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Fabrications of LBMO Thin Films at High Temperature by IBS

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Thin films of La-Ba-Mn-O were fabricated by ion beam sputtering on MgO and LAO ($LaAlO_3$) at 750℃ with supply of oxygen molecules or plasma at oxygen partial pressures of 0.5-1.5 mTorr. The θ-2θ half-widths (W) of XRD of the films are roughly the same for MgO and LAO, while half-widths (Δ) of rocking curve are much smaller for LAO than for MgO. The c-parameters are much larger for LAO and the surface roughness is much smaller for LAO near 1 mTorr. P_O-dependences of W and Δ show regular correlation on LAO whereas they show inverse correlation on MgO.

Key word: LBMO thin films, MgO and LAO, Oxygen molecule and plasma, Crystallinity

1. INTRODUCTION

In recent years, wide variety of researches on colossal magnetoresistance (CMR) have been actively conducted [1, 2]. The CMR thin films have the high potential for various device applications such as magnetic sensors and magnetic memories. Manganite thin films have been successfully grown epitaxially by pulsed laser deposition and molecular beam epitaxy [2-5]. However, more flexible thin-film-processing techniques with high controllability for various deposition parameters are desirable, because properties of manganite thin films seriously depend on various film-factors such as oxygen content, composition and lattice strain [6-8]. We developed new techniques of ion beam sputtering (IBS) employing ion beam or plasma-assist for fabrications of perovskite oxide thin films [9-13]. Using these techniques, we can grow $Bi_2Sr_2CuO_X$, $YBa_2Cu_3O_X$ (YBCO) and manganite thin films at ultralow temperatures around 450℃. Moreover, we can totally control a/c axis preferential orientations of YBCO thin film growth by controlling substrate temperature, oxygen partial pressure and oxygen excitation in plasma-assisted IBS deposition [14]. In this sense, the plasma-assisted IBS method must be very useful for the fabrication of the delicate manganite thin films.

We have been preparing the manganite thin films of La-Ba-Mn-O system (LBMO) employing the plasma-assisted IBS. In this experiment, we found that the crystalline LBMO thin film can be grown down to substrate temperature (T_S) of 470℃ on $LaAlO_3$ (LAO) substrate, while it can be grown above 600℃ on MgO substrate. The crystallinity is much better for LAO than for MgO in the low Ts range, whereas it becomes almost the same with increasing Ts up to 700℃. We found a "window

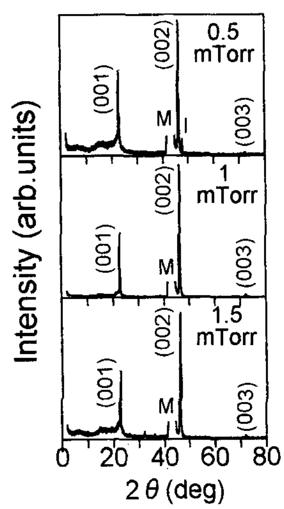

Fig. 1 XRD patterns for the deposited films on MgO with supply of oxygen plasma at various oxygen partial pressure P_O indicated. M: substrate peak.

effect" as that the crystallinity is improved on MgO more than on LAO at 700℃ only in narrow oxygen partial pressure (P_O) range. The crystallinity can also be improved by the oxygen plasma in the higher Ts region on MgO. In this work, we investigated in detail by varying P_O values whether there are some effects of the substrate species and the oxygen plasma on the thin film growth of LBMO at a very high Ts of 750 ℃ where the film growth is usually predominated by thermal energy.

2. EXPERIMENTAL

LBMO thin films were fabricated on MgO (100) and LAO (100) substrates simultaneously by the plasma-assisted IBS. A target of sintered $La_{0.9}Ba_{0.4}MnO_X$ was sputtered by 4 keV Ar^+ ion, and sputtered particles were deposited on the heated substrates. During the deposition, oxygen plasma, produced by discharging oxygen gas in a plasma source, was supplied to the substrate surface. When oxygen molecules were supplied, oxygen gas was emitted from the same plasma source without discharge. The substrate temperature (T_S) was fixed at 750℃ and the oxygen partial pressure (P_O) was varied in the range of 0.5-1.5 mTorr.

Crystallinity of the films were characterized by X-ray diffraction (XRD) on θ-2θ scan using Cu Kα radiation. The film crystallinity was estimated by full widths at half maximum of the θ-2θ peaks (W) and rocking curves (Δ). The θ-2θ half width indicates a measure of uniformity of plane-distance in the crystal grains parallel to the substrate plane (spread of inter-plane spacing). We call this "crystallinity of plane-distance" in this paper. On the other hand, the rocking half width indicates a measure of fluctuation of crystal plane deviated from the substrate plane (spread of orientation of crystallites). We call this "mosaicity". Surface roughness (R_S) was estimated by root mean square value using atomic force microscopy (AFM). Film composition was measured by energy dispersive X-ray microanalysis (EDX) calibrated by inductively coupled plasma analysis. Magnetization was measured by SQUID and magnetoresistance was measured on some of the films.

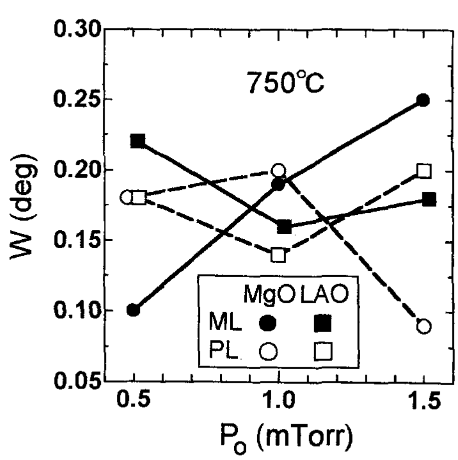

Fig. 2 Averaged W of θ-2θ peaks of (001) and (002) vs P_O. ML: molecular supply, PL: plasma supply.

3. RESULTS AND DISCUSSION

3.1 Crystallinity

The XRD patterns of the LBMO thin films deposited on MgO with the plasma supply are shown in Fig. 1 for various P_O values. The patterns show well oriented single phase of cubic (infinite layer) structure expressed as (La, Ba)MnO_3. According to EDX analysis, Mn composition is slightly rich from the nominal composition of (La, Ba)MnO_3 in all of the films. All of the films are around 350Å thick. Figure 2 shows a P_O-dependence of averaged W of the (001) and (002) XRD lines for the films with the molecular supply (ML) and plasma supply (PL). The averaged rocking half-widths (Δ) are plotted in Fig. 3 as a function of P_O for the same films on (a) MgO and (b) LAO, together with the rocking half-widths of (002) line of the corresponding substrates.

A. Substrate dependence

The films on MgO and LAO for ML and PL have similar values of W (Fig. 2), however, the rocking half-widths (Δ) are much different between them (Fig. 3). The magnitudes of Δ are much larger for the films on MgO than on LAO. For LAO, the values of Δ of the films are very small and close to those of the LAO substrate. Therefore, the crystallinity of plane-distance of the films is approximately the same for MgO and LAO, however the mosaicity is much better for the films on LAO than on MgO. We have previously obtained an experimental fact that the crystalline phase grows from the beginning of deposition on LAO due to small lattice mismatch, while only amorphous phase grows at initial stage of the deposition on MgO due to large lattice mismatch [11]. Then epitaxial growth is promoted on LAO, leading to well-aligned grain parallel to the substrate plane and to the excellent mosaicity (improvement of orientation uniformity) on LAO. On the contrary, the crystal grains grow on the amorphous layer on MgO, leading to considerable fluctuation of the grain alignment and the poor mosaicity on MgO.

Roughly speaking, the values of W of the films show a maximum at Po=1 mTorr for MgO while a minimum at Po=1 mTorr for LAO both for ML and PL (Fig. 2). This means that the crystallinity of plane-distance of the films is worst at 1 mTorr on MgO while it is best at 1 mTorr on LAO. This tendency for LAO is roughly consistent with the tendency of mosaicity (Δ) for LAO (Fig. 3b). Then the more intergrain aligned films have the more uniform plane-distance in the grain which is expected by the epitaxial growth concept. Contrary to this, the mosaicity of the films on MgO is best at Po=1 mTorr (Fig. 3a) whereas the crystallinity of plane-distance is worst at Po=1 mTorr on MgO. Then the grains in the films deposited on MgO at 1 mTorr are comparatively aligned to the substrate plane but have the fluctuated plane-distance probably due to intragrain stress induced by intergrain alignment. It should be noted that the behaviors of film Δ are not always affected by that of substrate Δ.

B. Plasma effects

On MgO, the values of W and Δ are smaller for ML in Po range of 0.5-1.0 mTorr, while they are smaller for PL at Po=1.5 mTorr.

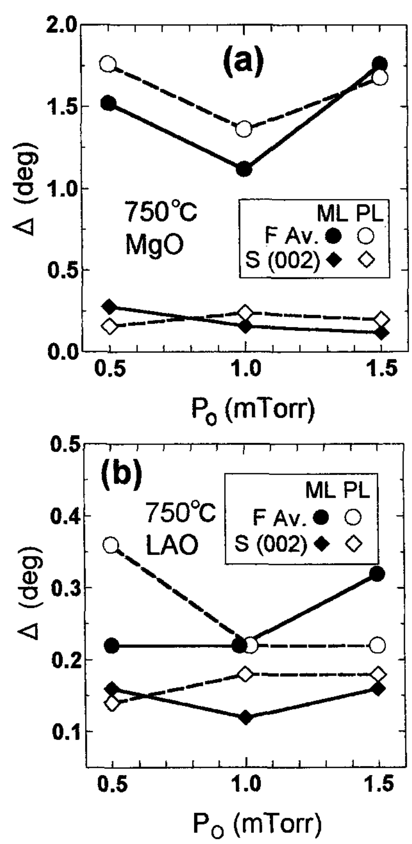

Fig. 3 Averaged rocking half-width Δ vs Po for the films on (a) MgO and (b) LAO. F Av.: film averaged Δ over (001) and (002) peaks, S(002): substrate Δ of (002) peak.

Therefore, both of the crystallinity of plane-distance and the mosaicity are improved by ML at lower Po and by PL at higher Po on MgO. On the other hand, on LAO, the values of W are smaller for PL but that of Δ are smaller for ML in the lower Po region of 0.5-1.0 mTorr. Therefore, the intragrain crystallinity of plane-distance is improved by PL while the intergrain mosaicity is improved by ML at the lower Po, and vice versa at the higher Po of 1.5 mTorr. As far as only the mosaicity is concerned, the tendency that the mosaicity is improved by ML at the lower Po (smaller Δ for ML), while it is improved by PL at the higher Po (smaller Δ for PL), is common to MgO and LAO.

3.2 c-parameter and surface roughness

The c-axis length (c-parameter) was estimated by averaged XRD peak positions. The c-parameters are plotted in Fig. 4 as a function of Po for the films on MgO and LAO both for ML and PL. The surface roughnesses (Rs) are plotted in Fig. 5 as a function of Po for the same films. All the values of c-parameters are larger than the bulk value of 3.87 Å. Especially the c-parameters are exceptionally large on LAO at Po=1 mTorr. As stated above, the crystalline phase grows at the initial stage of the deposition on LAO (lattice constant is 3.79 Å) at Po=1 mTorr, while the amorphous phase grows initially on MgO (lattice constant is 4.21Å) [11]. Then the in-plane a-b axes are compressed by the lattice matching, resulting in the expansion of c-axis on LAO. The exact reason why the c-parameter is large only at 1 mTorr is not known, but it can be deduced as follows. The both of crystallinity of plane-distance (W) and mosaicity (Δ) are better at 1 mTorr on LAO in the Po range of 0.5-1.5 mTorr (Figs. 2 and 3b). Then the epitaxial growth must be promoted at this growth condition. This indicates that the

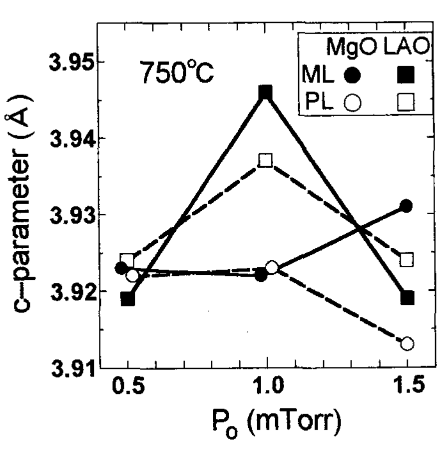

Fig. 4 c-parameter vs Po for the films.

lattice strain at the interface induced by the lattice mismatch is larger, leading to the larger expansion of c-axis at 1 mTorr. The promoted epitaxial growth results in the two-dimensional film growth and smoother surface on LAO at 1 mTorr as shown in Fig. 5. The strain free crystalline film grows on the amorphous buffer layer on MgO, then the c-axis is shorter on MgO and closer to the bulk value compared with that on LAO. This 3D grain growth on the amorphous layer results in the rough surface on MgO as show in Fig. 5. Contrary to this, 2D epitaxial growth results in the smooth surface on LAO as shown in Fig. 5.

The magnetization and resistance were measured on a film deposited on LAO with ML at Po=1.5 mTorr. It showed Curie temperature of 174 K and metal-insulator transition temperature of 84.2 K.

4. SUMMARY

LBMO thin films were fabricated by IBS on MgO and LAO substrates at 750℃ with supply of oxygen molecules or plasma in Po range of 0.5-1.5 mTorr. Neglecting slight differences for ML and PL, the crystallinity of plane-distance and the surface roughness are worst while the mosaisity is best at 1 mTorr on MgO. The crystallinity of plane-distance, the mosaicity and the surface roughness are best at 1 mTorr on LAO, and further the c-parameter is largest at 1 mTorr. The mosaicity is much better on LAO than on MgO, the c-parameter is larger on LAO than on MgO, and the surface roughness is much better on LAO than on MgO. These results can be basically explained by the difference in initial growth modes due to the lattice mismatch. The crystalline phase grows initially in 2D mode on LAO, whereas the amorphous phase grows initially then the 3D crystalline grain grows on the amorphous buffer layer on MgO. The effect of plasma supply is not so clear because of the large thermal energy at Ts=750℃. Its minor effects are that the crystallinity of plane-distance and the mosaicity are improved by PL at the higher Po on MgO, however, the crystallinity of plane-distance is improved by PL at the lower Po while the mosaicity is improved by PL at the higher Po on LAO.

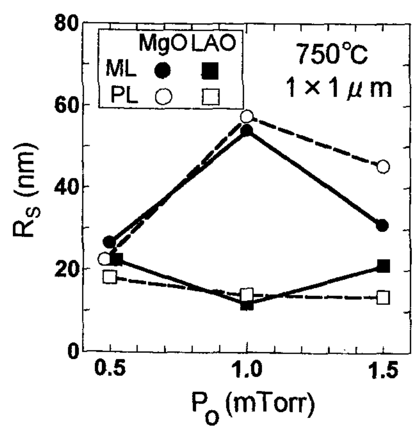

Fig. 5 Surface roughness (Rs) vs Po for the films.

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