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Effects of Oxygen Partial Pressure on Thin Film Growth of La-Ba-Mn-O System

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Thin films of LaBaMnO system were grown at 700°C on MgO and LAO substrates by ion beam sputtering with supply of oxygen molecules at partial pressures (P_O) of 0.05-4 mTorr. All the films showed c-oriented single phase of cubic $(La,Ba)MnO_3$. Two kinds of crystallinity were estimated on the films by X-ray diffraction; intragrain plane-distance (FWHM of θ-2θ peaks) and mosaicity (rocking half-width Δ). P_O-dependences of FWHM and Δ show regular correlation for LAO while inverse correlation for MgO. P_O-dependence of surface roughness (RMS) shows the same U-shape behavior with FWHM and Δ for LAO. FWHMs are roughly the same for MgO and LAO (0.15-0.2°), however Δs are extremely smaller for LAO (0.01° by subtraction) than for MgO. RMS values are much smaller for LAO (7.7 nm) than for MgO, indicating 2D growth on LAO.

Key words: Thin films of LaBaMnO, MgO and LAO substrates, oxygen partial pressure, θ-2θ and rocking half-width, surface roughness

1. INTRODUCTION

Material research for perovskite oxides involving Mn ion is attractive for variety of scientists in a decade of years. Especially, many people pay attention to a fact that resistances of the perovskite manganites suddenly decrease with decreasing temperature at Curie temperatures (T_C) where the materials show ferromagnetic phase transition. Application of magnetic field on these materials causes huge resistance drops near T_C. This negative magnetoresistance is called "Colossal Magnetoresistance (CMR)" [1-3].

CMR effect is greatly useful for magnetic devices. If these devices are used at room temperature, the material must show CMR effect at room temperature. Then we should develop manganite thin films showing CMR characteristics at room temperature. On the other hand, development of tunable microwave filter devices is highly expected using stacked thin films of high temperature superconductors and CMR manganites [4]. As far as this function is concerned, it is not always necessary for the manganite thin films to show CMR characteristics or large permeability change at room temperature. Then it is also valuable to develop the manganite thin films which show appropriate changes in magnetic properties at low temperatures where the tunable microwave filters work.

Properties of manganite thin films are strongly affected by their composition, oxygen content and lattice strain [5-7]. In order to realize the stacked tunable filters, we should prepare as-grown manganite thin films on various materials which can show the proper changes in magnetic characteristics by the small field application. Moreover, we should pay our attentions on surface roughness of the films and inter-diffusions of elements at the interface. Keeping these factors in view, we are trying to fabricate manganite thin films of La-Ba-Mn-O system (LBMO) employing ion beam sputtering (IBS) with supply of oxygen molecules or plasma on various substrates with varying substrate temperature (T_S) and oxygen partial pressure (P_O). In this paper, we report P_O-dependences of crystallinity, surface roughness and composition of the deposited films at T_S=700°C. We just touch upon magnetic properties of the films.

2. EXPERIMENTAL

LBMO thin films were prepared by IBS method as illustrated in Fig. 1 [8-10]. A target was sputtered by 4 keV Ar^+ ion, and sputtered particles were deposited on heated MgO (100) and $LaAlO_3$ (LAO) (100) substrates simultaneously. Substrate temperature (T_S) was measured using a corrected chromel-alumel thermocouple pressed on the substrate. During the deposition, oxygen molecules were supplied to the substrate surface from a PS nozzle located at 11 mm from the substrate. Then the actual oxygen partial pressure is higher than the average oxygen partial pressure (P_O) by factors of 5-10. In this work, T_S was fixed at 700°C and P_O-dependence of the film growth was examined in P_O range of 0.05-4 mTorr. The sintered target has a composition of La/Ba/Mn=0.94/0.40/1.

Crystallinity of the deposited films was characterized by X-ray diffraction (XRD) pattern on θ -2θ scan using Cu Kα line and FWHM half-width of the θ-2θ peaks. This indicates a measure of uniformity of plane-distance parallel to the substrate plane in the crystalline grains. It is called "crystallinity of plane-distance" in this paper. We also evaluated rocking half-width (Δ). This is a measure of fluctuation of crystal parallel plane with respect to the substrate plane. It is called "mosaicity". Surface morphology was characterized by atomic force microscopy (AFM) and the average roughness was estimated by RMS. Film composition was measured by energy dispersive X-ray microanalysis (EDX) corrected by ICP. Magnetization and Magnetoresistance were measured on some of the samples.

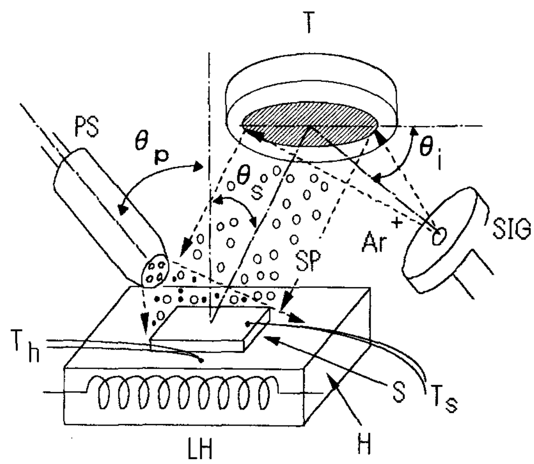

Fig. 1. Ion beam sputtering apparatus.

3. RESULTS AND DISCUSSION

3.1 Crystallinity

The XRD patterns are shown in Fig. 2 for the deposited films on (a) LAO at P_O=1 mTorr and (b) MgO at 0.1 mTorr. Their rocking curves of (002) peak are shown in Fig. 3. The XRD patterns show well oriented single phase of cubic (infinit layer) crystal expressed as (La,Ba)MnO_3. Averaged FWHM half-widths over (001) and (002) peaks are plotted in Fig. 4 as a function of P_O for the films on MgO and LAO, and the rocking half-widths (Δ) of (002) peak are plotted in Fig. 5 for part of the samples. Comparing FWHMs for the films on MgO and LAO, their magnitudes are almost the same in low P_O region (P_O<0.5 mTorr) just except for the plot for LAO at P_O=0.2 mTorr. In higher P_O region, FWHMs are obviously smaller for MgO than for LAO, indicating better crystallinity for MgO. FWHM for MgO at 1 mTorr is exceptionally large. At very low P_O and very high P_O, FWHMs are increased because the crystallinity of plane-distance gets worse due to shortage and excess of oxidation power. Therefore, the curve for LAO shows U-shape behavior on the whole (just except at P_O=0.2 mTorr), while the curve for MgO shows a curious behavior like a "window" around P_O=2 mTorr. The value of FWHM for MgO is smallest as 0.09° at this P_O. The result indicates that the better crystallinity of plane-distance can be obtained on MgO rather than on LAO if P_O is appropriately adjusted.

Two reasons are possible for these complicated behaviors of FWHM for MgO and LAO. One is that the crystal growth is controlled by total energy of this IBS system, i.e., thermal energy, sputtered particle energy and activated oxygen energy after collision with the sputtered particles [11]. The total energy is changed with varying P_O then if the total energy matches, the better crystalline film can be grown. The other is "least

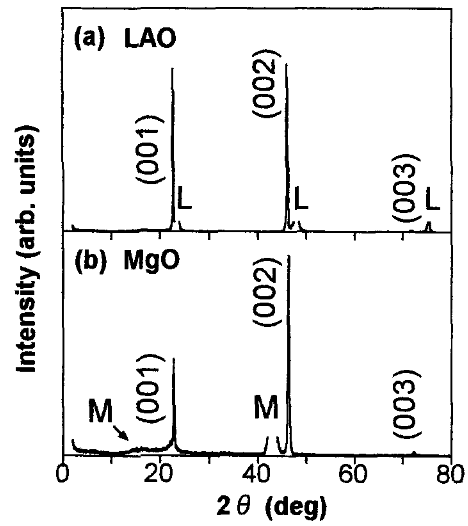

Fig. 2. XRD patterns of LBMO films grown on (a) LAO substrate at P_O=1 mTorr and (b) MgO substrate at P_O=0.1 mTorr. L and M indicate substrate peaks of LAO and MgO, respectively.

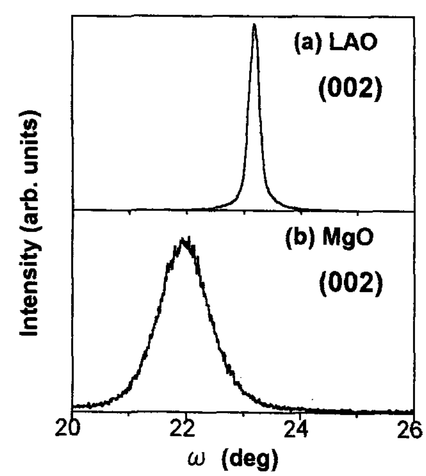

Fig. 3. Rocking curves of LBMO films grown on (a) LAO at P_O=1 mTorr and (b) MgO at P_O=0.1 mTorr.

common multiples" of lattice matching between the film and MgO substrate. As the total energy changes with varying P_O, the least common multiples of lattice matching changes. Then the crystallinity changes with changing P_O. This can be supported by our previous result that the behavior of FWHM vs P_O roughly corresponds to the behavior of c-parameter vs P_O [12].

The rocking half-widths for MgO are extremely large in the all P_O region (Fig. 5), however there is a remarkable feature in its behavior if it is related with FWHM behavior (Fig. 4). That is, there is inverse correlation between them; the maximum Δ at 2 mTorr corresponds to the minimum FWHM in the window region. There are many grains in which the crystal plane is aligned parallel to the substrate plane with uniform plane-distance (small FWHM) in the film, but these parallel grains are surrounded by grains with

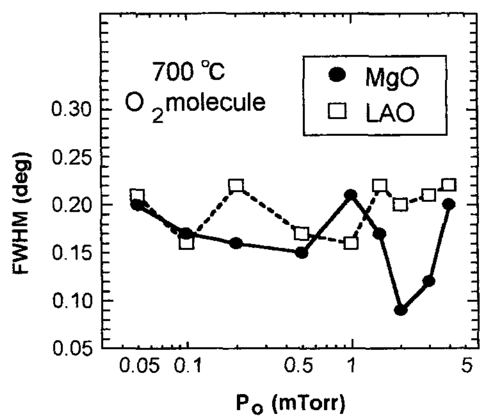

Fig. 4. The θ-2θ FWHM values averaged over (001) and (002) XRD peaks vs P_O for LBMO films on MgO and LAO.

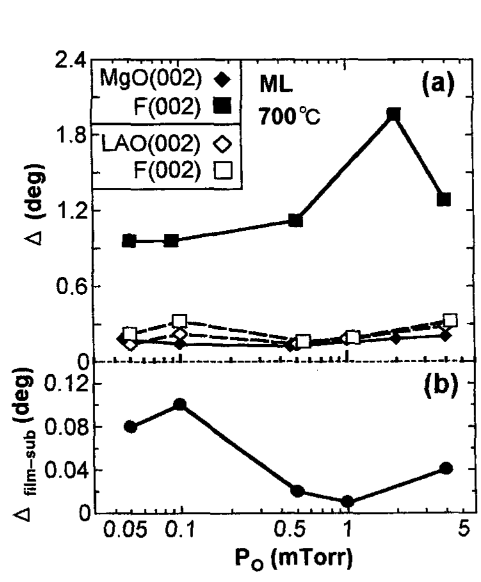

Fig. 5. (a) Rocking half-widths (Δ) of (002) peak vs P_O for LBMO films on MgO and LAO. Corresponding Δ for the substrate (002) peak are also shown. (b) The difference of $\Delta_{film\text{-}sub}$ for the films on LAO vs P_O.

considerably fluctuated crystal plane with respect to the substrate plane (bad mosaicity). Then such a film has two different sorts of grains, i.e., well aligned and much fluctuated grains. The films in the low P_O region have the opposite property that the intergrain crystal plane is well aligned (small Δ) while the intragrain plane-distance is much fluctuated (large FWHM), maybe due to the intergrain alignment induced intragrain stress.

On the other hand, U-shaped FWHM behavior (Fig. 4) has regular correlation with the same U-shaped Δ behavior (Fig. 5) on LAO. It is obvious from Fig. 5 that the Δ_{film} values of the films on LAO are affected by the Δ_{sub} values of the substrate (film mosaicity is affected by substrate mosaicity). Then we plotted their difference $\Delta_{film\text{-}sub}$ in Fig. 5(b). The result indicates that with increasing the mosaicity (Δ) or fluctuation in intergrain crystal plane, the fluctuation of intragrain plane-distance is increased. This is a quite normal behavior of crystalline thin film structure. Compared with Δ for MgO, Δ for LAO is extremely small. For example, $\Delta_{film\text{-}sub}$=0.01° at 1 mTorr. Then two-dimensional crystal growth must be realized on LAO. This induces higher strain in each grain then induces the comparably large fluctuation of intragrain plane-distance with that of the films on MgO. As the result, the films have the best crystallinity in the middle range of P_O around 1 mTorr on LAO.

3.2 Surface roughness and composition

The surface roughnesses (RMS) for the films on MgO and LAO are plotted in Fig. 6 as a function of P_O. The surface roughness is larger and considerably fluctuates with varying P_O for MgO. However, it has no correlation with the fluctuation of FWHM (Fig. 4). This fluctuation must be induced by the least common multiples of lattice matching stated above. The 3D grain grows on the whole on MgO.

On the contrary, the surface roughness vs P_O shows U-shape again just except for the plot at 0.2 mTorr for LAO. At P_O=0.5 mTorr, RMS=7.7 nm on

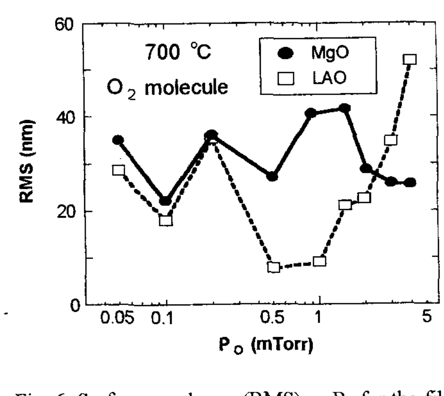

Fig. 6. Surface roughness (RMS) vs P_O for the films on MgO and LAO.

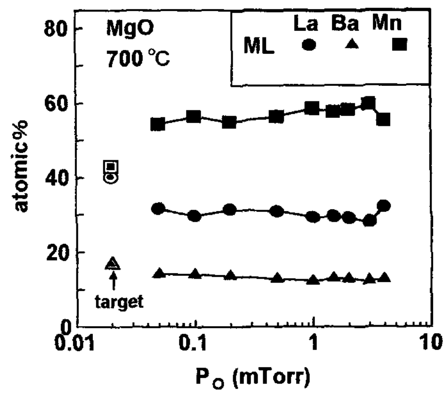

Fig. 7. Composition vs P_O only for the films on MgO.

LAO, then the surface is very smooth. The result clearly indicates that if the film has the excellent crystallinity of plane-distance (FWHM) and mosaicity (Δ), it has the smooth surface (RMS) at around P_O=0.5-1.0 mTorr. This correspondence between FWHM and RMS clearly holds even for the local fluctuation at P_O=0.2 mTorr. This also implies that the excellent crystalline film grows two-dimensionally on LAO.

The composition vs P_O is shown in Fig. 7 only for MgO substrate. We have expected that La and Ba elements must be reduced in the film from the target composition, then we used La and Ba rich target. The result show that La and Ba elements are excessively reduced then the films have slightly Mn-rich composition compared with the nominal composition of $(La,Ba)MnO_3$ on the whole. There are no impurity phases in the films, then Mn should substitutes for La site. This Mn-substitution may give some unusual magnetic properties.

A film deposited at 500 °C showed the magnetoresistance and metal-insulator transition at 149 K. The higher transition temperature can be expected for the films deposited at 700°C.

4. SUMMARY

LBMO thin films were fabricated on MgO and LAO simultaneously by IBS at 700°C with supply of oxygen molecules in the wide range of P_O from 0.05 to 4 mTorr, and film qualities were compared for MgO and LAO substrates. The magnitudes of FWHM are roughly the same between MgO and LAO, but MgO shows the window-like behavior at around 2 mTorr where FWHM is exceptionally small, namely, the intragrain crystallinity of plane-distance is excellent. The rocking half-widths Δ are much smaller for LAO than for MgO, then the mosaicity is more excellent for LAO. The surface roughness is much smaller for LAO than for MgO in the middle range of P_O. Therefore, the 2D growth mode is suggested for LAO due to the small lattice mismatch, while 3D grain growth mode is suggested for MgO due to the large lattice mismatch. On LAO, all the parameters of FWHM, Δ and RMS show the regular correlation and the U-shaped behaviors vs P_O. Then the excellent thin film can be grown at around 0.5-1 mTorr with small fluctuation of intragrain plane-distance, good mosaicity and smooth surface. However, on MgO, FWHM and Δ have the inverse correlation. Then the film deposited at 2 mTorr has the small fluctuation of the intragrain plane-distance but large fluctuation of the intergrain crystal plane.

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