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Growth of YMnO$_3$ Epitaxial Thin Film and Effect of the Magnetic Ordering on the Ferroelectric Polarization Switching

Kazuhiro Maeda

February 2011

Doctoral Thesis at Osaka Prefecture University
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Chapter 1: General Introduction

Transition metal compounds exhibit a wide variety of strongly correlated electron system properties, including ferromagnetism, superconductivity and colossal magnetoresistance, which are of great interest to the scientific and technological community. Ferromagnetic materials possess spin order (spontaneous magnetization) which can be switched by a magnetic field. The spin order has been used in magnetic recording devices, which form the basis of information technology. Similarly, ferroelectric materials possess an electric dipole order (spontaneous electric polarization), the direction of which can be switched by an applied electric field. A wide variety of functional devices using ferroelectric polarization have been put into practical use: ultrasonic and microwave devices; nonlinear optical devices; and pyroelectric infrared sensors. Furthermore, ferroelectrics are integrated into Si semiconductor technology as ferroelectric nonvolatile memory. Spin-based electronics using transition metal compounds are expected to overcome difficulties in current Si based electronics.

Multiferroics are materials where two or more ferroic orders, such as ferroelectricity and ferromagnetism, coexist simultaneously [1-4]. The magnetoelectric coupling properties of multiferroics make them promising candidates for next-generation technologies such as low-power-consumption spintronics devices [5].

Multiferroics have been studied both in single phase and composite materials. Composites of magnetostrictive and piezoelectric compounds exhibit a cross coupling between magnetic and electric properties via stress mediation [2]. Laminated ferromagnetic/ferroelectric structure and ferromagnetic nanostructure which is embedded in ferroelectric matrix are proposed [6, 7]. On the other hand, single-phase
multiferroics are prime candidates for displaying a giant magnetoelectric effect because enhancement of magnetoelectric effect can be expected by strong internal electromagnetic fields [2]. The single phase multiferroics has recently included materials which have ferroelectricity and not only ferromagnetism but also magnetic ordering simultaneously because electromagnetic effects have been found in several antimagnetic ferroelectric materials [8]. Currently four major types of multiferroics can be distinguished:

Multiferroics have attracted intense interest since the discovery in 2003 of colossal electromagnetic effects in orthorhombic manganite, TbMnO$_3$ [9]. TbMnO$_3$ has ferroelectricity induced by cycloid spiral spin ordering [10, 11]. When a magnetic field is applied, TbMnO$_3$ shows a spin-flip transition where the polarization vector rotates by 90°. This correlation between the cycloidal-spiral spin structure and ferroelectric polarization is thought to be associated with the Dzyaloshinskii–Moriya interaction [12]. A magnetic field-induced polarization flop has been observed in some materials with a spiral spin structure that exhibits spin-driven ferroelectricity, such as RMn$_2$O$_5$ [13], MnWO$_4$ [14], and LiCu$_2$O$_2$ [15]. Additionally, in CoCr$_2$O$_4$ which has a transverse-conical magnetic structure (transition temperature of ~25 K), the magnetic reversal of its polarization was demonstrated [16].

Ferroelectric perovskite BiFeO$_3$ displays G-type antiferromagnetic ordering at room temperature; thus, the nearest neighbor Fe moments are aligned antiparallel to each other in all three Cartesian directions [17]. The Curie temperature ($T_C$) and Néel temperature ($T_N$) of BiFeO$_3$ are ~1000 K and ~640 K, respectively. Ramesh et al. found that antiferromagnetic domain switching in BiFeO$_3$ was induced by ferroelectric polarization switching [18]. In addition, exchange bias systems using the
antiferromagnetic domain were proposed [19]. Ferroelectrics have also been explored for practical applications, because BiFeO$_3$ thin-films have large spontaneous polarization (~70 C/cm$^2$) [20].

Hexagonal RMnO$_3$ compounds (R = Ho, Er, Tm, Yb, Lu, Y, Sc, In) are both ferroelectric (T$_c$ > 1000 K) and antiferromagnetic (T$_N$ = 70-120 K) [21, 22]. The Mn$^{3+}$ ions form a triangular lattice ($\sqrt{3}$ $\times$ $\sqrt{3}$ superstructure) in which the moments are coupled antiferromagnetically in the ab plane. For YMnO$_3$, anomalies in the dielectric permittivity ($\varepsilon_\infty$) at T$_N$ provide some evidence of cross-correlation [23]. Atomic coordinates of a single crystal YMnO$_3$ have also been investigated by high resolution neutron diffraction and indicate strong spin-lattice coupling around T$_N$ [24].

The charge-frustrated system in RFe$_2$O$_4$ belongs to a new class of ferroelectrics. The ferroelectric polarization arises from charge ordering which is characterized as the regular arrangement of Fe$^{2+}$/Fe$^{3+}$ ions in the frustrated triangular lattice [25]. Furthermore, since RFe$_2$O$_4$ shows ferrimagnetism (T$_N$ = 240 K), which is closely related to Fe$^{2+}$/Fe$^{3+}$ charge ordering, RFe$_2$O$_4$ should show magnetoelectric cross-correlation [25, 26].

Magnetoferroelectric hexagonal RMnO$_3$ compounds are the focus of this work because of their strongly frustrated antiferromagnetism, which is attributed to the triangular antiferromagnetic structure of Mn$^{3+}$ ions. The structure of these compounds is described by the crystallographic space group P6$_{3}$cm. In hexagonal RMnO$_3$, each magnetic Mn$^{3+}$ ion is surrounded by five oxygen ions, which forms a corner-shared MnO$_5$ bipyramid. The rare earth atoms are surrounded by seven oxygen ions as shown in Fig. 1-1(a). Hexagonal RMnO$_3$ shows ferroelectricity along the c axis because of the tilting of the MnO$_5$ bipyramid, the change in distance between oxygen and rare-earth
ions and spontaneous polarization in the range of 5-6 µC/cm² (Fig. 1-1(b)). An antiferromagnetic spin arrangement is formed, where neighboring spins are rotated by 120° (Fig. 1-1(c))

Hexagonal RMnO₃ has a number of interesting features. It has a high Tₑ (~1000 K) and its ferroelectric polarization is enough large for practical use in devices, such as field-effects transistors (FETs) [27]. Si FETs need a polarization above 0.1 ?C/cm²; however, the spontaneous polarization of orthorhombic TbMnO₃ is small (0.04 ?C/cm²). Hexagonal RMnO₃ has a unique ferroelectric domain structure, which is driven by the triangular lattice as shown in Fig. 1-1(d) [28], and the Mn³⁺ ion moments have a frustrated antiferromagnetic spin arrangement [22]. The ferromagnetic properties of hexagonal RMnO₃ can be changed by A-site substitution with rare-earth ions [29]. Fiebig et al. have reported that, in an YMnO₃ single crystal, the ferroelectric domain wall is always accompanied by an antiferromagnetic domain wall, while a single antiferromagnetic domain wall can exist independently [31]. Hanamura and Tanabe revealed that theoretically, ferroelectric and antiferromagnetic order parameters in YMnO₃ are coupled at the ferroelectric domain boundary [32], indicating that the effect of the antiferromagnetic domain on the ferroelectric domain wall motion merit further investigation. If the antiferromagnetic domain wall follows the motion of the ferroelectric domain wall, its magnetic properties can be controlled by an electric field. Therefore, in hexagonal RMnO₃, large cross coupling can be expected when the ferroelectric polarization is switched because the ferroelectric polarization of hexagonal RMnO₃, is almost 100 times larger than that of representative multiferroics TbMnO₃ (~0.04 ?C/cm²).

Hence, it is essential that effect of the magnetic ordering on the ferroelectric
Fig. 1-1 (a) Crystallography, (b) tilting of MnO$_5$ bipyramids, (c) magnetic structure of Mn moment and (d) ferroelectric domain in YMnO$_3$. 
domain wall motion is clarified in order to make use of the multiferroic properties of RMnO$_3$. Therefore, this work has focused on YMnO$_3$, which has 2 order parameters: antiferromagnetism and ferroelectricity. Since the ferroelectric polarization of thin-films can be conveniently switched by large enough electric fields, the ferroelectric polarization switching behavior of YMnO$_3$ films around $T_N$ is investigated in this work.

Shigemitsu et al. have prepared YMnO$_3$ epitaxial films which have good crystallinity and show a polarization-electric field (P-E) hysteresis loop at room temperature [33, 34]. Additionally, ferroelectric gate FETs using YMnO$_3$ as a gate insulator have been developed [27, 35]. However, the ferroelectric polarization switching of YMnO$_3$ at low temperatures has not been widely reported. To investigate the effect of the antiferromagnetic domain on the ferroelectric domain wall motion, YMnO$_3$ thin films with a small number of defects are needed. The defects in ferroelectrics trap the ferroelectric domain wall; this is known as the pinning effect.

In this work, the YMnO$_3$ films were grown using a pulsed laser deposition (PLD) system which is a well-known technique for preparing crystalline oxide thin films with high epitaxial quality. Improvement of the crystalline quality of YMnO$_3$ films was attempted by optimizing the laser irradiation conditions for PLD. The laser irradiation conditions are the dominant parameters controlling material ablation, which mainly affects stoichiometric transfer. The ferroelectric polarization switching behavior, in particular nucleation and domain wall motion, of the YMnO$_3$ thin films around $T_N$ was then investigated in detail. Effect of the antiferromagnetic domain on the ferroelectric polarization switching is discussed.

This thesis consists of seven chapters as follows.

In Chapter 2, stoichiometry control of YMnO$_3$ thin film and the effect of the
film composition, such as metallic composition and oxygen, on the ferroelectric properties were investigated. Hexagonal YMnO$_3$ thin films were prepared using PLD. Correlation between laser condition and condition of the active species was investigated from the optical emission spectrum (OES) of the ablation plume of YMnO$_3$ [36-38]. The behavior of the active species in the plume was analyzed in terms of the laser spot area and the energy dependence of the composition and emission spectra. Moreover, it was inferred from the OES, that the plume consists of atomic Mn, Y, O and molecular YO species. Therefore, a reduction in the number of oxygen vacancies in the film was attempted by controlling the amount of oxygen-related active species in the plume.

In Chapter 3, the film characteristics were investigated as a function of thickness, in order to optimize the film thickness. During deposition, reflective high-energy electron diffraction (RHEED) was carried out to investigate the film surface and crystallinity. The structural characteristics of YMnO$_3$ films with thickness between 10 and 150 nm were evaluated by X-ray diffraction (XRD) and atomic force microscopy (AFM). In addition, X-ray photoelectron spectra of films with thickness of 10 and 100 nm were used to characterize the surface.

In Chapter 4, the ferroelectric polarization of the YMnO$_3$ film was investigated over the temperature range 300 to 10 K. Ferroelectric polarization switching is known to be affected by domain pinning, which is mainly caused by the space charge. The temperature dependence of the dielectric relaxation was assessed using $\varepsilon_r$-$f$ characteristics to measure the influence of trapped charge, and the P-E and C-V characteristics were measured to understand the ferroelectric switching process. The frequency dependence of the coercive field ($E_c$) was evaluated at various temperatures using Ishibashi–Orihara theory. Furthermore, the switching behavior of the YMnO$_3$ film
was compared with that of the typical ferroelectric film, Pb(Zr,Ti)O$_3$ (PZT).

In Chapter 5, neutron diffraction measurements were performed at various temperatures to investigate the magnetic structure of the YMnO$_3$ film, [22, 39]. The neutron diffraction profiles were measured at YMnO$_3$ 100 along 00l scan directions in the reciprocal space; magnetic diffraction is observed at YMnO$_3$ 100 when the spins of Mn$^{3+}$ are ordered antiferromagnetically. Additionally, Raman scattering was carried out for the YMnO$_3$ bulk and the film over the temperature range from 300 down to 15 K. The influence of magnetic spin ordering on the phonon in the YMnO$_3$ film is then discussed.

In Chapter 6, the temperature dependences of $\varepsilon_r$ and ferroelectric polarization were investigated. The effect of magnetic ordering on the ferroelectric properties of the YMnO$_3$ thin film should be observed around $T_N$. Because the ferroelectric domain wall is reported to always be accompanied by an antiferromagnetic domain wall, it is possible to see its influence on ferroelectric nucleation and domain wall motion. The temperature dependence of the ferroelectric nucleation density was then investigated using Rayleigh’s law. Additionally, a high-speed capacitance measurement system was developed to investigate the time constant of the domain wall motion in an electric field.

Chapter 7 summarizes the main results and presents the conclusions of this thesis.

Reference


Materials 9, 253 (2010).


Chapter 2: Stoichiometry Control of Hexagonal YMnO₃ Thin Film by Laser Condition on Pulsed Laser Deposition System

2-1. Introduction

To obtain ferroelectric thin films with good ferroelectric polarization switching characteristics, decrease of defects, such as off-stoichiometry and oxygen vacancies, in the film is needed, because the polarization switching, which is progressed by the ferroelectric domain wall motion, is interfered by the defects [1]. Therefore, growth of the YMnO₃ thin films with little off-stoichiometry and oxygen vacancies is attempted in this chapter. Shigemitsu et al. have successfully grown hexagonal YMnO₃ epitaxial thin films with extremely smooth surfaces and high crystallinity by reduction of the substrate temperature and the radiation heat effect, by exchanging the heating system for a pulsed laser deposition (PLD) method [2, 3]. In this study, stoichiometry control of YMnO₃ thin films and the effect of the film composition (Mn/Y) on the ferroelectric properties are investigated. It is known that the laser energy density is a significant parameter for PLD, mainly affecting stoichiometric transfer [4-6]. When a laser is irradiated on the target, the excited active species are ejected from the target surface, and a plume is generated due to the emission of active species. Influence of the laser irradiation conditions on the active species is analyzed by observation of the plume using optical emission spectrometry. In addition, the relationship between the properties of the active species and film composition is investigated. The laser energy dependences of the composition and the emission spectrum are measured using different laser spot areas. The influence of composition on the crystal structure and electrical properties of the films is examined. In addition, the effect of the oxygen-related active species such as
O and YO on the formation/annihilation of oxygen vacancies in YMnO$_3$ films is discussed. Such a discussion is warranted because a decrease in the number of oxygen vacancies because of an increase in the oxygen pressure during film growth influences the metallic composition ratio (Mn/Y) [7]. Decrease of the oxygen vacancies was attempted by controlling the oxygen related active species without changing the metallic composition in the films. Effect of the oxygen related active species on the ferroelectric polarization and the saturated property of the polarization of the YMnO$_3$ films is discussed.

2-2. Experiments

YMnO$_3$ films were deposited by PLD method using an ArF excimer laser (COMPex102: Lambda Physik Co., Ltd.). Ceramic targets of YMnO$_3$ were prepared via conventional ceramic processing. Mixed powders of Y$_2$O$_3$ and Mn$_3$O$_4$ were calcined at 1400°C for 6 h in air. The calcined powders were ball-milled for 24 h, then pressed at a pressure of 200 MPa and sintered at 1400 °C for 20 h in air. YMnO$_3$ ceramic pellets with Mn/Y from 1.05 to 0.95 were used as targets. The YMnO$_3$ target was placed at a distance of 30 mm from a substrate. The deposition rate depends on the laser energy and laser spot area which is controlled by the focusing lens position. The laser spot areas are changed from 0.03 to 0.12 cm$^2$. Since the deposition rate per laser pulse depends on the laser energy density, repetition rate was changed in range of 3.2-5.6 Hz to fix the deposition time. YMnO$_3$ thin films were grown on (111)Pt/(111)SrTiO$_3$ (STO) substrates. The substrates were heated by a semiconductor laser (? = 808 nm) and the substrate temperature ($T_s$) during the growth was 740 °C. Oxygen pressure was 5×10$^{-3}$ Torr. The optical emission of the plume was analyzed using OES (PMA-11: Hamamatsu
Photonics Co., Ltd.) in a wavelength of from 300 to 960 nm at $T_s$ of room temperature. The film composition was determined using electron probe micro-analysis (JXA-870: JEOL Ltd.). The crystal structure was analyzed by x-ray diffraction (XRD) measurements (X’Pert-MRD: Philips Co., Ltd.). Additionally reciprocal space mapping (RSM) measurements of XRD were performed to determine the a- and c- lattice constants. To evaluate the dielectric properties, Pt top electrodes with 100 $\mu$m diameter were formed on the YMnO$_3$ films through a metal mask by RF magnetron sputtering. The P-E hysteresis loops were measured using by a Sawyer-Tower Circuit. The leakage current was measured using a picoampere (pA) meter (Hewlett Packard 4140B). Raman scattering was observed by using an Ar gas laser at 514.5 nm for excitation. The laser was focused by a lens at the sample surface, and the scattered light was collected in a quasi-back-scattering geometry to a double monochromator of focal length 85 cm.

**Results and Discussion**

2-3-1. Control of Metallic Composition by Laser Condition for Pulsed Laser Deposition

The change in the plume shape with changing laser energy density or laser spot area can be observed directly. Figure 2-1 shows the pictures of the plume as a function of the laser energy at the laser spot areas from 0.04 to 0.08 cm$^2$. The emission intensity of the plume increases with increasing laser energy. In addition, the plume profile becomes broader for smaller laser spot area. This result indicates that the in-flight behavior of the active species depends not only on the laser energy density, but also on the laser spot area. To reveal the in-flight behavior of the active species, OES was carried out on the YMnO$_3$ plume [8-10].
Fig. 2-1 Pictures of laser energy dependence of plume at a laser spot area of 0.04 (upper panels), 0.06 (middle panels) and 0.08 cm$^2$ (lower panels).
Figure 2-2 (a) shows the emission spectrum of the plume near the substrate, when the YMnO$_3$ target is ablated at a laser energy density of 0.16 J/cm$^2$. Identification of the emission peaks was carried out by comparison with OES spectra of the ablation plumes of Y and Y$_2$O$_3$ targets, and using references [11, 12] as shown in Fig. 2-2 (b) and table 2-?. An emission peak at 403 nm corresponds to the emission of neutral Mn active species. Peaks at 602 and 615 nm correspond to the emission of YO active species. The peak at 777 nm corresponds to the emission of neutral O active species. Other peaks are from neutral Y active species. Conversely, no emission from diatomic species such as MnO is observed [20]. The spatial profile of the plume was also measured in order to investigate the origin of the change of plume shape by the varying laser conditions. In the profile, the strongest emission peaks of Mn, Y and YO active species (403, 643, and 615 nm, respectively) were used. Figure 2-3 shows the spatial profile of the emission peaks of Mn, YO and Y active species from the target surface to the substrate at a laser energy density of about 0.16 J/cm$^2$, and laser spot areas of 0.04 and 0.08 cm$^2$. The emission intensity near the target is particularly strong, and the plume profile expands all the way to the substrate. The decrease of the emission intensity between the target and the substrate from the Y active species is smaller than for Mn and YO active species. This result infers that the in-flight behavior of each active species is different. Despite using the same laser energy density, the emission intensity at a spot area of 0.04 cm$^2$ is higher than that at 0.08 cm$^2$. At 0.04 cm$^2$, a larger plume is also observed. Therefore, transfer of each of the active species from the target to the substrate is focused upon. Figure 2-4 shows the laser energy density dependence of the emission intensity ratios Mn/YO and Mn/Y for laser spot areas of 0.04 and 0.08 cm$^2$, respectively, which should relate to the metallic composition of the deposited films. As can be seen in Fig. 2-4 (a),
Fig. 2-2 (a) Optical emission spectra of YMnO$_3$ plume: atomic Mn (closed circles), Y (closed rhomboids), O (closed triangles) and molecular YO (closed squares) active species. (b) Optical emission spectra of YMnO$_3$ at 5.0×10$^{-3}$ Torr (O$_2$ pressure), Y$_2$O$_3$ at 5.0×10$^{-3}$ Torr (O$_2$ pressure), Y at < 1.0×10$^{-6}$ Torr.
Table 2. Wavelength of emission spectrum of active species in YMnO$_3$ plume.

<table>
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<th>Element</th>
<th>Wavelength of Spectrum (nm)</th>
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<tr>
<td>Mn</td>
<td>403</td>
</tr>
<tr>
<td>YO</td>
<td>408.4, 410.9, 412.9, 464.9, 546.7, 552.6, 558.6, 563.1, 619.7, 643.5, 656.1, 668.7, 679.8, 880.3, 923.2, 950.1</td>
</tr>
<tr>
<td>Y</td>
<td>602.6, 615.3</td>
</tr>
<tr>
<td>O</td>
<td>777, 812</td>
</tr>
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</table>
Fig. 2-3 Profile of the optical emission intensity of Mn, YO, and Y species at a laser energy density of 0.16 J/cm².
Fig. 2-4 Emission intensity ratios (a) Mn/YO and (b) Mn/Y, as a function laser energy density for neighborhood of target (open symbols) and substrate (closed symbols).
the emission intensity ratio Mn/YO increases for smaller spot area and higher laser energy density. The laser energy density dependence of the emission intensity ratio Mn/YO does not vary greatly between the neighborhood of the target and the substrate. It is known that two types of YO active species are ejected from the target surface and generated by reaction between the Y active species and O₂ gas at the top of the plume [14, 15]. The opportunity for collision between the active species and O₂ decreases with smaller spot area and higher laser energy, for which the density of the active species increases. Since the production of YO active species decreases, the emission intensity ratio Mn/YO increases for smaller spot area and higher laser energy density. Conversely, in Fig. 2-4 (b), the Mn/Y ratio near the target increases with increasing laser energy density. Compared to the emission intensity ratio Mn/Y near the target, the ratio near the substrate is approximately constant. Although the emission intensity ratio Mn/Y near the substrate has a large error below 0.11 J/cm², the difference in emission intensity ratio between the neighborhood of the target and the substrate is significant for a laser spot area of 0.04 cm² and a laser energy density of 0.16 J/cm².

The influence of laser conditions on composition ratio Mn/Y is also investigated. The laser energy dependence of Mn/Y in the film for laser spot areas of 0.04 and 0.08 cm² is shown in Fig. 2-5. With increasing laser energy, Mn/Y decreases at 0.04 cm². On the other hand, the composition is almost constant at 0.08 cm². The range of the laser energy density where the YMnO₃ films have stoichiometric composition depends on the laser spot area. For a laser spot area of 0.04 cm² and a laser energy density of 0.16 J/cm², in which the Mn/Y emission intensity ratio varies widely between the target and the substrate as shown in Fig. 2-4 (b), the film composition is Y excess as shown in Fig 2-5. The smaller the spot area and the higher the laser energy, the higher
Fig. 2-5 Laser energy density dependence of Mn/Y, for laser area spot of 0.04 (closed circle) and 0.08 cm² (open circle).
the density of active species ejected from the target surface. This indicates that the opportunity for collision between active species increases. Mn (mass: 54.9 au) active species, which have relatively low mass compared to Y (88.9 au) and YO (104.9 au) active species, appear to be readily scattered between the target and the substrate. The films have Y excess composition under plume conditions of high density of active species. Thus the in-flight behavior of ablated active species has a large influence on the metallic composition of the films. The difference in mass of the active species affects the collision rate and the collision effectiveness. It is expected that the control of metallic composition is more difficult with increasing difference in active species mass. The results in this section indicate that the in-flight behavior of ablated active species is one of the most important factors in determining film composition.

**2-3-2. Metallic Composition Dependence on Crystal Structure and Electric Properties**

Based on the results as described section 2-3-1, YMnO$_3$ films with various composition (Mn/Y = 0.8-1.4) were prepared by changing the laser condition in order to discuss the composition dependence on crystal structure and electric properties. Compositional analysis revealed that the metallic composition (Mn/Y) of films deposited at 0.16 J/cm$^2$ and 0.04 cm$^2$ and at 0.19 J/cm$^2$ and 0.08 cm$^2$ as shown in Fig. 2-5, are 0.89 and 0.99, respectively. Fig. 2-6 (a) shows XRD patterns of films grown on the (111)Pt/(111)STO substrate. Only strong YMnO$_3$ 000l peaks are observed. The 0008 diffraction peak at composition of 0.89 remarkably shifted lower angle than that of 0.99, indicating the increase of c-lattice constant. Additionally, a- and c-lattice constants were determined from the position of 1127 diffraction on RSM as shown in Fig. 2-6 (b).
Fig. 2-6 2?-? and RSM of YMnO$_3$ which were prepared at 0.16 J/cm$^2$ in the laser spot area of 0.04 and at 0.19 J/cm$^2$ in 0.08 cm$^2$. 
As a result, a-lattice constants of the films at composition of 0.89 and 0.99 are 6.17 and 6.15 Å, respectively. The c-lattice constants are 11.51 and 11.41 Å, respectively. The lattice constant of film at composition of 0.89 is larger than that at 0.99. In addition, on XRD 2θ-θ profile, all the films deposited exhibit only 000l diffraction, which indicates that several YMnO$_3$ films are single phase and has c axis growth. Figures 2-7 (a), (b) and (c) show the composition dependence of a-, c- lattice constants and volume. Composition is positively correlated with all parameter. In particular, the c-lattice constant varies greatly. The lattice constant and the volume tend to decrease with increasing Mn/Y ratio. This indicates that exceeded Y (Mn) ions are substituted the lattice location of Mn (Y) ions. Additionally, YMnO$_3$ films with different c-lattice constant are obtained at same metallic composition, which indicates c-lattice constant is affected by oxygen content also.

The ferroelectric property of the YMnO$_3$ films was characterized. YMnO$_3$ films were grown using laser condition at 0.16 J/cm$^2$ and 0.04 cm$^2$ and at 0.19 J/cm$^2$ and 0.08 cm$^2$ as shown in Fig. 2-5. The P-E hysteresis loops of the YMnO$_3$ films were measured as shown in Fig. 2-8 (a). The film with a Mn/Y ratio of 0.99 has a square-shaped P-E hysteresis polarization curve compared with the film with a ratio of 0.89. The slanted P-E hysteresis polarization curve of the Mn/Y = 0.89 film indicates that it contains a non-ferroelectric component. Since ferroelectricity in YMnO$_3$ originates from tilting of the MnO$_5$ bipyramid, it may be suppressed when the lattice constant of the sample changes from that of the bulk.

The relationship between the saturated polarization ($P_{sat}$) and the composition of the YMnO$_3$ films grown under various laser irradiation conditions is investigated in detail by P-E hysteresis measurements. The results are shown in Fig. 2-8 (b).
Fig. 2-7 Mn/Y dependence of (a) a-lattice constant (closed circles), (b) c-lattice constant (open circles) and (c) volume (closed triangles).
Fig. 2-8 (a) Polarization-electric field hysteresis loops for YMnO$_3$ epitaxial thin films which were prepared using a laser spot area of 0.04 cm$^2$ (dashed line) and 0.08 cm$^2$ (solid line). (b) Ferroelectric saturated polarization as a function of Mn/Y.
Whilst films with near stoichiometric composition have a $P_{\text{sat}}$ of about 2.60 ?C/cm$^2$, a comparable $P_{\text{sat}}$ in films with near stoichiometric composition is obtained, in the Mn/Y range from 0.9 to 1.1. In addition, a distribution of $P_{\text{sat}}$ is observed for the same composition. It appears that the decrease in $P_{\text{sat}}$ is caused by oxygen vacancies in the film. As a result, the effect of Mn/Y on ferroelectric polarization is less sensitive than that due to oxygen vacancies, because both Mn and Y ions are trivalent cations, whilst the oxygen ion is a divalent anion.

2-3-3. Control of Oxygen Content in YMnO$_3$ Films by Monitoring the Active Species in Plume

As described in section 2-3-1, the results of OES, indicates that atomic Mn, Y, O and molecular YO exist in the YMnO$_3$ plume. The O and YO active species are expected as oxidation source in the YMnO$_3$ film-growth process. The relationship between oxygen context in the films and the active species is investigated in this study. The relationship between oxygen content in the films and the active species is investigated in this study. Because the in-flight behavior of the ablated active species changes significantly with laser spot area, the laser spot area is selected as a deposition parameter. In this study, YMnO$_3$ films were prepared by varying the laser spot area from 0.04 to 0.08 cm$^2$. Moreover, it was found that the metallic composition of the films can be controlled by varying the laser energy for each laser spot area. Therefore, for each laser spot area, the laser energy was adjusted to prepare YMnO$_3$ films with the desired stoichiometric composition. Figure 2-9 (a) shows the laser-spot-area dependence of the emission intensities of the active species. The strong optical emissions from Mn, Y, O, and YO active species that have wavelengths of 403, 643, 777, and 615 nm,
Fig. 2-9 (a) Laser spot area dependence of optical emission intensity of the active species: Mn (closed circles), Y (closed rhomboids), O (closed triangles) and YO (closed squares) active species. (b) Emission intensity O/(Mn + Y + O + YO) (open triangles) and YO/(Mn + Y + O + YO) ratios (open squares) with laser spot area.
Fig. 2-10 Laser spot area dependence of (a) composition and (b) a- and c-lattice constants.
respectively, are used in this plot [10]. When the laser spot area is increased, the emission intensities of atomic Y, Mn, and O active species decrease. Emission from the O active species ceases for a laser spot area greater than 0.06 cm$^2$. On the other hand, the amount of YO active species remains constant, which indicates that the YO active species are generated by a reaction between Y active species and O$_2$ gas. As shown in Fig. 2-9 (b), with increasing laser spot area, the emission intensity ratio O/(Mn+Y+O+YO) decreases and the ratio YO/(Mn+Y+O+YO) increases. These results indicate that, in the plume, the abundance ratio of O active species decreases, while that of the YO active species increases with laser spot area. The amount of oxygen-related ablated active species such as O and YO is successfully controlled by controlling the lasing conditions.

The prepared YMnO$_3$ films are characterized by XRD and electrical measurements to investigate the effect of oxygen-related ablated active species on their crystal structure and ferroelectric properties. It is verified that all the YMnO$_3$ films have a single phase and the desired stoichiometric composition. Figure 2-10 shows the a- and c- lattice constants of the films. These lattice constants determined from the RSM are recorded as a function of the laser spot area. With increasing laser spot area, the values of the a- and c-lattice constants approach that of the corresponding bulk material. This result suggests that the oxygen content of the films was different. To confirm that the lattice constants vary with the oxygen content, the YMnO$_3$ films were annealed at 400 °C in both oxidizing (O$_2$ gas) and reducing {N$_2$:H$_2$ (H$_2$: 5%)} atmospheres. The c-lattice constant of the YMnO$_3$ films decreases by 0.036 Å owing to post-annealing in O$_2$ atmosphere, while it increases by 0.014 Å in N$_2$:H$_2$ (H$_2$: 5%) atmosphere. This result indicates that the oxygen content affects the lattice constant of the YMnO$_3$ films [16].
Fig. 2-11 (a) Raman spectra of YMnO$_3$ film. Raman shifts of (b) A$_1$ mode (154 cm$^{-1}$) and (c) A$_1$ mode (683 cm$^{-1}$), as a function of laser spot area.
Because charge balance between anions and cations improves owing to a decrease in the number of oxygen vacancies, Mn$^{2+}$ ions (radius 0.89 Å) change to Mn$^{3+}$ (radius 0.72 Å). As a result, the lattice constant of the YMnO$_3$ films decreases with a decrease in the number of oxygen vacancies. Additionally, Raman scattering measurement was performed on the YMnO$_3$ films as shown in Fig. 2-11 (a). Because the vibrations of each element such as O, Mn, and Y are observed in Raman scattering measurements, the oxygen content in the YMnO$_3$ films can be determined [17]. Figure 2-10 (b) shows the Raman shift in the A$_1$ mode of Y (at 135 cm$^{-1}$) and O (at 680 cm$^{-1}$) for the YMnO$_3$ films. With increasing laser spot area, the A$_1$ mode of Y remains constant; however, the A$_1$ mode of O approaches the value of the bulk material. From these results, it is suggested that the oxygen content in the YMnO$_3$ films increases with increasing laser spot area. A greater amount of oxygen is introduced into the films and their oxygen content is close to the stoichiometric content. It is indicated that the YO active species affect oxygen content, whereas the O active species have little effect on it.

To discuss the effect of oxygen content on the dielectric properties of the films, current–voltage measurement were performed at room temperature. Although the slope of the log(I)–log(V) plot is 1.1–1.4 at a low electric field, it increases to 1.6–2.1 at a high electric field. We believe that at a high electric field, the bulk-limited space-charge-limited conduction mechanism is dominant in all YMnO$_3$ films. Differences in the leakage current among samples are not remarkable. In this respect, it appears that structural differences such as surface roughness have a greater influence on the leakage current than the oxygen content of the films. Figure 2-12 shows P–E characteristics and the saturation property of the YMnO$_3$ films. The YMnO$_3$ films show well-saturated P–E hysteresis loops at 100 kHz. The $P_{sat}$ of the film grown at laser spot
Fig. 2-12 P-E hysteresis loops of the YMnO$_3$ films deposited at laser area spot of (a) 0.08 and (b) 0.05 cm$^2$. (c) Saturated property at laser area spot of 0.08 (closed circles) and 0.05 cm$^2$ (open squares).
areas of 0.08 and 0.05 cm$^2$ are 2.49 and 2.17 µC/cm$^2$, respectively. $P_{\text{sat}}$ at a laser area spot of 0.08 cm$^2$ is greater than that at 0.05 cm$^2$. Additionally, the slope of the saturation curve at 0.08 cm$^2$ is greater than that at 0.05 cm$^2$. As a result, ferroelectricity of the YMnO$_3$ films is improved by a decrease in the number of oxygen vacancies, which is achieved by increasing laser spot area. It is suggested that an increase in YO active species effectively decreases the number of oxygen vacancies. Precise control of the amount of YO active species in the ablation plume could provide a method to control the oxygen content in the films. Because the active species that is a combination of a metallic atom and oxygen is observed by OES in the plume of several oxide materials [18, 19], the active species is useful in the deposition of oxide thin films by PLD.

2-4. Conclusions

Growth of YMnO$_3$ epitaxial thin films with little off-stoichiometry and oxygen vacancies, which affect ferroelectric polarization switching behavior was attempted using PLD. To reveal the mechanism of compositional variation by changing the laser irradiation conditions, the in-flight behavior of active species in the plume was investigated by OES. It was revealed that Y, Mn, O, and YO active species exist in the YMnO$_3$ plume. For smaller laser spot area and high laser energy density, low mass active species are scattered by collisions within the plume, and therefore arrive at the substrate with lower frequency than high mass active species. It was found that a stoichiometric film can be obtained easily for large laser spot area, because scattering of the active species is suppressed. Thus, the elemental composition of YMnO$_3$ films can be successfully controlled by varying the laser irradiation conditions. Moreover, YMnO$_3$ films with various metallic compositional ratios were prepared in order to investigate
effects of film composition on the crystal structure and the ferroelectric properties. The lattice constant and the volume tend to decrease with increasing Mn/Y. There was no significant decrease in the saturated polarization in the Mn/Y range from 0.9 to 1.1.

The effect of oxygen-related active species such as O and YO present in the ablation plume on the crystal structure and electrical properties of the prepared YMnO$_3$ thin films was investigated. It was found that the emission intensity ratio of the YO active species in the plume increases with increasing laser spot area because of a decrease in the active species density. With increasing laser spot area, the values of the lattice constants of the prepared films approached that of bulk material, and the ferroelectric properties of the films improved. However, the influence of O active species on film characteristics was not observed. The effect of YO active species on the oxygen content of the prepared films is greater than that of the O active species. Therefore, it was concluded that YMnO$_3$ films with lower number of oxygen vacancies can be prepared under lasing conditions wherein the emission intensity ratio YO/(Mn+Y+O+YO) of the YO active species is large.

Reference

Chapter 3: Growth Process of YMnO$_3$ Epitaxial Thin Films

3-1. Introduction

As described in Chapter 2, stoichiometric YMnO$_3$ films exhibiting good ferroelectricity were obtained by optimizing the laser conditions for PLD. However, concerning the growth of YMnO$_3$ films, there is an issue of Mn ion evaporation from the target induced by radiation heat [1]. To resolve this issue, Shigemitsu et al. reported that the radiation heat effect can be minimized by changing the heating system from a lamp to an infrared laser [2]. In this chapter, to consider the growth of YMnO$_3$ films, an investigation into the dependence on film thickness of film characteristics such as surface morphology, structure, composition and electrical properties is discussed [3-6].

3-2. Experiments

YMnO$_3$ films with a thickness from 10 to 150 nm were prepared by changing the number of laser shots at a laser spot area of 0.05 cm$^2$, which is relatively small. During deposition, thin-film growth was monitored in situ by using a reflective high-energy electron diffraction (RHEED) system. Film surface morphology was observed by atomic force microscopy (AFM, Digital Instruments, NanoScope ?). Film composition was determined by electron probe microanalysis (EPMA, JXA-870: JEOL Ltd.) and X-ray photoelectron spectroscopy (XPS) at h? = 3.1 keV. XPS was performed at BL27A of the High Energy Accelerator Research Organization. Film structure was evaluated by 2?–? and reciprocal space mapping (RSM) on an X-ray diffraction system.
3-3. Results and Discussion

3-3-1. Dependence of Emission Spectra of Plume on Number of Laser Shots

The characteristics of YMnO$_3$ films as functions of film thickness were investigated to analyze film growth. Film thickness was controlled by varying the number of laser shots. Takahashi et al. have reported that preablation is needed in film growth by PLD because the emission intensity of a plume is unstable at the start of the deposition [7]. The dependence of the emission spectra of the films on the number of laser shots was verified using OES and is shown in Fig. 3-1. It is found that the emission intensity of Mn is decreased, whereas that of Y and YO is increased at the start of the deposition and becomes stable after 8,000 laser shots. Since the deposition is carried out after the preablation, there seems to be little change in the composition with the number of laser shots.

3-3-2. Film Thickness Dependence of Surface Morphology and Crystallinity

To investigate the thickness dependences of surface morphology and crystallinity for YMnO$_3$ films, the in situ RHEED patterns of the films were observed during deposition and are shown in Fig. 3-2 (a). Simulation patterns of RHEED in the incident direction of YMnO$_3$ [11\overline{2}0] and [10\overline{1}0] are also shown in Figs. 3-2 (b) and (c), respectively. The observed RHEED patterns consist of simulation patterns in the incident direction YMnO$_3$[11\overline{2}0]. Since sharp streaks in the RHEED patterns of YMnO$_3$ are observed immediately after the start of the deposition, the surface conditions of the films at the initial stage may be smooth. Although fine streak patterns are observed below 104 nm, spots appear on YMnO$_3$ 11\overline{2}0 and \overline{T}20 streaks above 116 nm.
Fig. 3-1 Dependence of emission intensity of Mn, Y, O and YO active species on number of laser shots, determined using OES.
Fig. 3-2 (a) RHEED patterns are observed with varying film thickness. Simulated RHEED patterns of YMnO$_3$ are drawn. The incident directions of the electron beam are (b) YMnO$_3$ [1 1 2 0] and (c) YMnO$_3$ [1 0 1 0]. (d) Enlarged RHEED patterns for 104- and 106-nm-thick films are shown. Spots are indicated with dashed circles.
(dashed circles in Fig. 3-2 (d)). This result indicates that large grains form above 116 nm. The surface morphology of the Pt/SrTiO$_3$ substrate and the films with different thicknesses were observed by AFM (Fig. 3-3). The Pt grains are 500 nm in diameter and 2 nm in height. The roughness of YMnO$_3$ films of 10-82 nm in thickness reflects the Pt grains. Since grains of 30-40 nm in diameter are observed in films with thickness from 10 to 82 nm, the grain size of the YMnO$_3$ films is almost constant up to a film thickness of 82 nm. On the other hand, at a film thickness of 150 nm, where the spots start to appear on the RHEED pattern, abnormal grain growth is noted. To investigate the cause of this abnormal grain growth, film composition was evaluated by EPMA. As a result, the metallic composition ratios (Mn/Y) of the films of 82 and 150 nm in thickness were 0.99 and 0.90, respectively. The Mn/Y ratio appreciably decreases with increasing film thickness from 82 to 150 nm. To analyze the composition of ultrathin films, XPS was performed for YMnO$_3$ films of 10 and 82 nm in thickness. To examine the crystal structure of the films, XRD analysis was carried out. Figures 3-4 (a), (b) and (c) show the 2?-? XRD patterns of all the samples. All the films of 10-150 nm in thickness exhibit only 000$\theta$ diffractions. It is found that the abnormal grains at a film thickness of 150 nm consist of YMnO$_3$. The full width at half-maximum (FWHM) of the 2?-? scan was examined to determine the composition variation of the films with increasing film thickness. Therefore, YMnO$_3$ 0004, which is the strongest peak among the 000$\theta$ diffractions, and YMnO$_3$ 0008, which has good measurement accuracy for calculating lattice constants, are taken under consideration. Figures 3-4 (b) and (c) show the 2?-? profiles of YMnO$_3$ 0004 and YMnO$_3$ 0008, respectively. The 0008 diffraction of the 10-nm-thick film is too weak to be observed. The FWHM of the 0004 profile of YMnO$_3$ 0004 for the 10-nm-thick film is fairly broad. Thus, it is possible that the
Fig. 3-3 Surface morphology of films of different thicknesses investigated using AFM. Upper panel: x-y scale is 3 μm. Lower panel: x-y scale is 1 μm.
Fig. 3-4 (a) XRD patterns of all the samples are measured in the angle range of 10-80°. (b), (c) Enlarged images for YMnO$_3$ 0004 and YMnO$_3$ 0008, respectively.
initial layer has a large distribution of lattice constants due to epitaxial strain. Compared with that of the 10-nm-thick film, the FWHM of the films above 40 nm thickness is small. In the 150-nm-thick film, the diffraction profile of YMnO$_3$ 0008 exhibits asymmetry at a lower angle. Moreover, Fig. 3-5 (a) shows the dependence of RSM on film thickness for YMnO$_3$ 0008 and YbMnO$_3$ 10 16. The FWHM values of the ? scan of YMnO$_3$ 0008 and YbMnO$_3$ 10 16 increase with increasing film thickness. In particular, the values increase to a greater extent at thickness between 82 and 150 nm. Therefore, the degree of orientation decreases with increasing film thickness. Figures 3-5 (b) and (c) shows the a- and c- lattice constants as functions of film thickness for YMnO$_3$ 0004, YMnO$_3$ 0008 and YbMnO$_3$ 10 16. The peaks are fitted using the Gauss function. In the 10-nm-thick film, c-lattice constant is 11.42 Å, while a- lattice constant cannot be determined exactly, owing to the very low diffraction intensity of YMnO$_3$ 10 16. a- and c- lattice constants are mostly constant in films with thickness from 40 to 80 nm. At 150 nm, the YMnO$_3$ 0008 diffraction indicates the presence of two c-lattice constant values of 11.49 and 11.54 Å. This result indicates that abnormal grains have a longer c-lattice constant in the 150-nm-thick film. From these results, the growth of abnormal grains corresponds to the composition distribution. Although the composition distribution appears to originate from the evaporation of Mn ions from the substrate, this is difficult to accept because the evaporation continues during deposition. Therefore, it appears that film growth changes in films above 120 nm in thickness. Film growth may be affected by epitaxial strain because the lattice constant of the 41-nm-thick film is the same as that of the 82-nm-thick film. It is thus possible that the amount of ions incorporated into the films varies as the growth process changes.
Fig. 3-5 (a) Reciprocal space mappings of YMnO$_3$ 0008 and YMnO$_3$ 1016 were investigated as functions of film thickness. (b) a- and (c) c-lattice constants were calculated using YMnO$_3$ 0004, YMnO$_3$ 0008 and YMnO$_3$ 1016.
3-3-3. Dependence of Electrical Properties on Film Thickness

Figure 3-6 shows the thickness dependence of I-V characteristics for the YMnO$_3$ films. The electric properties of the 10-nm-thick film could not be measured owing to the shorting of all electrode pads with the bottom electrode. The leakage current density of the 40-nm-thick film is 10 times larger than that of the 82- and 150-nm-thick films. The thickness dependence of the P-E hysteresis loops for the YMnO$_3$ film was next examined. Ferroelectric polarization increases with film thickness, as shown in Fig. 3-7. The 40-nm-thick film has a large leakage current density, owing to the presence of unformed YMnO$_3$ grains. The I-V and P-E characteristics indicate that the number of grains exhibiting ferroelectricity increases with film thickness up to 120 nm.

As a result, in films with thickness above 120 nm, the growth of abnormal grains is observed and the film contains excess Y. This result indicates a change in the growth process in films with thickness above 120 nm. Moreover, an increase in ferroelectric polarization with film thickness is observed. Although ferroelectric polarization is large for films with thickness above 120 nm, abnormal grains are observed on the surface of these films. Therefore, YMnO$_3$ thin films with thickness of 80-120 nm are next used to investigate ferroelectric properties at low temperatures, as described in the following chapter.

3-4. Conclusions

Epitaxial (0001)-oriented YMnO$_3$ thin films with thickness from 10 to 150 nm were grown by PLD on (111) Pt/(111) SrTiO$_3$ substrates. For YMnO$_3$ films with thicknesses greater than 120 nm, abnormal grain growth was observed on their surface.
Fig. 3-6 Thickness dependence of leakage current density.
Fig. 3-7 Saturated properties of ferroelectric polarization with film thickness.
In addition, they were shown to contain excess Y. These results indicated that film growth changed in films with thickness above 120 nm. On the other hand, it was found that ferroelectric polarization increased with film thickness. From the results, it appeared that the adequate thickness range of YMnO$_3$ films for investigating ferroelectric domain switching behavior at low temperatures was 80-120 nm.

Reference


Chapter 4: Investigation of Ferroelectric Polarization Switching Behavior in YMnO$_3$ Thin Film

4-1. Introduction

As described in chapter 2 and 3, stoichiometric YMnO$_3$ epitaxial films show excellent ferroelectric properties at room temperature. To investigate effect of magnetic ordering to ferroelectric nucleation and domain wall motion, the switching behavior of ferroelectric polarization of the YMnO$_3$ film needs to be characterized at around magnetic ordering transition temperature. However, domain pinning which is caused by space charge, such as trapped charge, in the film is known as a factor to inhibit the ferroelectric polarization switching [1, 2]. Thus, to examine the influence of domain pinning on the switching behavior, temperature dependence of the trapped charge density was measured in the YMnO$_3$ film.

The polarization switching in ferroelectric materials has been intensively studied both theoretically and experimentally such as transient current during polarization switching [3-5], function of frequency of E$_c$ [6, 7], C-V measurement [8], electro-optic imaging microscopy [9] and domain imaging method using AFM [10]. Features of each measurement method are given as follows;

In the switching current method, the charge associated with the change of polarization in the ferroelectric is analyzed by integration of the current response to voltage pulse. The switching speed and the switching behavior can be determined by the switching current as a function of voltage and time.

It is found that shape of P-E hysteresis loop becomes broader as the frequency is increased [6]. The polarization does not saturate at high frequencies, suggesting that
the nucleation and growth of domains can not follow the change of electric field. To explain measurement frequency dependence of the domain switching of ferroelectric films, some models have been proposed [7]. The domain switching models can be explained using the frequency dependence of $E_c$.

On C-V measurements, capacitance is measured using an AC electric field with small amplitude superimposed over a bias electric field. The dielectric permittivity ($\varepsilon_r$) of ferroelectrics decreases when a large bias voltage is applied, and shows a maximum at the $E_c$. It is known that the large $\varepsilon_r$ at around $E_c$ is caused by the domain wall motion [11]. Therefore, the temperature dependences of C-V characteristics are useful to investigate domain wall motion as well as P-E characteristics.

Observation of ferroelectric domain in single crystal is widely demonstrated using the electro-optic imaging microscopy due to the convenience to prepare the system. However, there is problem that ferroelectric domain with the size below 1 μm can not be observed because the space resolution is limited by wavelength.

The polarization switching is studied by means of AFM in conjunction with lock-in-amplifier. The AFM tip vibration signal originating from the induced local piezoelectric activity is detected. To image the ferroelectric domain and surface microstructure at the same, the domain movement and the microstructure are correlated. The method achieves spatial resolution of 10 nm. The domain nucleation and growth during the polarization switching can be interpreted using two different models, the forward and sidewise domain growth model [10].

Switching current measurement is inadequate in low-temperature because it is difficult to convey current to a long cable for cryostat. There is little system which can perform the electro-optic imaging microscopy and the AFM at ultra-low temperature.
Therefore, in this study, P-E hysteresis loop as a function of frequency and C-V characteristics were measured at a wide temperature range from 10 to 300 K.

Moreover, the switching behavior of YMnO₃ film is discussed by comparison with that of Pb(Zr,Ti)O₃ (PZT) film, which is typical ferroelectrics.

4-2. Experiments

YMnO₃ epitaxial films with a thickness of 100 nm were deposited on (111) Pt/(0001) sapphire substrates. The Mn/Y ratio of film is 0.99. The laser spot area is 0.05 cm² which is small spot area. Since c-lattice constant of the film accords with that of bulk, the film seems to have little oxygen vacancies as described in chapter 2. The PZT film was deposited on Pt/TiO₂/Ti/SiO₂/Si substrate. The Ti/Zr ratio was 30/70 and thickness was 300nm. The XRD pattern of the PZT film indicated that the film have (111) orientation and no second phases. The spontaneous polarization and the remanent polarization of the PZT film at 120 K were 39.5 and 33.9 ?C/cm², respectively. C-f characteristics were measured using an LCR meter (Hewlett Packard 4284A).

4-3. Results and Discussion

4-3-1. Effect of Trapped Charge on Ferroelectric Polarization Switching Behavior

Figure 4-1 shows P-E hysteresis loops and C-V characteristics of the stoichiometric YMnO₃ epitaxial film. The saturated polarization and the remnant polarization of the film at room temperature were 2.74 and 1.27 ?C/cm², respectively. The leakage current density is 1.5×10⁻⁴ A/cm² at electric field of 500k V/cm.

It is well known that ferroelectric polarization switching is affected by domain
Fig. 4-1 (a) P-E hysteresis loop and (b) C-V characteristic of YMnO$_3$ film were measured at room temperature.
pinning and that the dominant origin of the domain pinning is space charge. One method of evaluating trapped charge densities is measurement of the dielectric relaxation current [12]. However, the leakage current of the YMnO$_3$ film below 140 K is less than $10^{-9}$ A/cm$^2$, which is the measurement limit. Therefore, the temperature dependence of the dielectric relaxation was evaluated using $\varepsilon_r$-$f$ characteristics. It was reported that the frequency dependence of the dielectric constant is expressed as

$$\varepsilon_r f^\alpha$$

where $\varepsilon_r$ is the dielectric constant at very high frequencies, $k_0$ is a constant, and $\alpha$ is the same constant as that in the time dependence of the dielectric relaxation current, $J \propto t^\alpha$. $J$ is current density and $t$ is time. To apply eq. (4-1) to ferroelectrics, the effect of the domain wall on the dielectric constant must be eliminated. Therefore, the temperature dependence of the $\varepsilon_r$-$f$ characteristics was measured in a bias electric field of -500 kV/cm, which is sufficiently large to saturate the polarization of the YMnO$_3$ film as shown in Figs. 4-2 (a) and (b). With decreasing temperature, $\varepsilon_r$ and tan $\delta$ decrease. $\alpha$ in eq.(1) corresponds to the slope of the $\varepsilon_r$-$f$ characteristics. The results are shown in Fig. 4-2 (c). $\alpha$ gradually increases with decreasing temperature from 300 to 180 K. From 175 to 165 K, $\alpha$ is constant, and then decreases below 160 K. In Fig.4-2 (c), tan $\delta$ diverges with decreasing measurement frequency in temperature range of 300-200K. It is possible that the $\varepsilon_r$-$f$ characteristics include not only the trapped charge but also the leakage current. The effect of leakage current on the $\varepsilon_r$-$f$ measurement is estimated from the AC conduction. The AC conduction is expressed as,

$$\varepsilon_r \tan \delta \propto \frac{G}{\omega},$$

where $\varepsilon_r$ is the dielectric constant, $\omega$ is the frequency, and $G$ is the AC conductance.
Fig. 4-2 Measurement frequency dependence of (a) $\tau_r$ and (b) $\tan \delta$ at various temperatures. (c) Temperature dependence of $\tau_r^{-1}$. The dashed lines show effects of trap density and leakage current of $\tau_r$ characteristics. (d) The temperature dependence of AC conduction.
The frequency dependences of $\tan \delta$ at various temperatures are shown in Fig. 4-2 (d). A linear relationship between $\tan \delta$ and $1/T$ is obtained from 300 to 200 K. This result indicates that $\tan \delta$ characteristics in this temperature region are affected by the leakage current. Therefore, it appears that the negative slope of $\tan \delta$ from 300 to 180 K is attributable to the leakage current. On the other hand, the positive slope below 160 K indicates an increase in trapped charge with decreasing temperature. Below 160 K, the trapped charge gradually increases with decreasing temperature. Although the temperature dependence of the trapped charge above 180 K is not revealed, it can be expected that the trapped charge gradually increases with decreasing temperature. The pinning effects on ferroelectric properties of the YMnO$_3$ film should decrease with decreasing temperature, because ionized defects trap the charge and it is then neutralized with decreasing temperature. Therefore, little effect of domain pinning on ferroelectric polarization switching behavior is observed at around magnetic transition temperature.

**4-3-2. Temperature Dependences on Polarization Switching Behavior**

To reveal ferroelectric polarization switching behaviors of the YMnO$_3$ film in detail, the temperature dependence of P-E hysteresis loop was investigated. Temperature dependence of spontaneous polarization ($P_s$) and $E_c$ of the second-order ferroelectrics the equations is given by Devonshire’s theory.

\[
P_s^2 = \frac{4}{C_b g^2} T_c^0 T_c^{-1}, \quad \text{eq. (4-3a)}
\]

\[
E_c^{2/3} = \frac{4}{27 b C^3} T_c^{1/3} T_c^{-1}, \quad \text{eq. (4-3b)}
\]

where $T_c$ is the Curie temperature, $C$ is the Curie constant, and $b$ is the coefficient of the
second order of the elastic force between neighboring atoms. Thus, according to Devonshire’s theory, $E_c^{3/2}$ has a linear relationship with temperature. $E_c$ in Devonshire’s equation is defined for static electric field. However, since P-E hysteresis loop is measured using AC electric field, the influence of the measurement frequency on $E_c$ needs to be eliminated to discuss the agreement of the temperature dependence of the experimentally obtained $E_c$ with Devonshire’s theory. Therefore, P-E hysteresis loop was measured at various frequencies. Figures 4-4 (a) and (b) show P-E hysteresis loops of the YMnO$_3$ and PZT films at 1, 100 and 10k Hz in 80 K. In YMnO$_3$ film, $E_c$ increases with increasing frequency. On the other hand, $E_c$ is independent on frequency in PZT film. Figure 4-3 shows the temperature dependence of $E_c^{3/2}$ of the YMnO$_3$ film measured at 1, 100 and 10k Hz. With decreasing temperature, the $E_c^{3/2}$ increases without a linear relationship. It can be expected that $E_c$ at static electric field is obtained at low frequency, however, log($E_c$) of the YMnO$_3$ film shows linear relationship with log($f$) in the measured range from 1 to 10k Hz as shown in Fig. 4-4 (c). Moreover, P-E hysteresis measurements below 1 Hz were difficult due to the influence of the leakage current. Therefore, $E_c$ of the YMnO$_3$ film at static electric field could not be obtained. However, the temperature variation of static $E_c$ of the YMnO$_3$ film can be predicted from measurement frequency of dependence $E_c$. Because there is not frequency dependence on $E_c$ at extremely low temperature and high temperature. As shown in Figs. 4-5, the frequency dependence of $E_c$ is the largest at 40 K, and it becomes smaller below 40 K. The relationship between $E_c^{3/2}$ and temperature shows larger curvature with decreasing frequency as shown in Fig. 4-3. Therefore, it can be expected that the temperature dependence of $E_c^{3/2}$ of the YMnO$_3$ film at static electric field does not have linear relationship which indicates the disagreement with Devonshire’s theory.
Fig. 4-3 Temperature dependence of $E_c^{2/3}$ of the YMnO$_3$ film measured at 1 Hz (closed circles), 100 Hz (open circles), 10k Hz (closed triangles) and the PZT film at 1 Hz (open triangles) and Devonshire’s line (dashed line)
Fig. 4-4 Frequency dependence of P-E Hysteresis loops of the (a) YMnO$_3$ and (b) PZT films measured at 1, 100 and 10k Hz in 80 K. Frequency dependence of $E_c$ of the (c) YMnO$_3$ and (d) PZT films measured at from 1 to 10k Hz in the region of from 300 to 10 K.
The frequency dependence of P-E hysteresis loops of PZT thin film was measured. $E_c$ of the PZT thin film is independent on the frequencies at each temperature as shown Fig. 4-4 (d). The temperature dependence of $E_c^{3/2}$ for the PZT film from 10 to 260 K was also investigated to compare with that of the YMnO$_3$ film. Since $E_c$ of the PZT film is independent on frequency, $E_c$ measured at 1 Hz are plotted in Fig. 4-3. As can be seen, it is well fitted by Devonshire’s theory. The $C$ and $b$ for the PZT film were $3.51 \times 10^5$ K and $3.11 \times 10^9$ m$^5$C$^{-2}$F$^{-1}$, respectively. These values were also comparable with reported values [13]. Based on these results, it can be concluded that the abrupt increase of $E_c$ at low temperature for the YMnO$_3$ film is the quite unique.

Since it is found that $E_c$ of the YMnO$_3$ film depends on frequency significantly, the effect of measurement frequency on $E_c$ is focused. The ferroelectric switching behavior can be analyzed using $E_c$ as a function of frequency. Therefore, the P-E hysteresis loops of the YMnO$_3$ and PZT films were measured in the frequency range from 1 to 10 kHz and in the temperature range from 10 to 300 K. Although some models for the ferroelectric domain switching have been proposed, Ishibashi-Orihara theory, which describes the nucleation and domain wall motion on the ferroelectric polarization switching, is suitable to explain the frequency dependence of $E_c$ [6, 14]. Ishibashi-Orihara theory gives the frequency dependence of $E_c$ as

$$E_c \sim 2^{n/2} \ln \frac{2}{\text{Const.}} f^n,$$  \hspace{1cm} \text{eq. (4-4)}

where $f$ is the frequency, $n$ is a coefficient, and $\text{Const.}$ is a constant. Proportional relationships between $\log E_c$ and $\log f$ are obtained at all temperatures, which indicate that the frequency dependence of $E_c$ for the YMnO$_3$ film is in accordance with Ishibashi-Orihara theory as shown in Fig. 4-4 (c). Therefore, it is suggested that
sidewise growth of the domain is dominant in the ferroelectric polarization switching for the YMnO$_3$ film. The value of n, corresponding to the slope of log $E_c$-log $f$ plots, is constant above 150 K, increases gradually from 140 to 40 K and decreases below 30 K, which indicates that ferroelectric polarization switching has difficulty following these measurement frequencies below 140 K as shown in Fig. 4-5. Below 30 K, n decreases with decreasing temperature, which indicates that the ferroelectric polarization switching easily follows these frequencies. On the other hand, $E_c$ of the PZT thin film is independent on the frequencies at each temperature in Fig. 4-4 (d). The n is less than 0.014 as shown in Fig. 4-5. This result is quite different from that of the YMnO$_3$ film, and the difference might be explained by the difference of the domain structure of these films. Since the YMnO$_3$ film is epitaxially grown with (0001) orientation and the direction of the spontaneous polarization is $<0001>$, the YMnO$_3$ film has only 180° domain wall, which is perpendicular to the electrodes. On the other hand, the ferroelectric domain structure of the PZT polycrystalline film is the coexistence of 180° domain wall and non-180° domain wall. It appears that the nucleation for the domain switching in the YMnO$_3$ film is more difficult than that in the PZT film.

4-3-3. Domain Wall Density as a function of Temperature

It is suggested that the nucleation and domain wall density in the YMnO$_3$ film are smaller than that in the PZT film as described in section 4-3-2. In this section, the domain wall density is investigated by C-V characteristics. As the C-V characteristics of the YMnO$_3$ film is shown in Fig. 4-1, $\tau_r$ increases around $E_c$ due to the contribution of the domain wall motion. $\tau_r$ under electric field larger than $E_c$ corresponds to the intrinsic $\tau$, of the ferroelectrics. Hereafter, $\tau$, at $E_c$ and $\tau$, where ferroelectric polarization is
Fig. 4-5 Temperature dependence of $n$ of the YMnO$_3$ (solid circles) and the PZT (open circles) films
saturated are described $\alpha_r(SW)$ and $\alpha_r(Sat)$, respectively. Therefore, \{\alpha_r(SW)-\alpha_r(Sat)\} should correspond to the domain wall density. Since it is known that \{\alpha_r(SW)-\alpha_r(Sat)\} is corresponding to domain wall density [11], C-V characteristics were measured at various temperatures to investigate the domain wall densities of the YMnO$_3$ and PZT thin film. Figures 4-6 (a) and (b) show the temperature dependence of C-V characteristic of the YMnO$_3$ and the PZT film, respectively. $\alpha_r(SW)$ and $\alpha_r(Sat)$ decrease with decreasing temperature. $\alpha_r(SW)$ shows a larger decrease than $\alpha_r(Sat)$ and approaches $\alpha_r(Sat)$ at around 10 K. These results indicate that domain wall density decreased with decrease temperature. To compare temperature dependence of \{\alpha_r(SW)-\alpha_r(Sat)\} between YMnO$_3$ and PZT film, \{\alpha_r(SW)-\alpha_r(Sat)\} are normalized using the value of each film at 300 K. \{\alpha_r(SW)-\alpha_r(Sat)\} of the both films decrease with decreasing temperature as shown in Fig. 4-7. The decrease of \{\alpha_r(SW)-\alpha_r(Sat)\} for the YMnO$_3$ film is larger than the PZT film, which suggests that the YMnO$_3$ film have larger decrease of the nucleation density at low temperature than the PZT film. Therefore, for the YMnO$_3$ film, an increase in the domain size with decreasing temperature is suggested. This result is consistent with the decrease ionized defects at lower temperature as described in section 4-3-1.

Given the results shown in Figs. 4-5 and 4-7, which indicate that the domain size increases with decreasing temperature, the temperature dependence of $n$ can be explained as follows. Above 150 K, the YMnO$_3$ film has a high nucleation density and a small domain size. Thus, the ferroelectric polarization switching easily follows these frequencies because the distance that the domain wall needs to move for the switching to occur is small. From 140 to 40 K, ferroelectric polarization switching has difficulty following these frequencies because the nucleation density decreases and the domain
Fig. 4-6 $r$-$V$ characteristics of (a) the YMnO$_3$ and (b) the PZT films at 40K (black solid line), 80K (gray solid line) and 160K (black dashed line).
Fig. 4-7 Temperature dependence of \( r_{(SW)} - r_{(Sat)} \) of the YMnO\(_3\) (closed circles) and the PZT (open circles) films.
size increases. Below 30 K, while the nucleation density decreases and the domain size increases further, the pinning effects on the domain wall motion decrease and the ferroelectric polarization switching easily follows these frequencies with decreasing temperature.

4-4. Conclusions

In this chapter, the switching behavior of ferroelectric polarization in YMnO$_3$ film at around magnetic transition temperature is investigated. First, domain pinning which affected on the switching behavior was verified using $\tau_r f$ measurement at low temperature. With decreasing temperature, the pinning effects on ferroelectric properties decreased. There was little effect of the domain pinning in the YMnO$_3$ film at around magnetic transition temperature. Second, frequency dependence of the P-E hysteresis loops were measured at various temperatures. Although it was difficult to eliminate the contribution of frequency dependence of the conceive field for the YMnO$_3$ film, the result indicated that conceive field for the YMnO$_3$ film increased rapidly at low temperature, which was the quite unique. Additionally, It was found that the YMnO$_3$ film showed the larger frequency dependence of conceive field than that of polycrystalline PZT film. The switching behavior accords with Ishibashi-Orihara theory. Therefore, it was suggested that sidewise growth of the domain governed the ferroelectric polarization switching for the YMnO$_3$ film. Furthermore, with decreasing temperature, it was appeared that nucleation decreased and domain size increased from temperature dependence of the slope of log $E_c$-log $f$ plots and {?r(SW)-?r(Sat)}.

Reference


Chapter 5: Investigation of Magnetic Ordering Using Neutron Diffraction and Raman Scattering

5-1. Introduction

Hexagonal YMnO₃ consists of closed-packed layers of bipyramidal MnO₅ where each Mn ion is surrounded by three equatorial and two apical O²⁻ ions. Since Y³⁺ (4p⁶) is nonmagnetic, the magnetic properties of YMnO₃ originate from Mn³⁺ (3d⁴) with spin S=2. The Mn ions form a triangular lattice in which the moments are coupled antiferromagnetically in the ab plane. This gives rise to spin frustration effects and the antiferromagnetic spin arrangement with neighboring spins rotated by 120° below the Néel points (Tₐ) at 70-130 K in RMnO₃ [1-3]. In single crystals of YMnO₃ and LuMnO₃, a critical magnetocapacitance is observed below Tₐ [4]. However, the magnetic structure has not been investigated in YMnO₃ samples in which the ferroelectric polarization can be switched. In this chapter, the magnetic ordering of YMnO₃ films with excellent ferroelectricity is investigated using a superconducting quantum interference device magnetometer (SQUID), neutron diffraction and Raman scattering.

Neutron diffraction is one of the most important methods for determining magnetic ordering. There are several reports in which the magnetic structure of multiferroics was determined using neutron diffraction [5-7]. The frustrated magnetic order and the spin dynamics of Mn³⁺ have been reported in hexagonal RMnO₃ [6, 8]. Additionally, the magnetic ordering of RMnO₃ thin films on insulating substrates has also been investigated [9]. However, since the ferroelectric properties were not evaluated due to the insulating substrate, a relationship between ferroelectric switching
and magnetic ordering was not discussed. Therefore, it is important that the magnetic structure of YMnO$_3$ films which display good ferroelectricity is investigated.

It has been reported that optical and acoustic phonons are affected by antiferromagnetic ordering in hexagonal and orthorhombic RMnO$_3$ [10, 11]. Moreover, displacements for every atom in hexagonal RMnO$_3$ below $T_N$ have been found by high-resolution neutron diffraction experiments. Thus, the lattice and the phonon modes of RMnO$_3$ are affected by magnetic ordering. Consequently, the magnetic transition temperature of polycrystalline bulk, and thin films of YMnO$_3$ are herein investigated using Raman scattering.

5-2. Experiments

The YMnO$_3$ film investigated in chapter 4 was further studied in this chapter. YMnO$_3$ polycrystalline bulk was also prepared as a reference. The magnetization was measured in the temperature range 2 to 300 K using SQUID (Magnetic Properties Measurement System MPMS-5XL, Quantum Design). Neutron diffraction measurements were performed on the epitaxial thin film using a triple-axis spectrometer, PONTA, installed by the Institute for Solid State Physics (University of Tokyo), in the Japan Research Reactor No. 3 reactor of the Japan Atomic Energy Agency. Incident and final beam energies, $E_i$ and $E_f$ were 30.5 meV. Raman scattering was observed using an Ar gas laser with a wavelength of 514.5 nm. For measurement at 15 to 300 K, the sample was fixed to a cold finger in a closed-cycle He-gas cryostat. The laser was focused by a lens at the sample surface, and the scattered light was collected in a quasi-back-scattering geometry to a double monochromator of focal length 85 cm.
5-3. Results and Discussion

5-3-1. Magnetization Behavior of YMnO$_3$ Bulk and Thin Film

Figure 5 shows the XRD pattern of bulk YMnO$_3$. Diffraction peaks from a second phase are not observed, indicating that the bulk sample exists as a single phase. The a- and c- lattice constants are 6.14 Å and 11.38 Å, respectively. The magnetic and inverse susceptibilities of the bulk sample were measured as a function of temperature, as shown in Fig. 5-2 (a) and (b), respectively. Representative fitting using the Curie-Weiss law is shown in the inset in Fig. 5-2 (b). Although an inflection point indicating $T_N$ could not be observed clearly, the slope significantly decreases at around 77 K. This behavior seems to be caused by the magnetization of Mn at grain boundaries and impurities. Additionally, the inverse susceptibility $[d(1/\chi)/d(T)]$ was investigated, as shown in Fig. 5-2 (c). The inverse susceptibility is constant from 300 to 150 K, and increases gradually from 77 to 150 K. Below 75-77 K, $d(1/\chi)/d(T)$ varies greatly. These results indicate that the YMnO$_3$ bulk has antiferromagnetic ordering below 77 K. The increase of $d(1/\chi)/d(T)$ below 150 K may indicate magnetic short range order.

The magnetic and inverse susceptibilities of the film were also investigated as a function of temperature. The sapphire substrate is diamagnetic, i.e., it creates a magnetic field in opposition to an externally applied magnetic field. The volume of the sapphire substrate is 5000 times larger than that of the YMnO$_3$ thin film. The raw data for the film sample gives negative values. Furthermore, when the magnetization of the YMnO$_3$ film is calculated based on the temperature of magnetization in a Pt/sapphire substrate, the magnetization of the YMnO$_3$ film is 200 times smaller than the theoretical value calculated from the Brillouin function. Therefore, the antiferromagnetic transition temperature of the film can not be determined from the susceptibility measurements.
Fig. 5-1 XRD patterns of bulk YMnO$_3$. 
Fig. 5-2 (a) Temperature dependence of magnetization, (b) 1/\(\theta\) and (c) d(1/\(\theta\))/d(T) of bulk YMnO$_3$. 

Magnetization (\(10^{-3}/\theta\_B\))

Temperature (K)

Magnetization (\(10^5\theta\_B\))

Temperature (K)

\(\theta\) (\(10^5\theta\_B\))

T (K)

\(\theta\) (\(10^5\theta\_B\))

T (K)

\(d(1/\theta)/d(T)\)

Temperature (K)
Consequently, neutron diffraction experiments were carried out at various temperatures.

5-3-2. Investigation of Magnetic Ordering in YMnO₃ Thin Films by Neutron Diffraction Studies

In early neutron diffraction experiments on YMnO₃ powder, diffraction of the antiferromagnetic ordering of Mn³⁺ spins was observed at the reciprocal lattice point of YMnO₃ 100, below T_N = 77 K [3]. Neutron diffraction of YMnO₃ thin films was measured along the 100 diffraction plane [100].

To investigate T_N and the magnetic structure of YMnO₃ films, neutron diffraction was carried out. l and h scans were performed around YMnO₃ 002 and 300 to estimate YMnO₃ 100. Fig. 5-3 shows l and h scans at YMnO₃ 300 at 6 K. The Gauss function was used for fitting of the neutron diffraction. The peak intensity is 110 count/min and the FWHM of l scan is 0.05 r.l.u. It was found that magnetic diffraction was large enough to detect by scanning for 10 minutes per point, because the calculated peak intensity of magnetic diffraction YMnO₃ 100 was 10 times smaller than that of YMnO₃ 300. Consequently, the temperature dependence of the YMnO₃ 100 diffraction was investigated. These results are shown in Fig. 5-4. At 6 K and 40 K, the 100 neutron diffraction can be observed, which is associated with antiferromagnetic ordering of Mn³⁺ spins. The peak intensities at 6 K and 40 K are 135 and 68.5 count/min, respectively. In contrast, no neutron diffraction is observed at 80 K. Therefore, the YMnO₃ film grown in this study has a T_N below 80 K, which is consistent with T_N of a YMnO₃ single crystal [12].
Fig. 5-3 Neutron diffraction at YMnO$_3$ 300 along; (a) YMnO$_3$ [001] (l scan) and (b) YMnO$_3$ [100] (h scan)
Fig. 5-4 Neutron diffraction at YMnO$_3$ 100, along YMnO$_3$ [001]
5-3-3. Temperature Dependence on Raman Scattering of Bulk and Thin Film YMnO$_3$

Figure 5-5 shows Raman spectra of the bulk and thin film YMnO$_3$ at 15 K. 20 phonon peaks are clearly observed, and assigned to A$_1$, E$_1$, and E$_2$ modes via a polarized Raman study and with reference to the reported result of Iliev et al. [14]. In the A$_1$ and E$_2$ modes, strong peaks are observed at 141 [Y (E$_2$)], 160 [Y (A$_1$)], 226 [Mn-O (E$_2$)] and 680 [O-O (A$_1$)] cm$^{-1}$. Figure 5-6 shows the temperature dependence of the Raman spectra of the bulk YMnO$_3$. In the bulk sample, a peculiar temperature variation of the phonon mode is found at around 80 K [13]. For example, the A$_1$ mode at 160 cm$^{-1}$ exhibits a remarkable frequency shift at around 80 K. The frequency as a function of temperature reflects the anharmonicity effects reproduced by the following relation [14]:

\[ ?(T) ?_0 ? C \frac{\gamma_1}{?} ? \frac{2}{?_1} ? \frac{3}{?_1} \frac{D}{?} \frac{\gamma_2}{?_1} \frac{3}{?_1} \frac{3}{(e^y - 1)^2} \frac{\gamma_3}{?_1} \text{ eq. (5-1)} \]

where $?(T)$ is the phonon frequency at $T$, $x$ $\gamma$ $\gamma_0$ $2kT$, $y$ $\gamma$ $\gamma_0$ $3kT$, and $?_0$. C, and D are adjustable parameters. The value of the ratio D/C is 0.06 - 0.08, because the three-phonon process is small. The anomalous behavior is found in several peaks, and is most evident for the A$_1$ (160 cm$^{-1}$) and the E$_2$ (226 cm$^{-1}$) modes. Since the E$_2$ mode corresponds to ab plane displacement of basal O$_3$ and O$_4$ ions in phase with the motion of the apical O$_1$ and O$_2$ ions, the E$_2$ mode is one of the vibrational modes which connect the Mn-Mn exchange interaction strongly. Therefore, it is reasonable that the E$_2$ mode has an anomalous variation at around $T_N$ in which magnetic ordering is formed. The anomalous variation of these phonon modes at $T_N$ indicates that the antiferromagnetic spin ordering is accompanied by small structural modification of relevant ions.
Fig. 5-5 Raman scattering spectra of bulk and thin film YMnO$_3$. 
Fig. 5-6 Temperature evaluations of the phonon mode of (a) Y $E_2$, (b) Y $A_1$, (c) Mn-O $E_2$, and (d) O $A_1$ modes. Solid lines correspond to anharmonicity predictions. Vibrational modes of (e) $A_1$ (221cm$^{-1}$) and (f) $E_2$ (226cm$^{-1}$) are illustrated. The arrows show the direction of vibration.
Fig. 5-7 Raman spectra of (a) A\textsubscript{1} (160 cm\textsuperscript{-1}) and (b) E\textsubscript{2} (226 cm\textsuperscript{-1}) modes at 15-300 K. Voigt functions are fits to the experimental results for YMnO\textsubscript{3} bulk and thin films in at 15 K at in the Raman shift range of 180-280 cm\textsuperscript{-1}. 
Fig. 5-8 Raman scattering spectra of YMnO$_3$ bulk and thin film verse versus temperature. The full solid curve shows the expected Raman shift expected for from anharmonicity fitting. Anomalous variations appear below 150 K in film.
5-7 (a) and (b) show Raman scattering for the YMnO$_3$ epitaxial thin film as a function of temperature from 300 to 15 K. Raman spectra in which spin-phonon coupling are observed in the bulk are focused upon. Based on the results of the bulk sample, the experimental results of the film are fitted by the Voigt function (or Lorentz function), as shown in Fig. 5-7 (c). Figure 5-8 shows temperature dependence of the Raman shift for the YMnO$_3$ film. The solid line shows the Raman shift expected for anharmonicity fitting. Lattice hardening is observed below 150 K in the film, which is higher than $T_N$ of the YMnO$_3$ film (~80 K) as described in section 5-3-2. In orthorhombic RMnO$_3$, since anomalous variations appear at temperatures higher than the magnetic transition temperature, formation of magnetic short range ordering is suggested. Therefore it is indicated that the origin of lattice hardening is a precursor to the phenomenon of magnetic ordering of Mn$^{3+}$ spins, because the lattice hardening is observed below 150 K, which is higher than $T_N$ of the YMnO$_3$ film.

5-4. Conclusions

In this chapter, the magnetic structure of YMnO$_3$ films with excellent ferroelectricity was investigated. To determine the Néel point of the YMnO$_3$ film, magnetic measurements, neutron diffraction, and Raman scattering were carried out. Since it was difficult to determine the antiferromagnetic transition temperature accurately from the magnetic susceptibility, neutron diffraction experiments were carried out at various temperatures. Temperature dependence of the diffraction of the antiferromagnetic ordering of Mn$^{3+}$ spins indicated that the Néel point of the YMnO$_3$ thin film was ~80 K. Furthermore, temperature dependence Raman scattering for the YMnO$_3$ thin film was investigated. Spin-phonon coupling was observed below 150 K,
which was higher than $T_N$ of the YMnO$_3$ film. These results indicate that magnetic short range ordering exists as a precursor phenomenon in YMnO$_3$ films.

Reference


Chapter 6: Ferroelectric Properties of YMnO$_3$ Epitaxial Thin Film at around Magnetic Transition Temperature

6-1. Introduction

In chapter 5, it was found that $T_N$ of YMnO$_3$ film was $\sim$80 K and the spin phonon coupling which indicated the magnetic short range ordering was observed below 150 K. In this chapter, a cross-correlation between ferroelectric properties and antiferromagnetic ordering, in particular ferroelectric nucleation and domain wall motion, was investigated.

Abnormal $\xi$ and ferroelectric polarization below magnetic phase transition temperature are emerged in some multiferroics [1, 2]. In YMnO$_3$, an evidence of cross-correlation has also been observed in the in-plane $\xi$, at the $T_N$ [3]. If the magnetic ordering affects to ferroelectric nucleation and domain wall motion in YMnO$_3$, anomaly may appear in fundamental physical quantity of ferroelectrics, such as out-of-plane $\xi$ and ferroelectric polarization. Temperature dependence of C-V characteristics and P-E hysteresis loops of the YMnO$_3$ film were measured.

Fiebig et al. have been reported that in YMnO$_3$ single crystal, the ferroelectric domain wall is always accompanied by an antiferromagnetic domain wall, while a single antiferromagnetic domain wall can exist independently [4]. Hanamura and Tanabe revealed theoretically that ferroelectric and antiferromagnetic order parameters in YMnO$_3$ are coupled at the ferroelectric domain boundary [5]. In fact, $E_c$ of the YMnO$_3$ film is abruptly increased below $T_N$ as described in chapter 4. Therefore, if the ferroelectric domain wall accompanies the antiferromagnetic domain wall, it is possible that the ferroelectric domain wall switching is interfered. Therefore, ferroelectric
nucleation and domain wall motion is investigated at around magnetic phase transition temperature in detail.

It is widely known that the dielectric and piezoelectric properties of ferroelectric materials have nonlinear and hysteresis behaviors, even under relatively low amplitude of the driving electric field or mechanical stress. Under weak field conditions, the external field causes only vibration or small displacement of the domain wall, but the overall structure of the domain wall does not change. There is no switching of domain wall and no nucleation of wall. The primary contribution to dielectric and piezoelectric nonlinearity and hysteresis comes from the motion of existing ferroelectric or/and ferroelastic domain wall. The dielectric behavior as a function of AC electric field gives information of domain wall motion and density. The Rayleigh law, originally stated in order to describe the magnetic response of a ferromagnetic material to the action of an external magnetic field, has been used to describe the dielectric piezoelectric non-linear response in a piezoelectric ceramic [6-8]. Therefore, domain wall contribution to the dielectric response of YMnO$_3$ film is discussed using subcoercive AC electric field in order to discuss ferroelectric domain nucleation and wall motion of YMnO$_3$ film.

6-2 Experiments

Temperatures dependence of ferroelectric polarization, $P$, and domain wall motion, were measured using the YMnO$_3$ film shown in chapters 4 and 5. To observe ferroelectric domain wall motion, a high-speed capacitance measurement system was developed using a CV Analyzer (Keithley 590 CV Analyzer) as shown in Fig.6-1. Step voltage is applied to the sample by function generator. The output waveform is
Fig. 6-1 Sketch of a high-speed capacitance measurement system was developed using a CV Analyzer
converted into capacitance using CV Analyze. Capacitance is calculated by integration of output waveform at a constant time in LCR meter. On the other hand, since the integration is not performed in the high-speed capacitance measurement system, transient response of $\tau_r$ can be observed when the step voltage is applied.

AC electrical field dependence dielectric permittivity was measured with DC bias of $E_0$ and electric field in which ferroelectric polarization is saturated ($E_{\text{sat}}$) using LCR meter. The amplitude range of applied AC electrical field is from 1k to 200k V/cm and the measurement frequency is 100, 1k and 10k Hz.

6-3. Results and Discussion

6-3-1. Temperature Dependence on Dielectric Permittivity and Ferroelectric Polarization of YMnO$_3$ Film

The relationship between the magnetic ordering on fundamental ferroelectric properties, such as $\tau_r$ and ferroelectric polarization, is discussed. To investigate the temperature dependence of the $\tau_r$ and ferroelectric polarization for the YMnO$_3$ film, C-V characteristics and P-E hysteresis loops were measured in the temperature range from 300 to 10 K. Temperature dependences of $\tau_r$(SW) and $\tau_r$(Sat) are shown in Fig. 6-2 (a). While $\tau_r$(SW) is caused by the domain wall motion, $\tau_r$(Sat) is an intrinsic dielectric constant along the $c$-axis of YMnO$_3$. $\tau_r$(SW) and $\tau_r$(Sat) decrease with decreasing temperature. $\tau_r$(SW) shows a larger decrease than $\tau_r$(Sat) and approaches $\tau_r$(Sat) at around 10 K. As shown in chapter 4, this behavior corresponds to the decrease of the domain wall density with decreasing temperature. At around 80 K, an inflection point is also observed on $\tau_r$(Sat), as shown in Fig. 6-2 (a). Katsufuji et al. reported an anomaly in the temperature dependence of the $\tau_r$ to the $c$-axis on YMnO$_3$ [3].
Fig. 6-2 (a) $r_r$ (SW) (closed circles) and $r_r$ (Sat) (open circles) and (b) $P_{\text{sat}}$ as a function of temperature.
Although the results shown in Fig. 6-2 (a) are the \( ?_r \) along the c-axis, it seems that magnetoelectric coupling is the decrease of \( ?_r \text{(Sat)} \) at around 80 K of \( T_N \).

Figure 6-2 (b) shows the temperature dependence of the \( P_{\text{sat}} \). Note that, \( P_{\text{sat}} \) increases gradually from 280 to 130 K and becomes constant at around 3.8 \( \mu \text{C/cm}^2 \) in the temperature range of 80-120 K. Then, \( P_{\text{sat}} \) increases with decreasing temperature from 70 to 20 K. This result indicates that the spontaneous polarization (\( P_s \)) of the YMnO\(_3\) film is switched well by an electric field as low as 10 K. Moreover, inflection points of \( P_{\text{sat}} \) are observed at around 80 and 120 K, as shown in Fig. 6-2 (b). Change in \( P_s \) for YMnO\(_3\) at \( T_N \) was reported by Lee et al. [9]. They investigated the atomic positions of a YMnO\(_3\) single crystal using high-resolution neutron diffraction and revealed strong spin-lattice coupling and an increase in \( P_s \) due to variation in the in-plane Mn-O bond distance below \( T_N \). Therefore, the inflection point of \( P_{\text{sat}} \) at around 80 K, which is close to the \( T_N \) of the YMnO\(_3\) film, should originate from the increase in \( P_s \).

Thus, it appears that magnetoelectric coupling is observed for the temperature dependence of \( P_{\text{sat}} \) and \( ?_r \text{(Sat)} \) at around 80 K. In addition, the temperature dependence of \( P_{\text{sat}} \) shows a plateau in the temperature range from 120 to 80 K, as described above. It is known that ferroelectric domain is pinned by the defects in ferroelectrics and ferroelectric polarization switching is difficult, leading to a decrease in remnant polarization [10]. The result of temperature dependence of the trapped charge described in chapter 4 suggests that anomalies in the temperature dependence of \( P_{\text{sat}} \) and \( ?_r \text{(Sat)} \) at 80 K are not caused by the domain pinning at ionized defects but by change in ferroelectric polarization switching behaviors.
6-3-2. Nucleation of Ferroelectric at around Magnetic Transition Temperature

In the chapter 4, it was found that ferroelectric domain nucleation decreased and domain size increased with decreasing temperature from the measurement frequency dependence of $E_c$ and the temperature variation of $\gamma_r(SW) - \gamma_r(Sat)$. The result indicates that sidewise growth of the domain is dominant on the ferroelectric polarization switching process. In this section, the ferroelectric domain nucleation and wall motion is further investigated using Rayleigh law. The Rayleigh law assumes that the dielectric response of ferroelectric material can be described by this equation;

$$\gamma_r(E) \approx \gamma_{int} \cdot \gamma(E < E_c), \quad \text{eq. (6-1)}$$

where $E$ is the amplitude of the applied electric field, $\gamma$ is the Rayleigh coefficient and $\gamma_{int}$ is the dielectric constant which is at zero-field amplitude. Then, the ferroelectric domain nucleation density in YMnO$_3$ film is analyzed using $\gamma_r$ as a function of AC electric field.

Since the ferroelectric domain size increases with increasing electric field, ferroelectric domain wall density can be controlled by magnitude of applied electric field. AC electrical field dependence $\gamma_r$ was measured with DC bias of $E_c$ and electric field in which ferroelectric polarization is saturated ($E_{sat}$). The analysis is carried out in a temperature range of 80 to 200 K because the effect of the leakage current is included above 200 K. The dielectric response at $E_c$ and $E_{sat}$ in temperature range from 80 to 200 K show in Fig. 6-3 (a) and (b), respectively. Since the $\gamma_r$ at $E_c$ increases more largely than that at $E_{sat}$, contribution of the domain wall motion to the $\gamma_r$ at $E_c$ is suggested. Thus, the dielectric response was analyzed using the eq.(6-1) at low electric field region ($< 50$ kV/cm) because Rayleigh law is adapted at subcoercive electric field region.
Fig. 6-3 Dielectric responses depend on AC electric field at (a) $E_c$ and (b) electric field when ferroelectric polarization saturated in temperature range of 80-200 K.
Fig. 6-4 Inverse of Rayleigh coefficient ($1/\theta$?) as a function of temperature at $10^2$ (open circles), $10^3$ (closed circles) and $10^4$ (closed triangles) Hz.
Figure 5-8 shows the temperature dependence of inverse Rayleigh law \( (1/r^2) \). It is reported that the Rayleigh coefficient corresponds to the defect density and domain wall density as described by following equation;

\[
\frac{1}{r^2} = \frac{L_D N}{F_D}, \quad \text{eq. (6-2)}
\]

where \( L_D \) is average distance between domain walls, \( N \) is defect concentration and \( F_D \) is domain wall area [11]. Below 180 K, it was revealed that the tarp density decrease with decreasing temperature as described in chapter 4. Therefore, it seems that \( 1/r^2 \) is related to the domain wall density. Note that, \( 1/r^2 \) is constant in the temperature range of 150 - 180 K and increases gradually below 130 - 140 K. This result indicates that the ferroelectric domain wall density of the YMnO\(_3\) film begins to decrease at 140 K. This is consistent with the decrease of the ferroelectric nucleation and the increase of the domain size discussed in chapter 4.

**6-3-3. Dynamics of Ferroelectric Domain Wall in Multiferroic YMnO\(_3\) at around Magnetic Transition Temperature**

Since it is known that the ferroelectric polarization switching time for thin films is on the order of 10-100 ns and can not be determined easily [12, 13], a high-speed capacitance measurement system was developed for observing the ferroelectric polarization switching behavior. The velocity of the domain wall motion under an electric field is a function of the magnitude of the electric field. Therefore, measurement using a small step voltage is suitable to investigate the ferroelectric polarization switching behavior. Moreover, since the domain wall motion affects \( r \), as shown in Fig. 6-2 (a), the ferroelectric polarization switching behavior can be observed by measurement of the time dependence of \( r \) when applying a bias voltage with a small
step. The results are shown in Fig. 6-5. The time variations of $\tau$ at around the $E_c$ of the YMnO$_3$ film and at a voltage large enough to saturate the ferroelectric polarization, which correspond to $\tau$(SW) and $\tau$(Sat), respectively, were measured. Note that, the time variation of $\tau$ corresponding to the bias voltage waveform is obtained. In addition, a transient response (TR) is observed on $\tau$(SW), while no TR is observed on $\tau$(Sat). This result suggests that TR is attributable to domain wall motion. The TR of $\tau$(SW) was analyzed using the following equation:

$$\tau = \tau_0 A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right),$$

where $\tau_0$ and $\tau$ are the time constants, $A_1$ and $A_2$ are coefficients. As a result, the TR of $\tau$(SW) shown in Fig. 4(a) can be divided into regions (1), (2) and (3) corresponding to the domain wall motion as follows. (1) $\tau$(SW) shows an abrupt increase due to fast domain wall motion upon applying a voltage. (2) When the applied voltage is constant, the velocity decreases ($\tau_1$). (3) Domain wall motion is suppressed by ionized defects ($\tau_2$). The temperature dependences of the time constants are shown in Fig. 6-6. Both time constants decrease with decreasing temperature, which suggests that domain wall motion becomes faster at a lower temperature. The behavior is consistent with the results described above. For ferroelectric polarization switching, it is suggested that sidewise growth is dominant, the domain wall density decreases owing to a decrease in nucleation density, and the domain wall motion increases with decreasing temperature.

As described in chapter 4, it was found that the domain pinning gradually decreased with decreasing temperature below 140 K. On the other hand, the $\tau_2$ began to increase at around 150 K in which spin-phonon coupling was observed. It is suggested that domain wall motion is inhibited below 150 K, which is higher than the $T_N$ of 80 K. It is suggested that the precursor to the formation of magnetic ordering interact strongly with
Fig. 6-5 Time variation of (a) $r_t$(SW) and (b) $r_t$(Sat) (solid line) measured by step voltage (dashed line).
Fig. 6-6 Time constants $\tau_1$ and $\tau_2$ of transition response for $\tau_{i}(SW)$ as a function of temperature.
the ferroelectric domain wall motion.

6-3-4. Interaction between Ferroelectric and Magnetic Domain

Based on the experimental results, interaction between ferroelectric and magnetic domain is discussed. It is reported that crystallographically-defined antiphase domain which correspond periodicity of $\text{Mn}^{3+}$ exists in YMnO$_3$ [14]. The cross-correlation between ferroelectricity and antiferromagnetism in antiphase domain boundary is expected because the antiphase domain boundary accompanies ferroelectric domain wall. Based on the reports, the ferroelectric polarization switching of the YMnO$_3$ film is discussed around the magnetic phase transition temperature. Figure 6-7 illustrates the antiphase domain in film. By applying electric field, antiphase domain boundary works as nucleation of the ferroelectric domain. The ferroelectric domain penetrates to direction of film thickness and domain growth progresses. Below 130-140 K, the domain growth is suppressed because magnetic short range order exists near antiphase domain. Then, it is appeared that nucleation density decreases at the temperature in which magnetic ordering formed. The drastic increase of $E_c$ at low temperature seems to originate from the decrease of nucleation density.

6-4. Conclusions

The ferroelectric properties of a magnetic ferroelectric (0001) YMnO$_3$ epitaxial film at around the $T_N$ were investigated to discuss the effect of antiferromagnetic ordering on the ferroelectric polarization switching behavior. It was appeared that $T_N$ of YMnO$_3$ film was $\sim$80 K and the magnetic short range ordering was observed at 150 K. The temperature dependences of P-E and C-V characteristics were measured in the
Fig. 6-7 Illustration is ferroelectric domain nucleation behavior in Y\textsubscript{2}MnO\textsubscript{3} film (a) above and below (b) 150 K in which magnetic short range is formed. In addition, the crystallographically-defined antiphase domain which is correspond periodicity of Mn\textsuperscript{3+} exists in the film. (a) Above 150 K, the antiphase domain boundary works as nucleation of the ferroelectric domain. While (b) domain growth is suppressed due to form of magnetic short range ordering near antiphase domain.
temperature range from 300 to 10 K. Anomalies of ferroelectric properties of the YMnO$_3$ film such as an increase in $P_{\text{sat}}$ and a decrease in $\gamma_r(Sat)$ were observed at 80 K, which were caused by magnetoelectric coupling. Moreover, contribution of the magnetic ordering to the ferroelectric nucleation and domain wall motion was investigated. The YMnO$_3$ film had little domain pinning below 160 K. Temperature dependence of the ferroelectric nucleation density was examined using Rayleigh law. The result indicated that nucleation density also decreases below 140 K. The ferroelectric nucleation may be suppressed due to magnetic short range order. The velocity of domain wall motion began to decrease at around 150 K in which lattice hardening was observed. These results suggested that domain wall motion is inhibited below 150 K, which was higher than the $T_N$ of 80 K. It is seems that ferroelectric nucleation and domain wall motion is prevented by formation of magnetic short range order.

Reference


Chapter 7: Summary

This thesis provides a comprehensive study of “Growth of YMnO$_3$ Epitaxial Thin Film and Effect of the Magnetic Ordering on the Ferroelectric Polarization Switching”. This chapter briefly summarizes the major findings in this thesis.

In Chapter 2, growth of stoichiometric YMnO$_3$ epitaxial thin films with small amount of oxygen vacancies was attempted using PLD. Effect of the laser irradiation conditions for PLD on the metallic composition and oxygen content of YMnO$_3$ films was also investigated using OES. The plume consists of atomic Mn, Y, O and molecular YO. With the smaller laser spot area and the higher laser energy density, light mass Mn particle was scattered by collision among the active species and was hard to arrive substrate than heavy active species Y, YO. The effect of the oxygen related active species on the formation/annihilation of the oxygen vacancies in the YMnO$_3$ films was investigated. The emission intensity ratio of YO/(Mn+Y+O+YO) can be controlled by changing the laser spot area. With increasing the laser spot area, the lattice constants of the films approach to that of bulk and the saturated polarization increased suggesting that the active species of metal oxide molecule can be effective to decrease the oxygen vacancies in the YMnO$_3$ films without changing the metallic composition. Based on the result, YMnO$_3$ films with little off-stoichiometry and oxygen vacancies can be successfully obtained using laser conditions at which density of the active species is low and YO/(Mn+Y+O+YO) ratio is large in the plume.

In Chapter 3, influence of thickness on the film characteristics was observed in order to investigate growth process of YMnO$_3$ film. It was found that abnormal grain grew on the film surface above a thickness of 120 nm-thickness. While the film
composition was stoichiometry below 120 nm-thickness, that was Y exceed above 120 nm-thickness. Effect of the radiation heat from heating system and laser irradiation on composition of target surface was little. These results indicated that film growth changed in films with thickness above 120 nm. Therefore, it revealed that the adequate thickness range of YMnO$_3$ films for investigating the ferroelectric domain switching behavior at low temperatures was 80-120 nm.

In Chapter 4, the switching behavior of ferroelectric polarization in YMnO$_3$ film was investigated at a wide temperature range of 10-300 K. Effect of domain pinning on the switching behavior was examined. The pinning effect on ferroelectric properties decreased with decreasing temperature. It was appeared that the YMnO$_3$ film had little effect of the domain pinning at around magnetic transition temperature. Frequency dependence of the P-E hysteresis loops were measured at various temperatures. The frequency dependence of $E_c$ of the YMnO$_3$ film was accordance with Ishibashi-Orihara theory. This result suggested that sidewise growth dominants the ferroelectric polarization switching for the YMnO$_3$ film. Furthermore, with decreasing temperature, it was appeared that nucleation decreased and domain size increased from result of the P-E and C-V characteristics.

In Chapter 5, the magnetic structure of the YMnO$_3$ films was investigated. Magnetic measurement, neutron diffraction and Raman scattering were performed in order to determine the Néel point of YMnO$_3$ film. Since it was difficult to determine the antiferromagnetic transition temperature accurately from the magnetic susceptibility, neutron diffraction experiment was carried out at various temperatures. This result suggested that the Néel point of YMnO$_3$ film was ~80K. Furthermore, Raman scattering for the YMnO$_3$ thin film was investigated as a function of temperature. As a result, the
spin-phonon coupling which corresponded to magnetic short range orderings was observed below 150 K. These results indicated that the YMnO$_3$ film had magnetic precursor phenomenon below 150 K which is higher than $T_N$ of 80 K.

In Chapter 6, the ferroelectric properties of YMnO$_3$ epitaxial film at around the $T_N$ were investigated to discuss the effect of antiferromagnetic ordering on ferroelectric polarization switching behavior. Temperature dependence of the ferroelectric nucleation density was measured using Rayleigh law. This result indicated that nucleation density decreased below 140 K. Furthermore, a high-speed capacitance measurement system was developed for measuring domain wall velocity. With decreasing temperature, the domain wall velocity increased. This result corresponded to temperature dependence of pinning effects. On the other hand, the velocity of domain wall began to decrease at around 150 K in which spin-phonon coupling was observed. It is suggested that domain wall motion is inhibited below 150 K, which is higher than the $T_N$ of 80 K. These results appeared that ferroelectric nucleation and domain wall motion was interfered by the magnetic short range order.

In hexagonal RMnO$_3$, $E_c$ increased by formation of the magnetic short range order. This result indicated that the ferroelectric polarization stabilized by the magnetic order. It was revealed that the cross-correlation on magnetic and ferroelectric domain wall was observed.
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## Original Articles Regarding This Thesis

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