In this article it is reviewed on enigmatic electrical and magnetic properties of La(Ba)MnO₃ thin films, useful for tunable microwave filters. As-grown films have well separated insulating to metallic \( (T_p) \) and paramagnetic to ferromagnetic \( (T_c) \) transition temperatures, which can be understood from the phase separation model. The film shows negative magnetoresistance (MR) caused by normal double exchange coupling effect, and positive MR which is interpreted by a magnetostriction effect. The phase separation is caused by crystal strain in the film. By annealing these two temperatures, \( T_p \) and \( T_c \), become more separated, implying a size reduction of ferromagnetic grains. The phase separation scenario can be confirmed by ferromagnetic resonance (FMR) showing doublet signals. The FMR indicates anisotropic phase transition which supports the magnetostriction model. Moreover, the narrow FMR signals suggest high spin ordering and good crystallinity.

Key words: Manganite LBMO Thin Films, Ion Beam Sputtering, Resistance, Magnetoresistance, SQUID Magnetization, FMR, Phase Separation, Magnetostriction

1. INTRODUCTION

Although oxide materials have been widely utilized since the dawn of humanity, they have only had a minor impact in modern electronics so far. Nevertheless, after the discovery of perovskite oxide High \( T_c \) Superconductors (HTS), the interest in oxide materials grew enormously [1]. This was indeed a turning point for oxide materials, which triggered a huge amount of research on these types of materials. This has resulted in yet another breakthrough, i.e., colossal magnetostrictive manganites, which have the same perovskite crystal structures [2]. Interestingly, even traditional oxide materials such as ZnO, TiO₂ and SrTiO₃ have been gaining a renewed interest, resulting in extremely fine thin film growths of SrTiO₃ and ZnO [3]. These new developments have led to novel approaches in Oxide Electronics, where all-oxide electronics is now emerging, leading to Function Harmonized Oxides (FH-Oxides), where novel functional devices are designed based solely on oxides. Here we introduce two examples of FH-Oxides composed of double layers, and review the peculiar properties of versatile manganites which can be used as one part of double-layer devices.

2. FUNCTION HARMONIZED OXIDES

2.1 Novel p-n junctions

Recently manganites (say, La(Ba)MnO₃ (LBMO)) and ZnO are being widely investigated and thin films with excellent crystallinity of both materials have been grown. When they are combined into a double layer, they may give rise to completely new functional device [4]. LBMO is a p-type semiconductor at higher temperatures due to acceptor (Ba) doping, while ZnO is normally a n-type semiconductor due to intrinsic oxygen vacancy donor. Then the double layers should lead to atypical p-n junctions. The junction has a function of UV-light enhanced detection because ZnO has a wide band-gap (3.4 eV) then UV-generated high density carriers are injected into diffusion layer. On the other hand, LBMO has enigmatic properties due to colossal magnetoresistance. Then I-V characteristics of the p-n junction can be sensitively modified by magnetic field as well as temperature. However, such stacking is not so easy to grow due to different crystal structures of the two materials, i.e., LBMO has cubic structure while ZnO has hexagonal structure. Thus investigations of orientation growths are important. This subject of double-layer regarding the enigmatic properties of LBMO is very new and interesting, but it is not involved in this article. It will be reported in a different review article [5].

2.2 Tunable microwave filters

Currently dielectric resonators are used as microwave filters at most mobile phone base stations. Such filters,
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However, have large insertion losses, consequently high power signal amplification is required after the filtering. Furthermore, the skirt performance of the filters is not so good. However, the number of mobile phones is continuously increasing, in addition, the amount of functionalities of the mobile phones is expected to increase considerably in the near future. To keep up with such increasing demands, the filtering problems must be solved. Moreover, downsizing the devices is also an important factor, since there is no space for the large base stations in big cities. Further, if the insertion loss is reduced, it can contribute to energy saving owing to the lower power amplification.

HTS thin films have a great potential for the microwave filters. The fundamental mechanism of the filtering for a primitive strip line filter made of HTS thin film is schematically shown in Fig.1. Surface resistances are very small for HTS, then the insertion loss is extremely small and the skirt performance is improved. The total size can be reduced using excellent cryo-coolers, leading to a possible solution for crowded base stations. Microwaves of different frequencies are filtered by a resonant standing wave. Then, as shown in the figure, the center frequency $F_o$ is selected by the line length $L$ according to eq.(1)

$$F_o = \frac{c}{2L\sqrt{\varepsilon \mu}}.$$  \hspace{1cm} (1)

It should be noted that $F_o$ depends also on dielectric constant $\varepsilon$ and permeability $\mu$ of medium.

Based on HTS microwave filters, an other possible example of FH-Oxides is a tunable microwave filter [6]. Superconducting YBa$_2$Cu$_3$O$_{x}$ (YBCO) and ferromagnetic LBMO can be stacked into a double layer as shown in Fig.2 (a). This is desirable because both have perovskite crystal structures. When a magnetic field $H_a$ is applied, the permeability $\mu$ of the medium ferromagnetic layer is modified, then microwave propagation mode (velocity $v$) in the superconducting layer is modified, leading to shift of resonant center frequency $F_o$ of the microwave according to eq.(1) as schematically shown in Fig.2 (b). Thus we can tune the filter frequency easily by adjusting $H_a$ even after the device is fixed in the base station. Since usually YBCO thin films are grown as a-axis oriented or c-axis oriented structures, then we have investigated the double-layer growths for a/c-YBCO and LBMO systems [7-9]. Nevertheless, in this review we focus on the growth and properties of the LBMO ferromagnetic layer.

An important factor for the ferromagnetic layer is that it must be insulator and ferromagnetic at device working temperatures as shown by the schematic curves for the resistance $R$ and the magnetization $M$ as a function of temperature $T$, in Fig.3. Note that if the ferromagnetic layer is metallic, the microwave is absorbed by high density free carriers of the metal, causing the insertion loss of filter. Yet, it is usually difficult to obtain a ferromagnetic-insulator LBMO since it would violate the DEC (double exchange coupling) model [10]. To satisfy this demand, we tried to deposit LBMO thin films at various deposition conditions. The dependences
of the interesting electrical and magnetic properties of LBMO on the growth and annealing conditions are the main focus of this article. Ideas of phase separation and magnetostriction models are proposed to interpret such enigmatic properties.

3. EXPERIMENTAL

3.1 Thin film fabrication

We selected La$_{0.7}$Ba$_{0.3}$MnO$_3$ as the manganite ferromagnetic layer because its intrinsic Curie temperature $T_c$ is very high. LBMO thin films were deposited on MgO (100) and LaAlO$_3$ (LAO) (100) substrates by ion beam sputtering as shown in Fig. 4 [11,12]. A La-Ba-Mn-O target was sputtered by an Ar$^+$ ion beam. Sputtered particles were deposited on the heated substrates at different substrate temperatures $T_s$. Oxygen molecules (ML) or oxygen plasma (PL) was supplied to the substrates during the deposition at various oxygen partial pressures $P_o$. The crystallinity of LBMO thin films was estimated by the half-width $\Delta \theta_p$ of X-ray diffraction (XRD) peaks. Moreover, some of the samples were annealed at 900°C for 5 hr in 1 atom oxygen atmosphere after the depositions. Thickness of the films is around 100 nm.

3.2 Electrical, magnetic and ferromagnetic resonance measurements

Electrical resistance $R$ of the films was measured at various temperatures $T$ down to 4 K by the four-probe method. Magnetoresistance (MR) was measured under magnetic fields $H_a$ applied perpendicular to the film plane ($H_a \perp$). Magnetization $M$ was measured using SQUID magnetometer for $H_a \perp$. Measurement of ferromagnetic resonance (FMR) was done on the samples for $H_a$ perpendicular to the film plane ($H_a \perp$) and $H_a$ parallel to the film plane ($H_a \parallel$) at various $T$ using microwaves at 9.3 GHz. The FMR signal intensities, resonant fields $H_r$ (line positions) and peak half-widths $\Delta H_r$ were evaluated. Effective magnetizations, $4\pi M_{\text{eff}}$, were calculated for $H_a \parallel$ and $H_a \perp$ using the corresponding resonant fields of $H_r \parallel$ and $H_r \perp$. We use the resonance equations of Kittel according to Landau-Lifshitz-Gilbert [13]

$$\frac{\omega_r}{\gamma} = \frac{1}{4\pi M_{\text{eff}}} \left( \frac{1}{4\pi M_{\text{eff}}} + H_a \parallel \right)^{-1/2} \quad (\text{for } H_a \parallel). \quad (2)$$

$$\frac{\omega_r}{\gamma} = \frac{1}{4\pi M_{\text{eff}}} \left( 1 - H_a \perp \right) \quad (\text{for } H_a \perp). \quad (3)$$

In these equations, $\omega_r$ is a resonant frequency and $\gamma$ is the gyromagnetic ratio. This $\gamma$ is expressed as

$$\gamma = g\mu_B / \hbar, \quad (h = \hbar / 2\pi),$$

where $\mu_B$ is the Bohr magneton, and for $g$-factor $g = 2.00$ is used to estimate $M_{\text{eff}}$. The magnitudes of $H_r \parallel$ and $H_r \perp$ are defined as a center fields between positive and negative peaks of the derivative signal. The half-width $\Delta H_{pp}$ was evaluated from peak-to-peak field of the derivative signal. When the signal has a doublet peak, the $\Delta H_{pp}$ value has some error. Nevertheless, the magnitude of error can be estimated to be smaller than 20-30% at most.

4. THIN FILM CRYSTALLINITY

Typical XRD patterns are shown in Fig. 5 (a) for LBMO thin films grown on LAO at $T_s=500^\circ$C and (b) for $T_s=750^\circ$C grown on LAO. For both $T_s$, single phase cubic perovskite crystalline films are grown in with (001) orientation. The crystallinity estimated by XRD is particularly good for $T_s=750^\circ$C, with $\Delta \theta_p=0.09$ deg. Remarkably, LBMO films with excellent crystallinity could be grown at various $T_s$ from 750°C down to 650°C on MgO, and even down to 480°C on LAO substrates.
cannot be explained merely by the DEC model. In fact, the insulating (In) to metallic (Mt) transition (In $\rightarrow$ Mt) is observed in the Mt-regime as indicated by two opposite arrows in Fig.6. Thus, the MR was investigated under $H_a$ $= 1$ kOe. The film shows $T_c$ $= 140$ K as indicated by an arrow.

The extended range of high quality LBMO growth for LAO is caused by the different lattice mismatching for MgO and LAO, where the latter has a much better lattice match with LBMO [14-16]. Note that a good crystallinity is crucial for double-layer fabrication, in particular, textured growth. This is a very important subject for double-layer fabrication, i.e., crystalline orientation growth, but this subject is skipped here. It will be reported in ref.[5].

5. RESISTANCE, MAGNETIZATION AND MAGNETORESISTANCE

The experimental plots of $R$-$T$ and $M$-$T$ are shown in Fig.6 (a) and (b), respectively, for the film S-2 deposited on LAO at $T \text{crit}$ $= 750$°C at $P_{\text{crit}}$ $= 0.5$ mTorr with plasma supply (PL). With decreasing $T$, the $R$-$T$ curve shows insulating (In) to metallic (Mt) transition (In $\rightarrow$ Mt) at $T_p$ $= 82.2$ K. This film shows a paramagnetic (PM) to ferromagnetic (FM) transition (PM $\rightarrow$ FM) at a Curie temperature of $T_c$ $= 140$ K. In the double exchange coupling (DEC) model [10] for manganites the In $\rightarrow$ Mt transition should be accompanied by the PM $\rightarrow$ FM transition [17-19]. It indicates that $T_p$ must be closely located to $T_c$ which is real in the bulk manganites. However, $T_p$ does not coincide with $T_c$ in this thin film sample, implying that these transitions in the thin film cannot be explained merely by the DEC model. In fact, in LBMO thin films $T_p$ and $T_c$ can be controlled to a certain extent, although they depend on the deposition and annealing conditions in a complex way [20]. However, interestingly, we could obtain films which are insulating and ferromagnetic in the temperature range $T_p$ $< T < T_c$ (82-140 K), as desired for HTS/Ferromagnetic tunable microwave filters.

Careful inspection of the $R$-$T$ curve, reveals a slight negative-MR effect in the In-regime while positive-MR is observed in the Mt-regime as indicated by two opposite arrows in Fig.6. Thus, the MR was investigated more in detail. The $R$ and MR ratio ($\Delta R$/$R$) are plotted as a function of $H_a$ in Fig.7. In the middle temperature region (100-150 K) of the In-regime, the MR clearly shows the negative-MR which is explained by the DEC. Whereas in the lower temperature region (50-77 K) of the MT-regime, it clearly shows the positive-MR which cannot be explained by the DEC. In order to explain this apparent contradiction with the DEC model we propose to combine it with the “Phase Separation” model [21].

6. PHASE SEPARATION AND MAGNETOSTRICTION

As schematically shown in Fig.8, the film consists of ferromagnetic-metallic (FMt) grains and charge ordered insulating (COI) phases in the middle and low temperature regions. In the DEC the FMt grains have a conventional colossal magnetoresistive nature, then the manganese d-electron states are split into two states, localized $t_{2g}$ and non-localized $e_g$, in the crystal structure as shown in Fig.9. If there are vacant sites of the $e_g$-electron due to hole doping (Ba), the $e_g$-electron can be transferred from one site to the neighboring site.

Fig.6 (a) $R$-$T$ and (b) $M$-$T$ curves for the as-grown S-2 sample on LAO ($T_{\text{crit}}$ $= 750$°C, $P_{\text{crit}}$ $= 0.5$ mTorr, PL) shown in Fig.5. (a) The values of $R$ are plotted under $H_a$ $= 0$ and 4.2 kOe. The $R$ is slightly decreased in the In-regime while it is slightly increased in the Mt-regime under 4.2 kOe as indicated by two opposite arrows. A thicker arrow indicates a position of $T_p$ $= 82.2$ K. (b) The magnetization was measured under $H_a$ $= 1$ kOe. The film shows $T_c$ $= 140$ K as indicated by an arrow.

Fig.7 $H_a$ plots and MR ratio ($\Delta R$/$R$)-$H_a$ plots for the as-grown S-2 sample at various $T$. The film shows negative-MR in the In-regime in the middle temperature region, while positive-MR in the Mt-regime in the low temperature region.
At low temperatures or under high magnetic fields, the localized t$_{2g}$-electron spins are well aligned, then the traveling eg-electron spin is not scattered. This means that the material is ferromagnetic and metallic. On the other hand, at high temperatures or under no (or even small) magnetic fields, the t$_{2g}$-electron spins are strongly fluctuating due to the high thermal energy, then the traveling eg-electron spin is scattered. This means the material is paramagnetic and insulating. Looking back to the MR results at the middle T regime in Fig.7, the resistance $R$ decreases with increasing $H_a$, showing a negative-MR as expected from the DEC model, thus the FMt grains should have the normal manganite nature. However, in other regimes the DEC model cannot explain the results. Namely, the material surely contains the FMt grains but they are surrounded by the COI phase (i.e., phase separation as shown in Fig.8). Thus the electrical properties should reflect not only the nature of the FMt grain but also the mixed nature of FMt and COI.

6.1 Ferromagnetic-Insulating behavior and phase separation

The phase separation in the material should progress with temperature as shown in Fig.10. In the high temperature region ① as shown in Fig.10 (a), it is homogeneous Paramagnetic Insulator (PI) as illustrated in ① in Fig.10 (b). In the middle temperature region ②, the FMt grains start to develop although they are surrounded by the COI phase due to the phase separation. Consequently, the material is weakly Ferromagnetic but still Insulating because the conductive FMt grains are isolated by the insulating COI matrix. With decreasing T within region ②, the magnetization M becomes larger due to growing size of the FMt grains. This should cause the corresponding reduction of $R$ in the grains. However, $R$ increases further due to preferential insulating behavior in the COI matrix phase. In the low temperature region ③ the FMt grains grow sufficiently to become in contact with each other forming a percolation path. Then the material becomes strongly...
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6.2 Positive MR and magnetostriction

DEC combined with phase separation can explain the ferromagnetic-insulating behavior, however they cannot explain the different MR behavior. Namely, while the negative-MR in the low temperature In-regime (Fig.7) can be interpreted by the DEC inside of FMt grains, the positive-MR in the low temperature Mt-regime cannot be interpreted by this model. Note that sometimes positive-MR is found in the manganites, and is explained in terms of superexchange interaction [22], domain structures [23] and other models [24]. However, it is difficult to interpret all our results by a particular model.

In order to explain the different MR behaviors we need to take into account magnetostriction (note that manganites are known to exhibit moderate magnetostriction [25]). As shown in Fig.11 (a), the localized spins (t$_{2g}$) in each FMt grain are aligned by the magnetic field, inducing a decrease in resistance in each grain. Then the total resistance $R$ decreases with increasing $H_a$ as indicated in the figure, causing the negative-MR in the In-regime and weak FM-regime in the middle-T region ②. In the low-T region ③, the current path is well connected, leading to very low $R$ under zero magnetic field as indicated in Fig.11 (b). With application of out-of-plane magnetic field ($H_a \perp$), the FMt grains are expected to expand in the field direction while contracting in the perpendicular direction due to magnetostriction, as shown in the figure. Consequently, the current path becomes disconnected as the field is applied, leading to an increase in $R$ for an in-plane current $I$ with $H_a \perp$. Hence, $R$ increases with increasing $H_a$ as indicated in Fig.11 (b), causing the positive-MR in the Mt-regime and the strong FM-regime in the low-T region ③. Thus the mechanisms are different for the negative-MR, caused by the DEC in the FMt grains, and for the positive-MR caused by the magnetostriction. The different MR mechanisms also cause the dissimilar rates of change in MR with $H_a$ and the larger MR ratio (having almost the same value of the change but in a narrower $H_a$ range) for the positive-MR at 77 K.

6.3 MR saturation and re-entry of slight negative-MR

In the $R$-$H_a$ plot of Fig.7 (d) at 77 K, in the Mt-regime, $R$ saturates for larger $H_a$ (as shown in the expanded plots in Fig.12). This saturation arises from the fact that once the current path is fully broken (i.e., the FM grains have no connection, Fig.11(b)), increasing the applied filed should have no effect in the resistance even the FM grains continue to grow along the field direction. However, careful inspection of the MR curve reveals a slight negative-MR after the saturation. This is caused by the decrease in resistance in each grain due to the DEC. Thus, the results confirm the twofold origin of MR in these samples. Although the negative-MR due to the DEC is always working at any temperatures inside of FMt grains, the positive-MR due to the magnetostriction effect dominates only in a certain temperature range. Namely, the positive-MR is not observed in the middle-T In-regime because the disconnection effect is very small since the grains are already well separated, even if the magnetostriction is effective on each grain. Therefore, the DEC plays dominantly in this In-regime. Finally, at 50 K no MR saturation is observed in the same $H_a$ range (0-4 kOe) (Fig.7(e)) because the full...
grain disconnection must occur at higher $H_a$ since at this temperature the FMt grains are already much larger than at 77 K.

6.4 Strain-induced phase separation

Interestingly, although phase separation does not normally occur in bulk manganites, it can be induced by strain [26]. Since La and Ba have almost the same ionic radius, and thus no strain, bulk LBMO does not show a FMI (ferromagnetic insulator) phase. However, bulk manganites do show the FMI phase at low $T$ when doping with impurities having smaller ionic radii, such as Sr and Ca (see Fig.13) [26].

Shown in Fig.14 are the $c$-lattice parameters, $C_{lp}$, of the as-deposited LBMO thin films on LAO and MgO substrates as a function of the substrate temperature $T_s$. $C_{lp}$ for the thin films grown on LAO at higher $T_s$ are much larger than the bulk value of 3.894 Å, although they approach the bulk value with decreasing $T_s$. This indicates that in-plane lattices are strongly contracted, hence inducing a large crystal strain, which supports the possibility of the existence of a COI phase [26].

Note that the origin of the strain in the LBMO films arises from the “lattice matching” between the film and substrate. Namely, the lattice constant of LAO is 3.79 Å while the bulk lattice constant of LBMO is 3.894 Å, thus the lattice matching induces an in-plane contraction of the film. This, in turn, results in an expansion of out-of-plane lattice parameter, as shown schematically in the inset of Fig.14. Notably, the $c$-lattice parameters of the LBMO thin films on MgO are not as large compared with those on LAO. The lattice constant of MgO, 4.21 Å, is much larger than that of LBMO. In this case, an exact lattice matching is difficult for LBMO in the initial deposition stages. Consequently, amorphous LBMO is grown initially, before crystallite nucleation occurs. The amorphous layer relaxes the strain from the substrate, therefore the LBMO films on MgO have lattice parameters similar to the bulk ones.

6.5 Enhanced phase separation and annihilated magnetostriction effects by annealing

6.5.1 $R$-$T$ and $M$-$T$

Importantly, the value of $T_p=82.2$ K shown in Fig.6 is not sufficiently low for the ferromagnetic layer of

Fig.13 Plots of Temperature-Tolerance factor for bulk manganites doped with impurities having different ion radii $r_A$. The ferromagnetic insulator (FMI) phase is introduced by smaller ion impurities, indicating the phase separation is induced by the crystal strain. (Ref. [26], Permission by APS No.9661).

Fig.14 $c$-parameters as a function of $T_s$ for the LBMO thin films deposited on LAO and MgO at $P_o=1$ mTorr with supply of ML and PL. The bulk value of 3.894 Å is indicated by an arrow in the figure. The inset shows the expansion of out-of-plane lattice due to a contraction of in-plane lattices.
HTS/Ferromagnetic tunable microwave filters. Having \( T_p=82.2 \text{ K} \) would imply that HTS should have a critical temperature \( (T_c) \) well above 82.2 K, as illustrated by the top figure in Fig.3, which is not easily achieved. To reduce \( T_c \) in order to have a feasible device, we tried to anneal the films at 900°C in atmospheric oxygen for 5 hr. The results of \( R-T \) and \( M-T \) for a LBMO film grown on LAO \((T_c=750°C, \ P_o=0.5 \text{ mTorr, PL})\) after the annealing \((S-2')\) are shown in Fig.15 (a) and (b), respectively. After annealing, the magnitude of \( R \) is reduced while the magnitude of \( M \) increases, implying apparently that the film has changed to be more metallic and ferromagnetic. Interestingly, although \( T_c \) was shifted to higher \( T \), \( T_p \) has decreased to lower \( T \). The higher \( T_c \) can be easily understood, since the crystallinity of the film was improved by the annealing to have stronger ferromagnetic nature at the higher temperatures due to higher crystal order. On the other hand, understanding the decrease in \( T_p \) is more complex, since it implies that the insulating temperature range \((T>T_p)\) was expanded though \( R \) was reduced in the annealed film.

Here we suggest one of models for this peculiar behavior. The \( T_p \) and \( T_c \) are separated, then we can apply the phase separation model again to this film. The result may suggest that the FMt grains are enlarged, and/or the metallic and ferromagnetic nature of each grain is enhanced. If the grains were enlarged, it should lead to an increase of \( T_p \) (rather than a reduction), since in this case the grains would be more easily contacted to cause the In\( \rightarrow \)Mt transition with decreasing \( T \). The reduction of \( T_p \) indicates the grains shrink by the annealing. Then the grains contact occurs at lower \( T \). This implies that the metallic and ferromagnetic nature of the shrunken grains must be enhanced.

Independently of the origin of the effects, the practical consequence is that the film is insulating and ferromagnetic in a wider temperature range of 31-180 K. In fact, \( T_p=31 \text{ K} \) is sufficiently low and \( T_c=180 \text{ K} \) is sufficiently high for a viable HTS/Ferromagnetic tunable microwave filters because it is not difficult to obtain HTS layers with \( T_c \) higher than 31 K (see Fig.3), and for the ferromagnetic layer to have comparatively large permeability \( \mu \) as needed. Moreover, it is expected that the filter device would be used around 60 K employing closed-cycle cryo-coolers. For the particular case of this annealed film, since the resistance is rather high and the magnetization is very large (both close to the maximum values at 60 K), it would be adequate for HTS/Ferromagnetic tunable microwave filters. Notably, although the film is indeed insulating in this temperature range, the microwaves should be absorbed by the free carriers in the metallic regions. Nevertheless, the total absorption is reduced due to the insulating regions (COI) having less carrier density compared with if the film was completely metallic.

6.5.2 Magnetoresistance (MR)

We examined MR ratio \((\Delta R/R)\) on the annealed sample as a function of \( H_a \) at various \( T \) in the In-regime, and the results are shown in Fig.16 (to be compared with the results of the as-grown sample in Fig.7). Interestingly, the annealed sample exhibits only negative-MR down to 50 K, although the as grown sample shows positive-MR at low \( T \) in the same temperature region. This seems to indicate that the magnetostriction effects disappear with the annealing. Moreover, the magnitude of MR is much larger for the annealed sample compared with the as-grown sample. This implies that the spins are more easily aligned by the magnetic field due to the well ordered crystal structure in the shrunken FMt grains. Actually the XRD peak half-width \( \Delta \theta \) was reduced then the crystallinity was improved after the annealing. Furthermore, high spin ordering was confirmed by FMR after the annealing [27], as will be discussed in more detail in the next section.

The MR depends much on \( T \) as indicated by a turning arrow in Fig.16, then the magnitudes of \( \Delta R/R \) at a fixed \( H_a=4 \text{ kOe} \) is plotted in Fig.17 as a function of \( T \). The MR ratio is small at lower \( T \), and its absolute value increases and subsequently decreases with increasing \( T \), showing its maximum values at about \( T=125 \text{ K} \).
maximum value is -17% for $H_p=4$ kOe. Usually the maximum MR temperature corresponds to $T_p$ in bulk manganites, but in the thin film samples it is located at much higher $T$ than $T_p=31$ K. This again confirms that the magnetic and electrical behaviors arise from different origins. The $T$-dependence of MR can be explained by using the schematic spin orientations shown on the top of Fig.17. At low-$T$, the spins are already aligned well due to small thermal energy, then there is no additional field alignment of the spins. Therefore the MR is very small. At high-$T$, as the spins are subjected to strong thermal fluctuations, it is difficult to align them by the moderate magnetic field. Therefore, the MR is again very small. At intermediate temperatures between the low- and high-$T$ regimes, the spins fluctuate only moderately, thus they are easily aligned by the magnetic field, resulting in a large MR. Hence, this behavior can be satisfactorily explained by DEC model. We can confirm that the DEC model is applicable for the thin film, and conclude that we are looking only inside of FMt grains by the MR measurement for the annealed sample.

Careful inspection of the MR-$H_a$ data in Fig.16, we can observe evidences of tiny traces of positive-MR only at 50 K as indicated by two oblique arrows. This temperature does not exactly correspond to the measurement for the annealed sample. However looking only inside of FMt grains by the MR measurement for both of as-grown and annealed samples the ferromagnetic resonance simply called FMR on the as-grown sample (LAO, $T_p=750$°C, $P_0=1.5$ mTorr, PL) and (b) the annealed sample (at 900°C in O$_2$ for 5 hr).

7. FERROMAGNETIC RESONANCE (FMR)

7.1 Doublet peak signal and phase separation

We investigated the magnetic properties in terms of the ferromagnetic resonance simply called FMR on the as-grown and annealed samples [20, 27, 28]. Shown in Fig.18 are typical FMR signals for $H_a\perp$ for the as-grown sample ($T_p=750$°C, $P_0=1.5$ mTorr, PL on LAO) and after annealing at 900°C in atmospheric oxygen for 5 hr [20]. The as-grown sample shows singlet peaks at higher $T$, above 145 K, while doublet peaks at lower $T$, below 145 K in the middle-$T$ In-regime. One of the doublet peak at $T=114$ K is shown in Fig.18. This change from single to doublet peak structure with decreasing $T$ indicates that phase separation takes place at this $T$. The singlet peaks at higher-$T$ and the lower-field-side peaks of the doublet peak signals at the lower-$T$, may come from FMR in the FMt grains. The higher-field-side peaks of the doublet peak signals at lower-$T$ may arise from the COI phase. It might be anti-ferromagnetic resonance (A-FMR) peak, although the reason why this peak is located so close to FMR peak, is not yet fully understood. Nevertheless, FMR results seem to confirm the phase separation proposed to explain the separated $T_p$ and $T_c$ [29, 30].

7.2 Doublet peak signal after annealing

After the annealing, the doublet peak structure is not observed at the same $T=115$ K in the In-regime as discussed above. Probably the A-FMR signal from the COI phase can no longer be detected due to change in its anti-ferromagnetic nature, or the anti-ferromagnetic nature is depressed.

We examined the doublet signal whether it always disappear or not after the annealing. Examples of the FMR signals for $H_a//\perp$ and $H_a\perp$ are shown in Fig.19 [28]. The sample was deposited at $T_p=750$°C at $P_0=1$ mTorr (ML) on LAO then annealed at 850°C for 13 hr (first annealing), and subsequently annealed at 800°C for 16 hr (second annealing). The FMR signals at 77 K for the first-annealed show a singlet peak for $H_a//\perp$ but a faint doublet peak structure for $H_a\perp$. The FMR signals at 77 K for the second-annealing reveal the faint doublet peak for both of $H_a\perp$ and $H_a//\perp$. This is evidence that the annealed samples actually show doublet peaks indicating the phase separation. The resonant fields are different for $H_a\perp$ and $H_a//\perp$; they are caused by demagnetizing effect for $H_a\perp$ and field concentration effect for $H_a//\perp$. Remarkably, in the room temperature (r.t.) data for the second-annealing shown in Fig.19, the sample shows clear FMR signals (although very small and broad) both for $H_a\perp$ and $H_a//\perp$, indicating that the annealed sample is ferromagnetic at room temperature.

7.3 Effective magnetization and half-width

The effective magnetizations, $4\pi M_{eff}$, of the films were calculated for $H_a//\perp$ and $H_a\perp$ configurations using
the resonant fields $H_r$ using eqs. (2) and (3), respectively. They are plotted as a function of $T$ in Fig. 20 for the as-grown ($T_c=750^\circ$C, $P_o=0.5$ mTorr, PL) and annealed ($900^\circ$C, O$_2$, 5 hr) samples. For the as-grown sample, the magnitudes of $4\pi M_{\text{eff}}$ are almost the same but slightly larger for $H_a \perp$ than for $H_a //$, indicating that the easy magnetization configuration may be perpendicular to the film plane. After annealing, the magnitude of $4\pi M_{\text{eff}}$ increases considerably for both of $H_a //$ and $H_a \perp$, and it is clearly larger for $H_a \perp$ than for $H_a //$. Consequently, we can conclude that easy magnetization configuration is clearly out-of-plane. It should be remembered that spins are aligned more easily for $H_a \perp$. The Curie temperature $T_c$ (defined as extrapolated $4\pi M_{\text{eff}}=0$) shifts from $T_c=185$ K in the as-grown state to $T_c=195$ K in the annealed state. Then ferromagnetic nature is enhanced by the annealing, in concordance with the SQUID measurements shown in Fig. 6 and 15.

The half-widths of the FMR signals, $\Gamma_{pp}$, are plotted as a function of $T$ in Fig. 21. In general, the magnitude of $\Gamma_{pp}$ decreases with increasing $T$. There are a variety of spins in the material contributing to the FMR signal, thus causing wider spread of resonance. The magnitude of $\Gamma_{pp}$ is a measure of the variation of spin orientations, corresponding basically to crystalline order. Usually at high $T$, only the stronger spins having equivalent orientations are contributing to the FMR, causing a decrease in $\Gamma_{pp}$ with raising $T$.

However, the $T$-dependence of $\Gamma_{pp}$ for the as-grown sample is somewhat unusual, taking into account the monotonic dependence of $4\pi M_{\text{eff}}$ with $T$. The values of $\Gamma_{pp}$ are smaller for $H_a //$ and $H_a \perp$ in a window range of $100<T<140$ K, especially they are extremely small, as low as 100 Oe, for $H_a \perp$ as compared with those in other $T$-regions [31]. This result indicates that the as-grown sample is extremely spin-homogeneous in the perpendicular to the film plane direction in this temperature window, confirming the excellent crystallinity of the sample in addition to the XRD result. Around 150 K, $\Gamma_{pp}$ shows maxima both for $H_a //$ and $H_a \perp$. The same behavior was reported by Loßland et al. [31] and Domingues et al. [32]. This might indicate...
some phase change, probably corresponding to the phase separation, because the doublet peak structure starts to be observed below this anomaly temperature. This phase transition is anisotropic [31] because the $I_{pp}$ shows a strong peak for $H_a⊥$ while only a weak hump for $H_a∥$, and the drop of $I_{pp}$ values in this temperature range is much larger for $H_a⊥$. This anisotropy has probably some relation with the magnetostriiction effect, because it takes place easily for $H_a⊥$.

For the annealed sample, the values of $I_{pp}$ are considerably reduced as compared to the values of the as-grown samples both for $H_a∥$ and $H_a⊥$. Thus, the spin homogeneity and the crystallinity are improved by the annealing. The anomaly of $I_{pp}$ around 150 K observed in the as-grown sample is eliminated for $H_a∥$ and weakened for $H_a⊥$ by the annealing. This corresponds to the disappearance of doublet FMR signal after the annealing. Hence, the phase separation of the annealed sample has a different nature than the as-grown sample, indicating perhaps a change in COI nature since the doublet signal may arise from A-FMR in the COI phase. The $I_{pp}$ is much smaller for $H_a⊥$ than for $H_a∥$ again for $T<150$ K, pointing to an enhanced homogeneity in the perpendicular field direction (as observed in the as-grown sample). Notably, the $I_{pp}$ values for $H_a⊥$ are similar to the values for the as-grown samples in the window range of 100<$T<$140 K, meaning that the as-grown sample is originally extremely homogeneous in the perpendicular direction. It means the ultimately fine crystalline LBMO thin film can be grown by IBS, concerning at least to the spin order.

We should point out the other notes. It is known by the SQUID magnetization data and FMR data (effective magnetization) that the magnetic nature is enhanced and the Curie temperature is raised by the annealing. While we can obtain further important information from the FMR, the doublet (corresponding to the phase separation) and the half-width (corresponding to the spin homogeneity). We can suggest the FMR technique is an important technique in this research work.

In the future, we should develop new ferromagnetic materials which have stronger ferromagnetic nature (larger $μ$) but low carrier density in fact. It is necessary that we can form the double layers easily if we employ such new ferromagnetic layers and HTS layers.

8. SUMMARY

The growth and structural, magnetic and transport properties of insulating ferromagnetic oxide La(Ba)MnO$_3$ films, suitable for HTS/Ferromagnetic tunable filter, are described. It is important that the ferromagnetic layer should have less carrier density (insulator) not to absorb the microwave. The LBMO film deposited at 750°C shows rather low $T_p$ of 82.2 K and rather high $T_c$ of 140 K, making this film potentially useful for the Ferromagnetic part of tunable filters. The separated $T_p$ and $T_c$ can be interpreted by the phase separation model in which the FMt grains (responsible for the ferromagnetic nature) are surrounded by the COI phase (responsible for the insulating nature). The phase separation is introduced by the crystal strains in the film. The film shows the negative-MR in the middle-$T$ range due to the DEC effect in the FMt grains, while it shows the positive-MR at low-$T$ due to the magnetostriiction effect.

These characteristic temperatures can be improved by the annealing, resulting in $T_p=31$ K and $T_p=180$ K. Therefore the annealed film can be actually used as the Ferromagnetic layer combined with the HTS layer because $T_p$ is well below $T_c$ of HTS. The reduction in $T_p$ is explained by the size reduction of FMt grains, although their ferromagnetic nature is enhanced by the annealing owing to the improvements of crystalline order and magnetic order in the FMt grains.

The FMR on the as-grown film shows doublet signals corresponding to the phase separation. One signal at lower-$H_a$ comes from the ferromagnetic resonance in the FMt grains, the other at higher-$H_a$ may arise from the COI phase. The extremely narrow half-widths $I_{pp}$ of the FMR indicate an excellent crystallinity and spin ordering both for the as-grown and annealed films. The anisotropic anomalous $T$-dependence of $I_{pp}$ around 150 K might be related to the magnetostriiction effect. It is suggested that the FMR is very unique and important techniqne in this research work.

References


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