論文の内容の要旨

論文題目　Epitaxial growth and physical properties of Garnet-type $Sm_3Fe_5O_{12}$ films and Wurtzite-type ZnO films

(ガーネット型 $Sm_3Fe_5O_{12}$ 薄膜およびウルツ鉱型 ZnO 薄膜のエピタキシャル成長とその物性)

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Abstract – Garnet-type $Sm_3Fe_5O_{12}$, SmIG, (001) films with thicknesses between 170 and 1450 Å, were grown epitaxially on $Gd_3Ga_5O_{12}$, GGG, (001) substrates. Strained and relaxed films were obtained with a critical thickness of 602 Å, as confirmed by x-ray diffraction (XRD). Moreover, dielectric measurements (*Q*-*V* curves) revealed that hysteresis loops were clearly observed on the films with thicknesses below 790Å. Thickness dependency of remnant charge amount Q_s and $d(Q_s/t)/dV(V=0)$ revealed that they remained the same below 602 Å, indicating that the crystal structure of strained films were tetragonally-distorted. On the other hand, wurtite-type ZnO (0001) films were grown epitaxially on GGG (111) and (001) substrates. X-ray diffraction revealed that the out-of-plane and in-plane epitaxial relations of ZnO films on the GGG (111) substrates [ZnO/GGG (111)] were the [0001]ZnO || [001]GGG and [10-10]ZnO || [1-12]GGG±21°, while ZnO films on the GGG (001) substrates [ZnO/GGG (001)] showed the out-of-plane and in-plane epitaxial relations with the [0001]ZnO || [001]GGG and [10-10]ZnO || [100]GGG, [010]GGG.

I. Research backgrounds

Rare earth (Re) irons-based garnets ($Re_3Fe_5O_{12}$: ReIG) have received much attention for their magnetic and magneto-optical properties. Thus far, practical applications such as bubble memories and microwave devices have been reported on garnet materials[1,2]. Recently, it was found interesting magneto-electric (ME) effects on garnets. The ME effects can control magnetization and electric polarizations by applying external fields such as magnetic and electric fields. Moreover, it is known that garnets show a magneto-dielectric (MD) effect that can control dielectric constants in the host by applying magnetic fields [3]. Crystal symmetry breaking based on tri-color superlattices demonstrated the ME effect in garnets [4].

A garnet structure belongs to the cubic centro-symmetric space group (Ia-3d). A unit cell is composed of 160 atoms. A chemical formula can be described as $\{Re_3\}[M_2]^O(M_3)^TO_{12}$, where Re is a rare earth ion with a dodecahedral coordination. M^O and M^T are occupied by Fe ions with octahedral and tetragonal coordination, respectively. In particular, Re ions occupy 24c Wyckoff sites that are known as special crystallographic positions, while Fe ions occupy both 16a octahedral sites and 24d tetragonal sites. On the other hand, the oxygen ions occupy 96h sites. ReIG exhibits ferrimagnetic behaviors with a Curie temperature of 550 K at room temperature. Moreover, ME and MD effect is observed in the

vicinity of 4 and 150K, respectively [3, 5]. Therefore, it is suggested that ReIG is candidate for one of multiferroic materials, which is expected to be promising for memory devices such as field-effect transistors with four-states.

II. Introduction

This work is devoted to two experiments: One experiment is focused on electric polarizations of ReIG induced by breaking crystal symmetry (research-A). The other is epitaxial film growth of ReIG on non-garnet substrates (research-B).

For research A, it is indispensable for realizing crystal symmetry breaking of ReIG with a cubic-type in order to obtain spontaneous polarizations from ReIG. J. H. Haeni *et al* reported $SrTiO_3$ films showed ferroelectricity at room temperature (RT) [6], which is ascribed to interface strains caused by lattice mismatches between films and substrates. For example, $SrTiO_3$ films, which were observed ferroelectricity at RT, were grown using $DyScO_3$ substrates with an orientation of (110) (a = 5.440 Å, b = 5.713 Å, and c = 7.887 Å). In addition, ferroelectric $SrTiO_3$ films could be realized using LSAT substrates (a = 3.869Å) that are known as $(LaAlO_3)_{0.29} \times (SrAl_{0.5}Ta_{0.5}O_3)_{0.71}$. These reports indicate that the centro-symmetry of $SrTiO_3$ breaks by the interface strains between the films and substrates. In this work, $Sm_3Fe_5O_{12}$ (SmIG) films are grown on $Gd_3Ga_5O_{12}$ (GGG) substrates (SmIG/GGG). It is expected that this heteroepitaxial film growth introduces interface strains between the films and substrates, and breaks crystal symmetry of the films. From a theoretical calculation, a critical thickness of SmIG/GGG system was estimated as 602 Å [7].

Research B is aiming at fabricating ReIG epitaxial films on non-garnet substrates. However, it is difficult to achieve heteroepitaxial growth of garnets using non-garnet substrates at the present time. As a consequence, we cannot obtain ReIG films with better magnetic and optical properties. Therefore, this study is focused on epitaxial growth of oxide materials on garnet substrates as a first step. Thereafter, we develop to film growth of ReIG on garnet substrates with oxide buffers. Finally, epitaxial film growth of ReIG is carried out using non-garnet substrates. J. Haisma *et al* reported heteroepitaxy of GaAs and InP films on garnet substrates on the basis of higher-ordered epitaxy [8, 9]. Epitaxial film growth of ZnO on garnet substrates also results from the higher-ordered epitaxy.

III. Experimental

The (111) and (001) planes of GGG substrate (Surface-Net GmbH; Germany) were mechano -chemically polished, and then thermally annealed at 1250 °C for 2.5 h for obtaining atomically flat surfaces. The height scales of both atomic force microscopy (AFM) images revealed that step and terrace structures at atomic scale were clearly observed on both GGG substrates. Step heights of GGG (111) and (001) substrates were 0.19 and 0.33 nm, respectively. AFM (Seiko SPI-3800) was used to observe the surface morphologies of the substrates and the films. Crystal quality and lattice parameters were investigated by X-ray diffraction (XRD: Philips X'-Pert) equipped with a double-crystal monochromator and an analyzer crystal. SmIG and ZnO films were grown on GGG substrates by a PLD apparatus with a background pressure of 1.4×10^{-5} Pa. The beam out of an ArF excimer laser with a wavelength of 193 nm (Lambda Physik) was focused to produce an energy density of 4 J/cm^2 on a SmIG (99.9%) and a ZnO target (99.999%) at a repetition rate of 3 Hz. The distance between the target and the substrate was fixed to 5 cm during film growth.

III-A. Physical properties of the SmIG films

The SmIG films were grown on the GGG (001) substrates at a temperature of 750 °C in an oxygen atmosphere of 1.0×10^{-1} Pa. The dielectric properties of obtained films were measured by a ferroelectric characteristic evaluation (FCE) system.

III-B. Heteroepitaxy

The ZnO films were gown at a temperature of 650 °C in an oxygen atmosphere of 1.2×10^{-3} Pa. Thicknesses of ZnO films on the GGG (111) and (001) substrates were in the range from 80 to 150 nm.

IV. Results and discussions

IV-A. Physical properties of the SmIG films

The SmIG films were successfully grown on GGG substrates with thicknesses from 390 to 1240 Å. The strained SmIG films were obtained blow the critical thickness of 602 Å, as confirmed by XRD. From AFM observations, step and terrace structures were observed on the SmIG films with thicknesses blow 602 Å. Over the critical thickness, step and terrace structures disappeared owing to a lattice relaxation.

The thickness (t) dependence of dielectric properties on SmIG films was measured. Figures 1 (a) and (b) showed Q-V and Q/t-V characteristics, respectively. The remnant charge amounts (Q_s and $d(Q_s/t)/dV$ (V=0) were proportional to a remnant polarization (P_s) and dielectric constant (ε), respectively. P_s and ε showed the same values in all films below thicknesses of 602 Å, while the values of P_s and ε of the samples with thicknesses of 790 Å and 620 Å decreased. It was thought that the lattice relaxations resulted in breaking of crystal symmetry in the SmIG films.

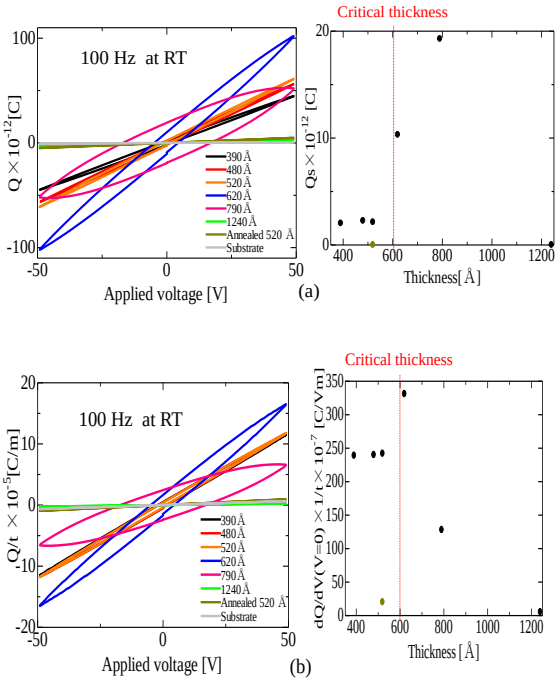

Fig. 1. The dielectric properties of SmIG films. (a) Q-V characteristics. (b) Q/t-V characteristics

VI-B. Heteroepitaxy

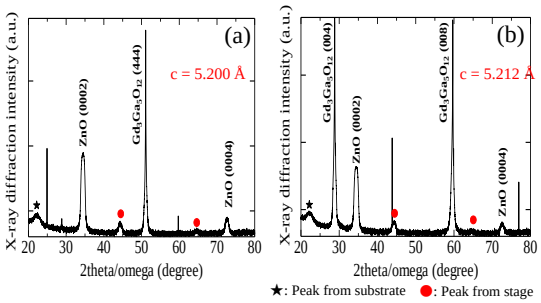

Fig. 2. 2θ/ω scans of (a) ZnO/GGG (111), (b) ZnO/GGG (001)

Figures 2(a) and 2(b) show the XRD patterns of ZnO/GGG (111) and ZnO/GGG (001), respectively. From 2θ/ω scans, we only found a diffraction peak of the (0002) plane of ZnO on both samples, revealing film growth of ZnO with the c-axis orientation.

Figure 3 (a) and (b) showed X-ray pole figure measurements for ZnO/GGG (111) and ZnO/GGG (001) as measured by the (10-11) plane of ZnO. The

pole figures showed that ZnO films with the *c*-axis direction possessed two types of in-plane rotation domains, which were identified with the 12 diffraction peaks. In the case of ZnO/GGG (111), the 12 peaks in the pole figure derived from the (10-11) plane of ZnO were two types of in-plane orientations. The rotation angle between these domains was 42°. The two domains were asymmetrically rotated with angles of ±21° with respect to the $[1\text{-}12]_{GGG}$ direction and the $[10\text{-}10]_{ZnO}$ direction. The in-plane epitaxial relations of ZnO/GGG (111) were determined as $[10\text{-}10]_{ZnO}$ || $[1\text{-}12]_{GGG}$±21°.While in the case of ZnO/GGG (001), 12 peaks derived from the ZnO (10-11) were also observed in the pole figure. The two types of in-plane orientations were measured with a rotation angle of 30° around the surface normal. The in-plane epitaxial relations of ZnO/GGG (001) were identified as $[10\text{-}10]_{ZnO}$ || $[100]_{GGG}$ and $[10\text{-}10]_{ZnO}$ || $[010]_{GGG}$.

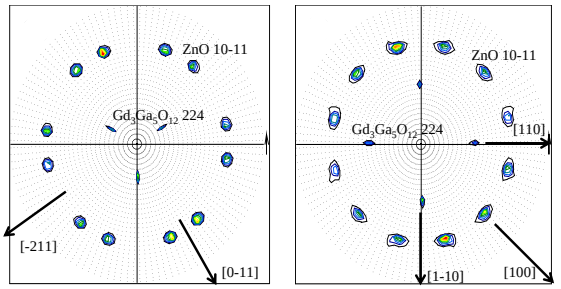

Fig. 3. X-ray pole figure measurements for (a) ZnO/GGG (111) and (b) ZnO/GGG (001).

V. Summary

V-A. Physical properties of SmIG films

We introduced the epitaxial lattice strains in the SmIG films. From the dielectric properties, Q_s and $d(Q_s/t)/V(V=0)$ were dependent on film thickness. We found the supplementary dielectric properties in the SmIG films.

V-B. Heteroepitaxy

ZnO films were grown epitaxially on GGG (111) and (001) substrates. The epitaxial relation of out-of-plane and in-plane epitaxial relations of ZnO films on the GGG (111) substrates [ZnO/GGG (111)] were the [0001]ZnO || [001]GGG and [10-10]ZnO || [1-12]GGG±21°, while ZnO films on the GGG (001) substrates [ZnO/GGG (001)] showed the out-of-plane and in-plane epitaxial relations with the [0001]ZnO || [001]GGG and [10-10]ZnO || [100]GGG, [010]GGG.

VI. References

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