Review paper

Peculiar Electrical and Magnetic Properties of La(Ba)MnO₃ Thin Films

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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 magnetoresistive 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,

Fig.1 Filtering mechanism for a strip line filter.

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_0 is selected by the line length L according to eq.(1)

$$F_0 = \frac{c}{2L\sqrt{\varepsilon\mu}} \quad (1)$$

It should be noted that F_0 depends also on dielectric constant ε and permeability μ of medium.

Based on HTS microwave filters, an other possible example of FH-Oxides is a tunable microwave filter [6]. Superconducting YBa₂Cu₃O_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 μ 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_0 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

Fig.2 (a) Stack of HTS and ferromagnetic layers. The microwave velocity v is modified by the magnetic field H_a through μ . (b) The filtered center frequency F_0 is shifted by the magnetic field.

Fig.3 Models of resistance R and magnetization M curves as a function of temperature for ferromagnetic layer. T_c : Curie temperature, T_p : metal-insulator transition temperature, T_d : device temperature range where both of R and M must be large. PM: paramagnetic, FM: ferromagnetic, In: insulator, Mt: metal. The top figure indicates resistance-temperature curves for HTS layer. Two cases are shown for different critical temperatures of T_{cr} and T'_{cr} .

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

Fig.4 Ion Beam Sputtering system. SIG: sputter ion gun, T: target, SP: sputtered particles, S: substrate, LH: lamp heater, H: holder, PS: plasma source, T_s : substrate temperature, P_o : oxygen partial pressure, T_h : holder temperature, ML: molecular supply, PL: plasma supply, θ_i , θ_s and θ_p : angles indicated.

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 $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ 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 diverse oxygen partial pressures P_o . The crystallinity of LBMO thin films was estimated by the half-width $\Delta\theta$ of X-ray diffraction (XRD) peaks. Moreover, some of the samples were annealed at 900°C for 5 hr in 1 atm 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

Fig.5 Typical XRD patterns of LBMO thin films deposited on LAO at (a) $T_s=500^\circ\text{C}$, $P_o=1$ mTorr, PL for S-1 sample and (b) $T_s=750^\circ\text{C}$, $P_o=0.5$ mTorr, PL for S-2 sample. The LBMO XRD peak indices are indicated in brackets. The symbol “L” shows LAO substrate peaks (only a part is shown).

Γ_{pp} were evaluated. Effective magnetizations, $4\pi M_{\text{eff}}$, were calculated for $H_a \perp$ and $H_a \parallel$ using the corresponding resonant fields of $H_r \perp$ and $H_r \parallel$. We use the resonance equations of Kittel according to Landau-Lifshitz-Gilbert [13]

$$\omega_r / \gamma = [H_r \parallel / (H_r \parallel + 4\pi M_{\text{eff}})]^{1/2} \quad (\text{for } H_a \parallel), \quad (2)$$

$$\omega_r / \gamma = H_r \perp - 4\pi M_{\text{eff}} \quad (\text{for } H_a \perp). \quad (3)$$

In these equations, ω_r is a resonant frequency and γ is the gyromagnetic ratio. This γ is expressed as

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

where μ_B is the Bohr magneton, and for g -factor $g = 2.00$ is used to estimate M_{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 Γ_{pp} was evaluated from peak-to-peak field of the derivative signal. When the signal has a doublet peak, the Γ_{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 $T_s=500^\circ\text{C}$ and (b) for $T_s=750^\circ\text{C}$ 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 $T_s=750^\circ\text{C}$, with $\Delta\theta=0.09$ 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.

Fig.6 (a) R - T and (b) M - T curves for the as-grown S-2 sample on LAO ($T_s=750^\circ\text{C}$, $P_o=0.5$ 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.

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 $T_s=750^\circ\text{C}$ at $P_o=0.5$ 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,

Fig.7 R - 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.

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.8 Schematic representation of the phase separation model. FMt: ferromagnetic-metallic grain, COI: charge ordered insulating phase. The FMt grains are surrounded by the COI phase.

Fig.9 Usual double exchange coupling (DEC) model. Manganese d-electron states are split into t_{2g} and e_g states. At high T , e_g -electron spin is scattered by fluctuating t_{2g} -electron spins. At low T or under high magnetic field, e_g -electron spin is not scattered by aligned t_{2g} -electron spins. In this model, metallic is always ferromagnetic.

At low temperatures or under high magnetic fields, the localized t_{2g} -electron spins are well aligned, then the traveling e_g -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 e_g -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

(a)

● Ferromagnetic Metallic grain
COI: Charge Ordered Insulating phase

(b)

Fig.10 Phase separation model to interpret the separated temperatures of T_p and T_c , as well as the electrical and magnetic properties. (a) Model R - T and M - T curves, (b) schematic phase separation models at different temperature regions corresponding to (a).

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

Fig.11 Combination of the phase separation and magnetostriction models to explaining schematically (a) the negative-MR in the middle- T region and (b) the positive-MR in the low- T region.

Ferromagnetic and Metallic. With further decreasing T , the FMt grains become larger and larger then the total contact area increases, leading to the decrease in R and further increase in M .

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 middle 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

Fig.12 Expanded view of part of Fig.7 (d). An arrow indicates the slight negative-MR after saturation.

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 field 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

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 $P_0=1$ 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.

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

Fig. 15 Plots of (a) R - T and (b) M - T for the LBMO film grown on LAO ($T_s=750^\circ\text{C}$, $P_0=0.5$ mTorr, PL) annealed at 900°C in atmospheric oxygen for 5 hr. The T_p is shifted to lower T of 31 K, while the T_c to higher T of 180 K. Then the film is insulating and ferromagnetic in 31-180 K.

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 $T_p=82.2 \text{ K}$ shown in Fig. 6 is not sufficiently low for the ferromagnetic layer of

HTS/Ferromagnetic tunable microwave filters. Having $T_p=82.2$ K would imply that HTS should have a critical temperature (T_{cr}) well above 82.2 K, as illustrated by the top figure in Fig.3, which is not easily achieved. To reduce T_p 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 ($T_s=750^\circ\text{C}$, $P_0=0.5$ 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, $T_p=31$ K is sufficiently low and $T_c=180$ K is sufficiently high for a viable HTS/Ferromagnetic tunable microwave filters because it is not difficult to obtain HTS layers with T_{cr} higher than 31 K (see Fig.3), and for the ferromagnetic layer to have comparatively large permeability μ , 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

Fig.16 MR ratios as a function of H_a for the annealed S-2' sample at various T in the In-regime shown in Fig.15. The MR depends strongly on T as indicated by a turning arrow. All the plots show negative-MR, but tiny traces of positive-MR can be observed at 50 K as indicated by the two oblique arrows.

Fig.17 MR ratio at 4 kOe as a function of T for the annealed S-2' sample. The arrows on the top of the figure indicate thermal spin orientations (lower) and their field alignment (upper).

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 $H_a=4$ 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 $T=125$ K. The

maximum value is -17% for $H_a=4$ 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 subject 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 Mt-regime, although it is close to $T_p=31$ K. This means we are observing a slight magnetostriction effect at 50 K, implying that the FMt grains are already weakly connected in some parts just above T_p . These weak connections are effectively broken (i.e., positive-MR) by the magnetostriction induced at small fields, but the negative-MR brought about by the DEC is not induced effectively yet at these low fields, resulting in the net positive-MR. With increasing the field, the weak connections are fully broken at rather low fields, leading to no positive-MR. Instead the normal negative-MR plays a dominant role. This probably indicates that if we measure MR at lower T than $T_p=31$ K, we should observe clear positive-MR due to the magnetostriction in the annealed sample also (as will be reported elsewhere).

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 ($T_s=750^\circ\text{C}$, $P_0=1.5$ 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 singlet 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

Fig.18 FMR signals for $H_a \perp$ for (a) the as-grown (LAO, $T_s=750^\circ\text{C}$, $P_0=1.5$ mTorr, PL) and (b) the annealed sample (at 900°C in O_2 for 5 hr).

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 shown in Fig.18. This is somewhat puzzling because the annealed sample should also have phase separation, 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 $H_a \parallel$ and $H_a \perp$ are shown in Fig.19 [28]. The sample was deposited at $T_s=750^\circ\text{C}$ 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 $H_a \parallel$ 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 $H_a \parallel$. 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 $H_a \parallel$, they are caused by demagnetizing effect for $H_a \perp$ and field concentration effect for $H_a \parallel$. 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 $H_a \parallel$, indicating that the annealed sample is ferromagnetic at room temperature.

7.3 Effective magnetization and half-width

The effective magnetizations, $4\pi M_{\text{eff}}$, of the films were calculated for $H_a \parallel$ and $H_a \perp$ configurations using

Fig.19 FMR signals for $H_a \perp$ and $H_a \parallel$ obtained for the annealed sample, (a) first-anneal, (b) and (c) second-anneal. Measurement temperatures are shown in the figure (r. t.: room temperature).

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 ($T_s=750^\circ\text{C}$, $P_0=0.5$ mTorr, PL) and annealed (900°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 $H_a \parallel$, 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 $H_a \parallel$ and $H_a \perp$, and it is clearly larger for $H_a \perp$ than for $H_a \parallel$. Consequently, we can conclude that easy magnetization configuration is clearly out-of-plane. It should be remembered the 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, Γ_{pp} , are plotted as a function of T in Fig.21. In general, the magnitude of Γ_{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 Γ_{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

Fig.20 Effective magnetizations, $4\pi M_{\text{eff}}$, as a function of T for $H_a \parallel$ and $H_a \perp$ for the as-grown and annealed samples.

Fig.21 Half-widths Γ_{pp} of the FMR signals as a function of T for $H_a \parallel$ and $H_a \perp$ for the as-grown and annealed samples corresponding to those shown in Fig.20.

decrease in Γ_{pp} with raising T .

However, the T -dependence of Γ_{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 Γ_{pp} are smaller for $H_a \parallel$ 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, Γ_{pp} shows maxima both for $H_a \parallel$ and $H_a \perp$. The same behavior was reported by Lofland 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 Γ_{pp} shows a strong peak for $H_a \perp$ while only a weak hump for $H_a \parallel$, and the drop of Γ_{pp} values in this temperature range is much larger for $H_a \perp$. This anisotropy has probably some relation with the magnetostriction effect, because it takes place easily for $H_a \perp$.

For the annealed sample, the values of Γ_{pp} are considerably reduced as compared to the values of the as-grown samples both for $H_a \parallel$ and $H_a \perp$. Thus, the spin homogeneity and the crystallinity are improved by the annealing. The anomaly of Γ_{pp} around 150 K observed in the as-grown sample is eliminated for $H_a \parallel$ and weakened for $H_a \perp$ 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 Γ_{pp} is much smaller for $H_a \perp$ than for $H_a \parallel$ again for $T < 150$ K, pointing to an enhanced homogeneity in the perpendicular field direction (as observed in the as-grown sample). Notably, the Γ_{pp} values for $H_a \perp$ 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 LBMTO 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 unique and very important in these materials sciences to get the various sides of magnetic natures.

8. SUMMARY

The growth and structural, magnetic and transport properties of insulating ferromagnetic oxide La(Ba)MnO₃ 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 LBMTO 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 magnetostriction effect.

These characteristic temperatures can be improved by

the annealing, resulting in $T_p = 31$ K and $T_c = 180$ 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_{cr} 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 Γ_{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 Γ_{pp} around 150 K might be related to the magnetostriction effect. We should investigate hereafter whether the magnetostriction model is really effective or not [33-36]. It is suggested that the FMR is very unique and 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.

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