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Fabrication of $YMnO_3$ Epitaxial Thin Films and the Magnetic-Ferroelectric Correlation Phenomena

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$YMnO_3$, a hexagonal $RMnO_3$ compound, has both antiferromagnetic and ferroelectric properties. Recently, cross-correlation in magnetic dielectric properties on hexagonal $YMnO_3$ single crystals has been investigated. However, cross-correlation in magnetic-ferroelectric properties has not yet been understood. In this study, we used $YMnO_3$ epitaxial films with excellent crystallinity to understand the correlation. The $YMnO_3$ epitaxial films show dielectric anomalies at around the Néel point of the films. It was suggested that the ferroelectric domain switching was suppressed by magnetic ordering. The relationship between the magnetic structure and ferroelectric properties are discussed in terms of the temperature dependencies of magnetization and dielectric permittivity.

Key words: $YMnO_3$, multiferroic, ferroelectric, antiferromagnetic, optical emission spectrometry

1. INTRODUCTION

A material group called multiferroics has attracted considerable attention due to their potential for future computing application. Multiferroics have multiple simultaneous properties such as ferroelectricitiy, ferromagnetism, ferroelasticity and show cross-correlation among the properties. [1-5]

In this study, we focused on $YMnO_3$, which is a hexagonal $RMnO_3$ compound and has simultaneous antiferromagnetic and ferroelectric properties. [2] In hexagonal $RMnO_3$, each magnetic Mn^{3+} ion is surrounded by five oxygen ions, forming a corner-shared MnO_5 bipyramid. $RMnO_3$ shows ferroelectricity along the c axis due to the tilting of MnO_5 bipyramid and the change of distance between oxygen and rare-earth ions. [6] Moreover, Below the Néel point ~70K, hexagonal $RMnO_3$ shows antiferromagnetism by the magnetic ordering of Mn^{3+}.

Recently, cross-correlation in the magnetic-dielectric properties on hexagonal $RMnO_3$ single crystals including $YMnO_3$ has been reported. [2] In single crystals of $YMnO_3$ and $LuMnO_3$, the dielectric permittivity is largely reduced below the antiferromagnetic Néel point. We examined the relationship between the ferroelectric domain switching and the ordering of magnetic moment using $YMnO_3$ epitaxial films deposited by the pulsed laser deposition method. [7-9]

2. EXPERIMENTAL

$YMnO_3$ films were deposited by the pulsed laser deposition method, which uses sintered ceramics are used as a target in many cases and the quality of the target has a significant influence on the quality of the deposited thin films. In this study, to obtain targets with high density, the ceramic bulk of $YMnO_3$ was prepared by the following process. Y_2O_3 (99.9%) and Mn_3O_4 (99.9%) were mixed in a ratio of 3:2 to achieve stoichiometry of $YMnO_3$. The mixture was calcinated three times at 950°C for 4 hours to compose a single phase at low temperature and sintered at 1400°C for 20 hours. The density of the obtained $YMnO_3$ target was above 95%. To grow high-quality thin films, the control of the metallic composition of the films is important. To investigate film composition dependence on the deposition condition, $YMnO_3$ films were deposited on silicon substrates at room temperature as an initial optimization for the deposition condition. The composition of the $YMnO_3$ films was determined by electron probe micro-analysis (EPMA) measurement. During the deposition, the plume was analyzed by optical emission spectroscopy (OES) to investigate the ablation condition.

$YMnO_3$ epitaxial films with a thickness of 100 nm were then deposited on (111) Pt/(0001) sapphire substrates at 740°C. The structural analysis was carried out by x-ray diffraction (XRD). To examine the dielectric properties, Pt top electrodes were deposited on the films through a shadow mask by an rf magnetron sputtering method. Magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer. The polarization-electric field (P-E) measurement was performed using a Sawyer-Tower circuit. Capacitance-voltage (C-V) characteristics were measured with an LCR meter (HA4282) at low temperature. Pulsed C-V measurement was also used to eliminate the influence of space charge. [10]

3. RESULTS AND DISCUSSION

Figure 1(a) shows the Mn/Y composition ratio of the films deposited at room temperature as a function of the laser power density. Two kinds of $YMnO_3$ targets (A and B) were used and the significant difference is illustrated in Fig. 1(a). In the films deposited by the target A, as the laser power density increased, the Mn/Y ratio increased and closed to 1 at the laser power density of 0.30J/cm^2. The Mn/Y ratio then decreased to 0.8-0.9 above 0.33J/cm^2. On the other hand, when target B was used, the Mn/Y ratio was saturated around 1 above the laser power density of 0.37J/cm^2. Another difference between target A and B could be found on the deposition rate as shown in Fig. 1(b). The deposition ratio of target A becomes higher than that of target B above 0.30 J/cm^2. Although the density and microstructure between the two targets were not

significantly different, there was a difference in the times used for the deposition. Target A was used for many depositions and target B was used only a few times. Therefore, the surface of target A being the inside of the original ceramics and the surface of target B is the surface region of the original ceramics. It is known that the density of ceramics is not constant from the surface to the inside. The difference between targets A and B shown in Fig. 1 was probably caused by the slight difference between the two targets. Laser ablation has two kinds of mechanisms: photo ablation in low laser power density region and thermal ablation in high laser power density region. Fig. 1 shows that the difference was significant at the laser power density above 0.30 J/cm^2; thus, it appears that the density of the target influences the thermal ablation.

To investigate the ablation condition of the two targets, OES was carried out for the plume. OES peaks at 467 nm and 615 nm are corresponds to Y and YO, respectively. [11] Figure 2 shows peak intensity ratio of YO/(Y+YO) from 0.23J/cm^2 to 0.40J/cm^2. At 0.23J/cm^2 and 0.27J/cm^2, the peak from Y was barely observed. As can be seen, the plume of target B has larger YO/(Y+YO) ratio than that of target A. A larger YO/(Y+YO) ratio is suitable for deposition because it can be expected that oxygen deficiency in the films is reduced. Given the results shown in Figs. 1 and 2, it

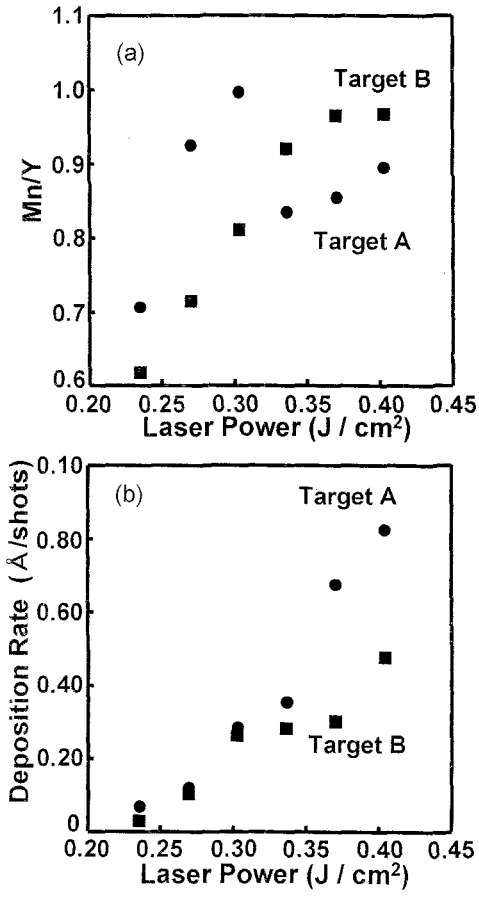

Fig.1. Laser power density dependence of (a) composition and (b) deposition rate by $YMnO_3$ target A (solid circle) and B (solid square).

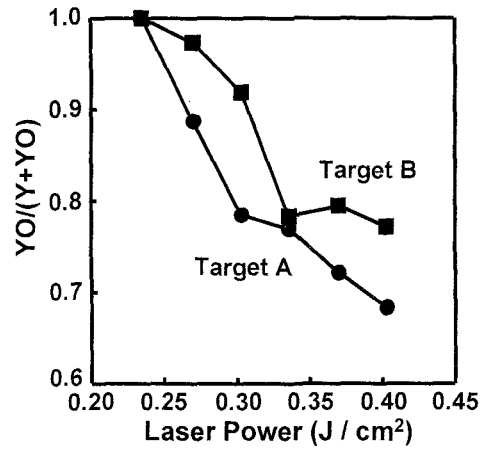

Fig.2. YO/(Y+YO) ratio of OSE for the plume as a function of laser power density. Solid circle, target A and solid square, target B.

was found that the quality of the target has influence on the composition of the deposited films and the species in the plume.

As a result of the optimization for the deposition conditions, $YMnO_3$ epitaxial thin films with high crystallinity were obtained at a substrate temperature of 740°C on (111) Pt/(0001) sapphire substrates. Details are described other studies in report. The full width at half maximums (FWHM) of rocking curve for $YMnO_3$ 0004 and 1122 were 0.49° and 1.12°, respectively [9].

Figure 3 shows the temperature dependence of the magnetization measured at a field strength H of 750Oe in which magnetization of the $YMnO_3$ films was saturated along the a axis below 300K. Magnetization increased with decreasing temperature from 300K to 130K, and deceased below 130K. This indicates that the $YMnO_3$ films have magnetic phase transition near 130K. It was reported that T_N of a $YMnO_3$ single crystal is around 70K. [2] There are a couple of possibilities to explain the increase of to increase the magnetic phase transition temperature of the films than that of the single crystal, such as precipitation of second phase or change of Mn-O-Mn distance. Although XRD indicated that the $YMnO_3$ films were single phase and had excellent crystalline, an undetectable amount of second phase by XRD might precipitate. It is possible that the small amount of magnetization from the second phase affected the M-T characteristics. YMn_2O_5, MnO, MnO_2 and Mn_3O_4 are the possible magnetic materials composed by Y, Mn and O. MnO and MnO_2 show antiferromagnetism and the Néel point were 120K and 80K, respectively. If magnetization of MnO or MnO_2 affected M-T characteristics, the film should show magnetic phase transition near 120K or 84K. Equally, YMn_2O_5 shows weak ferromagnetism at 20~40K and Mn_3O_4 shows antiferromagnetism blew 42K. Therefore, the second phase does not effect the magnetic phase transition of the $YMnO_3$ films.

It was reported that the spins of Mn ions are ordered by superexchange interaction mediating O ions. Therefore, another possibility is that the Mn-O-Mn bond distance is reduced by lattice distortion or defect, and the Néel point is increased by strengthening

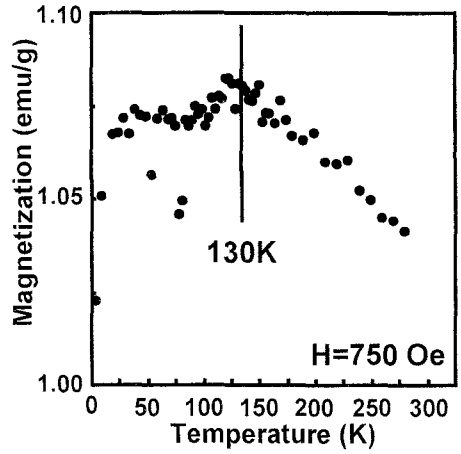

Fig.3. M-T characteristics of $YMnO_3$ films with applied magnetic field 750Oe.

superexchange interaction. The Change in Mn-O-Mn bond distance is caused by the lattice mismatch between the substrate and the film or the difference of the thermal expansion coefficient. However, the lattice constant of the film was consistent with that of the single crystal at 300K. Moreover, there is no significant difference on the thermal expansion coefficient between Pt and $YMnO_3$. Therefore, it can be concluded that Mn-O-Mn bond distance is not different between the single crystal and the film. Although the accurate Néel point of $YMnO_3$ film is unclear, it seems that the magnetic anomaly observed by M-T measurement near 130K indicates the pretransitional phenomenon for the antimagnetic ordering.

The P-E characteristics of the $YMnO_3$ films were measured from 20K to 300K. The $YMnO_3$ films showed well-saturated polarization-electric field hysteresis loops with a saturated polarization of 4.3 $\mu C/cm^2$, the remanent polarization of 3.9 $\mu C/cm^2$ and a coercive electric field of 85 kV/cm at 300K. [8] It was found that the coercive field increased gradually with decreasing temperature and it increased rapidly below

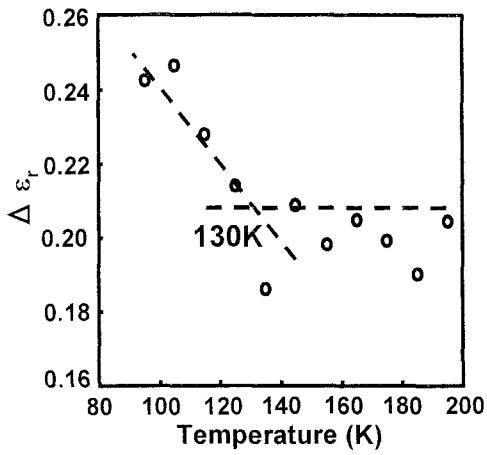

Fig.4. Temperature dependence of temperature derivative of dielectric permittivity at domain switching measured by conventional C-V and pulsed C-V.

130K. This result indicates that more the energy is needed to switch the ferroelectric polarization below 130K where the $YMnO_3$ films show magnetic phase transition.

In addition, the dielectric permittivity of the $YMnO_3$ films was evaluated by pulsed C-V measurement from 80K to 300K. In the C-V characteristics, the $YMnO_3$ films showed typical ferroelectric-type curves. While the dielectric permittivity measured by high DC voltage is linear component of the dielectric permittivity of $YMnO_3$, the maximum dielectric permittivity is attributed to the ferroelectric polarization switching. When there was a temperature dependence of the maximum dielectric permittivity, an anomaly was observed around 250K. However, in comparison with the results of conventional C-V measurement, it was found that the anomaly is attributed to leakage current, free ion, etc. On the other hand, $\Delta\varepsilon_r/\Delta T$ shows an anomaly at 130K as shown in Fig. 4. The rapid increase of $\Delta\varepsilon_r/\Delta T$ below 130K indicates that the decreasing rate of the maximum dielectric permittivity with decreasing temperature increases below 130 K. This result is probably caused by the suppression of the ferroelectric polarization switching, which is consistent with the result of the increase of the coercive electric field below 130K as described earlier. Therefore, the decrease of the dielectric permittivity below the antiferromagnetic Néel point might be caused by the magnetoelectric effect. Given the results shown in this paper, it can be concluded that the spin interaction by the antiferromagnetic ordering of Mn ions influences the ferroelectric polarization switching.

4. SUMMARY

$YMnO_3$ films were deposited by PLD method. From the optimization process of the deposition conditions using optical emission spectrometry, it was found that the quality of the target such as the density has great influences on the film composition, deposition rate, and ablation condition. Eventually, $YMnO_3$ epitaxial films with excellent crystallinity on epitaxial (111) Pt/(0001) sapphire substrates were obtained. The $YMnO_3$ films showed a magnetic phase transition at 130K. We attempted investigate the relationship between the magnetic structure and the dielectric properties. On the temperature dependence of the dielectric permittivity, an anomaly was observed below the magnetic phase transition near 130K.

5. ACKNOWLEDGEMENTS

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