many reports speculate the growth of thin films on different substrates, the selection of optimum one depends on the material to be grown and method of synthesis and hence the selection of particular substrate is one of the essential criteria in the thin film fabrication. Commonly used substrates are LaAlO$_3$, MgO, ZrO$_2$, SrTiO$_3$ and sapphire in [100], [110] or [111] orientations. As the thermal expansion coefficients of oxides are closer to those of the substrates, oxide films grown over such substrates are expected to be crack free. MgO and LAO substrates were widely used for the thin film fabrication of perovskite materials such as CMR manganites and high $T_c$ cuprates (Tanaka et al 2002) owing to its high stability and low interdiffusion between the substrate and the epilayer. While compared with LAO the suitability of MgO substrates are masked by its lattice mismatch, as shown in Figure 6.1. Although MgO shows lattice mismatch, it is known that magnetic thin films can be grown successfully. Thus lattice matching between the substrate and film is the first and foremost criteria to be dealt with in determining the suitability of the substrate. A detailed study regarding the fabrication and characterisation processes is given in the following sections of this chapter.
Figure 6.1 (a) Lattice matching for LAO (b) Lattice mismatch for MgO
6.2 EXPERIMENTAL

La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films have been grown by Ion beam sputtering (IBS) technique by varying the substrate temperature and oxygen partial pressure ($P_o$). In this technique the target is sputtered by argon ion beam and the sputtered particles are deposited on the heated substrates of LAO and MgO simultaneously. The important feature of IBS technique is that the deposition rate is extremely low (0.02-0.08 Å/s) compared to MBE growth (0.1 - Å/s) and the growth parameters are tabulated in Table 6.1 and Table 6.2. In the present work we used 4 keV Ar$^+$ ion because of its low cost and high sputtering yield (Chu et al 2002). For the growth of La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film a stoichiometric La-Sr-Mn-O bulk ceramic target was fixed using silver paint to the holder mounted at a distance of 40 mm from the substrate. As the substrate is farther from the target, the sputtered atoms undergo scattering before reaching the substrate and lose more kinetic energy (Cheng et al 2003). The substrates were placed parallel to the heater assembly (lamp source) and heated during the fabrication process and the substrate temperature was continuously monitored using a thermocouple. Before deposition the substrate surface was cleaned chemically with acetone. A more detailed description of the growth technique is explained in chapter-1.

During the growth, oxygen molecules (ML) or oxygen plasma (PL) were supplied to the LAO/MgO substrate and YBCO layer. For the growth of double layer LSMO, initially the YBCO films were grown on MgO substrate by varying the growth parameters and the as-grown YBCO layer was used for the growth of double layer. The main advantage of IBS technique is that the La$_{0.7}$Sr$_{0.3}$MnO$_3$ film was grown simultaneously on LAO and MgO substrates. The schematic diagram of single and double layer fabrication process of
Table 6.1 Sputtering conditions

<table>
<thead>
<tr>
<th>Substrate</th>
<th>LaAlO$_3$, MgO</th>
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<tbody>
<tr>
<td>Sputtering Ion Beam</td>
<td>Ar$^+$ (dc 4kV)</td>
</tr>
<tr>
<td>Oxidant</td>
<td>Oxygen molecule (ML)</td>
</tr>
<tr>
<td></td>
<td>Oxygen plasma (PL)</td>
</tr>
<tr>
<td></td>
<td>(ac 60 Hz, ~1 kV, 9.6 mA)</td>
</tr>
</tbody>
</table>

Table 6.2 Deposition conditions

<table>
<thead>
<tr>
<th>Target</th>
<th>La / Sr / Mn / O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature ($T_s$)</td>
<td>750°C – 700°C</td>
</tr>
<tr>
<td>Oxygen partial pressure ($P_o$)</td>
<td>1.5 m Torr – 0.5 m Torr</td>
</tr>
<tr>
<td>Deposition time</td>
<td>6h</td>
</tr>
<tr>
<td>Anneal</td>
<td>400°C, 20 min</td>
</tr>
</tbody>
</table>
La$_{0.7}$Sr$_{0.3}$MnO$_3$ is shown in Figure 6.2 and 6.3 respectively. The oxygen plasma is produced by discharging the oxygen gas into plasma source at the discharge voltage ($V_d$) of $\approx 1$ kV and discharge current ($I_d$) of 9.6 mA at 60 Hz. For the molecular supply, oxygen gas was emitted from the same plasma source without discharge. The oxidants PL or ML were supplied parallel to the substrate during the fabrication process. For a chamber base pressure of $1 \times 10^{-5}$ Torr the average oxygen partial pressure $P_o$ was varied between 0.5 to 1.5 mTorr and the substrate temperature was fixed between 700-750 °C. After the deposition process the films were annealed at 400 °C for 20 min and then slowly cooled to room temperature.

![Figure 6.2 Schematic diagram of single layer LSMO fabrication](image-url)
Figure 6.3 Growth of stacked La$_{0.7}$Sr$_{0.3}$MnO$_3$

The as-grown film thickness is found to be around 1000 Å and the results of La$_{0.7}$Sr$_{0.3}$MnO$_3$ grown with variable $P_0$ and $T_s$ for molecular assisted and plasma assisted thin films using the same target grown on MgO / LAO and YBCO layers were compared. The structural study of single layer La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film and stacked La$_{0.7}$Sr$_{0.3}$MnO$_3$ was performed by X-ray diffraction analysis using Philips X'Pert system on 0-20 geometry using CuKα radiation. From the FWHM of 0-20 peaks the intra-grain crystallinity of the as-grown samples was estimated. The as-grown single and double layer La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin film surfaces have been characterized by AFM in order to study the relationship between the surface morphology and the growth parameters and also surface roughness of the films.
6.3 CHARACTERISATION STUDIES

6.3.1 X-ray diffraction analysis

The X-ray diffraction patterns of the as-grown films at various oxygen partial pressures ($P_o$) for LAO and MgO substrates with oxygen molecules (ML) and oxygen plasma (PL) are shown in Figure 6.4 and Figure 6.5. The XRD peak intensities are normalized to LAO and MgO peak intensity. The observed (00l) diffraction peaks manifest the sample orientation with the c-axis parallel to the substrate. It is evident that the as-grown films crystallize in single phase without any impurity phases showing sharp characteristic peaks of cubic perovskite.

Figure 6.6 shows the X-ray diffraction patterns of LSMO on a-axis YBCO. Figure 6.7 and Figure 6.8 show the growth on a + c phase at 0.5 and 1.5 mT oxygen partial pressure. Figure 6.9 shows the growth on c + (110) phase of YBCO.

In the X-ray diffraction patterns of (001) and (003) peaks of LSMO for ML and PL assisted growth are similar as shown in Figures 6.4 and 6.5. To provide deep insight into the crystalline quality, the average FWHM of (001) and (002) peaks as a function of oxygen partial pressure ($P_o$) for the films grown on LAO and MgO substrate at Ts = 700 °C and 750 °C are plotted in Figure 6.10. The small FWHM is an indicative of epitaxial quality of grown LSMO thin films.
Figure 6.4  XRD pattern of LSMO grown at different $P_o$ on LAO with oxygen molecules and oxygen plasma
Figure 6.5 XRD pattern of LSMO grown at different $P_o$ on MgO with oxygen molecules and oxygen plasma
Figure 6.6 XRD pattern of ML assisted LSMO on a-axis YBCO at $T_s = 750 \, ^\circ\text{C}$ and $P_0 = 0.5 \, \text{mTorr}$
Figure 6.7 XRD pattern of PL assisted LSMO on a+c phase YBCO at $T_s = 750$ °C and $P_0 = 0.5$ mTorr
Figure 6.8  XRD pattern of ML assisted LSMO on a+c phase YBCO at $T_s = 750 \, ^\circ\text{C}$ and $P_o = 1.5 \, \text{mTorr}$
Figure 6.9 XRD pattern of PL assisted LSMO on c+110 YBCO phase at $T_s = 750 \, ^\circ\text{C}$ and $P_0 = 1 \, \text{mTorr}$
Figure 6.10 Average FWHM of (001) and (002) peaks of LSMO vs $P_o$.
6.3.2 Influence of plasma supply on crystallinity

For the plasma assisted thin films, the crystallinity is better for LAO with FWHM = 0.09 compared to MgO for an oxygen partial pressure of \( P_o = 1.0 \) mTorr corresponding to the substrate temperature \( T_s = 750 \) °C. But at lower oxygen partial pressure (\( P_o = 0.5 \) mTorr) the crystallinity is almost same for both the molecule assisted and plasma assisted films with \( T_s = 750 \) °C for the samples grown on LAO and MgO substrates. This apparently indicates that the influence of plasma was not effective rather the film growth is governed by thermodynamic process in both the series of molecular and plasma at low partial pressures (\( P_o = 0.5 \) mTorr). During the deposition process \( P_o \) plays a vital role in the growth of thin films. It is observed that the value of the FWHM for the plasma assisted thin films grown over MgO substrate shows a maximum at \( P_o = 1.5 \) mTorr and as a contrary a minimum value has been obtained at \( P_o = 1.0 \) mTorr for the thin film grown over LAO substrate.

The results indicate that the crystallinity of the plasma assisted plane distance of the films is low at 1.5 mTorr on MgO, while it is improved at 1 mTorr for LAO substrate. During the PL supply the strain energy and the surface energy are reduced. This is supported by the experimental facts that the crystallinity and surface morphology are improved by plasma. The better crystallinity on LAO may also be attributed to minimum lattice mismatch compared to MgO as shown in Figure 6.1.

6.3.3 Influence of molecular supply on crystallinity

The difference in FWHM for MgO and LAO is explained in two ways. Generally in IBS technique the film growth is influenced by thermal energy and sputtered particles energy. This total energy changes with varying
oxygen partial pressure $P_0$, which in-turn leads to changes in the crystallinity. This can be substantiated from the results obtained by AFM study. With increasing the $P_0$ or supplying the plasma, the multiple collisions are expected to be enhanced and the particle diameter is increased. It will be difficult for the expanded particle to migrate on the film surface. However this effect may not be so effective because the film surface is usually very smooth at the higher $P_0$ region and especially it is much more smoothened by plasma assisted growth compared with the molecular assisted thin films.

It is evident from Figure 6.10 that at low $P_0$ (0.5 mTorr), there is no much difference in crystalline quality for the plasma and molecule assisted thin films grown on LAO and MgO substrates. It is known from the published data that the $P_0$ influences the motion of sputtered atoms since in the sputtering process there is some energy loss during their transit to the substrate due to collisions with ambient gas atoms and sputtered atoms. Therefore it is well-understood that the collision decreases with $P_0$, so that there will be a decrease in the mean free path of sputtered atoms, which provide sufficient energy to transit the substrate resulting in the nucleation and growth of the films (Lee et al 2003 and Wang et al 2002). Thus by increasing the $P_0$, the crystalline quality is improved gradually on LAO and for MgO substrate the crystalline quality degrades for higher oxygen partial pressure ($P_0 = 1.5$ mTorr) compared to plasma assisted films. Molecule assisted film shows low crystalline quality, which is attributed to the shortage of oxidation power.

The X-ray diffraction patterns shown in Figure 6.6 clearly depict the decrease of intensity of $Y(200)$ and $Y(100)$. Further the patterns infer that La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films are not grown on $a$-phase YBCO at a substrate temperature of $T_s = 750$ °C for molecule assisted film at $P_0 = 0.5$ mTorr.
Peak positions are nearly the same but the peak intensities are different. Also Lao.7Sr0.3MnO3 film was not formed on a + c phase of YBCO at 750 °C for plasma and molecule assisted growth at P0 = 0.5 and 1.5 mTorr as shown in Figure 6.7 and Figure 6.8. This result infers that a and a + c phases of YBCO are not suitable for the growth of high quality stacked LSMO on YBCO layer because of the mismatch in the growth conditions. However from Figure 6.9 it is evident that LSMO thin film has been successfully grown on c + (110) phase YBCO at 750 °C for plasma assisted growth at P0 = 1 mT. The increase of intensity and the presence of LS (002) and LS (001) peaks substantiates the successful fabrication of LSMO in these deposition conditions. Hence it is concluded that double layer LSMO can be grown on c + (110) YBCO for plasma assisted growth at Tg = 750 °C and P0 = 1 mTorr by Ion beam sputtering technique.

6.3.4 Atomic force microscopy study

Atomic force microscope (AFM) is an advanced technique, which is capable of providing atomic scale images of the surface. AFM provides wide measurement range in X-Y direction with a high resolution of Z direction. It is a non-destructive technique and offers the possibility of imaging the surface without any surface treatment. AFM technique is a versatile technique for the study of surface morphology and powerful tool for surface imaging at the sub micrometer level (Falaras et al 2002). In this work, LSMO samples were examined using AFM (Digital Instruments) operated in the static contact mode at room temperature. Si cantilever with integrated tips were used for making observation. Though quite a lot of work has already been done on the fabrication of single and double layer thin films, the influence of the growth parameters on the surface roughness is still unclear. In the present study AFM
results substantiate the influence of plasma effect (PL) on the surface roughness, which includes a 3D perspective of surface topography. The plasma assisted and molecule assisted single and double layer La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films show significant difference as evidenced by AFM topograph shown in Figure 6.11 and Figure 6.12.

Since the growth mechanism for ML and PL assisted La$_{0.7}$Sr$_{0.3}$MnO$_3$ films are different, the influence of steps might also be different. On MgO surface the reconstruction induces a higher roughness, which is responsible for the poor quality of the films. Also with the increase of surface roughness the inter-diffusion between substrate and film increases. The surface roughness value has also been calculated from the AFM images. For MgO substrate, the surface roughness is low (3.570 nm) with molecule assisted ($P_o = 0.5$ mT) and higher surface roughness value (15.372 nm) is obtained for $T_s = 700$ °C and $P_o = 1$ mTorr. At high $T_s = 750$ °C ($P_o = 0.5$ mTorr) there is no much difference in the ML and PL assisted thin films. It is noteworthy that at $P_o = 1.5$ mTorr, there is no pronounced effect of oxidants. The low surface roughness at $T_s = 750$ °C ($P_o = 1.0$ mTorr) for plasma assisted thin films is due to the excess oxidation power.

In the case of LAO substrate, lower surface roughness is obtained for PL assisted film (2.691 nm) grown at $T_s = 750$ °C and $P_o = 1.0$ mTorr and surface roughness is higher for PL assisted thin film (18.541 nm) grown at $T_s = 700$ °C $P_o = 1.0$ mTorr. Therefore it is inferred that the supply of plasma influences the surface roughness of the as-grown films. AFM picture of the double layer LSMO is shown in Figure 6.13. From the figure it is evident that for the growth of stacked LSMO thin films with smooth surface, low surface roughness of YBCO is necessary.
Figure 6.11 AFM topograph of LSMO for ML assisted and PL assisted film grown on MgO.
Figure 6.12 AFM topograph of LSMO for ML assisted and PL assisted film grown on LAO.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RMS Value 1</th>
<th>RMS Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C 10 x 10 μm</td>
<td>16.858 nm</td>
<td>18.541 nm</td>
</tr>
<tr>
<td>750°C 10 x 10 μm</td>
<td>3.119 nm</td>
<td>2.91 nm</td>
</tr>
<tr>
<td>500°C 10 x 10 μm</td>
<td>6.200 nm</td>
<td>2.865 nm</td>
</tr>
<tr>
<td>500°C 10 x 10 μm</td>
<td>9.583 nm</td>
<td>2.91 nm</td>
</tr>
<tr>
<td>1500°C 10 x 10 μm</td>
<td>6.200 nm</td>
<td>2.865 nm</td>
</tr>
</tbody>
</table>
Figure 6.13 AFM topograph of LSMO grown over YBCO for ML
6.4 CONCLUSION

The single and double layer $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films have been grown on LAO/MgO substrates with YBCO layer by varying the oxygen partial pressure and substrate temperature by supplying different oxygen species (ML and PL). Investigations on the as-grown films on different substrates reveal that the films are smooth and the surface roughness depends strongly on growth conditions and deposition parameters. The improved crystallinity has been confirmed by structural and morphological studies.