Epitaxial growth of ferrimagnetic semiconductor
0.4Fe₃O₄·0.6Fe₂TiO₄ solid solution thin films on MgO(100) substrates

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Abstract. We have prepared the solid solution thin films with 0.4Fe₃O₄·0.6Fe₂TiO₄ composition
(molar ratio) on MgO(100) substrates by a pulsed laser deposition technique and examined their
magnetic and electrical properties. The thin films are epitaxially grown on the MgO substrate
cube-on-cube relationship and have a flat and smooth surface. The epitaxial thin films show
ferrimagnetism with Curie temperature beyond room temperature and exhibit n-type semiconducting behavior.

1. Introduction

Development of magnetic oxide semiconductors is a subject of strongly growing interest mainly
due to their potential applications in spintronics [1]. Among various oxides, intensive studies have
been performed on magnetite (Fe₃O₄) [2,3] and its related materials such as Fe₃O₄–Fe₂MO₄ (M = Co, Mn, Zn, Ni) [4–7] because of their high spin polarization and high Curie temperature (typically
\( T_C > 300 \) K). In this study, our attention is focused on the \((1-x)\)Fe₃O₄\( \times \)Fe₂TiO₄ (molar ratio: \( 0 < x < 1 \))
solid solutions. The uniqueness of this solid solution system lies in the fact that the conduction type
can be easily controlled by changing the chemical composition \( x \); n-type conduction is obtained for the
compositions of \( x \leq 0.6 \), while the compositions of \( x \geq 0.7 \) show p-type conduction [8]. The solid
solution system has also superiority that for \( x < 0.8 \), \( T_C \) is above room temperature regardless of the
conduction type [9]. We have recently shown that ferrimagnetic and semiconducting 0.4Fe₃O₄·
0.6Fe₂TiO₄ solid solution thin films can be grown on the \( \alpha \)-Al₂O₃(0001) substrates by a pulsed laser
deposition (PLD) technique [10]. Although the solid solution thin films were epitaxially grown on
\( \alpha \)-Al₂O₃(0001) substrates, twin domain boundaries were formed, presumably due to the large lattice
mismatch (10.7%) between the thin film and the substrate. In addition, the film surface was rough as
a result of a three-dimensional growth.

For device implementation, it is highly desirable to produce thin films with a flat surface so that
the heterostructures with a smooth interface can be obtained. A single crystalline MgO substrate has
been frequently utilized for the cube-on-cube epitaxial growth of Fe₂O₄ and the related solid solutions,
which is due to the small lattice mismatch (typically <1%) between the thin film and the substrate [11,12].
In this paper, we have demonstrated the epitaxial growth of 0.4Fe₃O₄·0.6Fe₂TiO₄ solid solution thin films on MgO(100) substrates by the PLD technique. The magnetic and electrical properties of the resultant thin films are also presented.

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2. Experimental Procedure
Thin films with 0.4Fe$_3$O$_4$·0.6Fe$_2$TiO$_4$ composition (molar ratio) were grown on the MgO(100) substrates by a PLD technique. Laser pulses launched from a KrF excimer laser ($\lambda = 248$ nm, 2 Hz) were focused on a 0.4Fe$_3$O$_4$·0.6Fe$_2$TiO$_4$ target at a fluence of 3 J/cm$^2$. The film growth was performed under an oxygen partial pressure ($P_{O_2}$) of $1.0 \times 10^{-5}$ Pa and at a substrate temperature ($T_s$) of 500 °C. An energy dispersive X-ray spectrometry revealed that the cation ratio of thin films was almost the same as that of target (Fe:Ti=2.4:0.6). The crystal structure was characterized by high-resolution X-ray diffraction (XRD), and the surface morphology of films was observed by an atomic force microscope (AFM). Magnetization ($M$) was measured by using a superconducting quantum interference device (SQUID) magnetometer. The measurement of electric resistivity ($\rho$) was carried out by the van der Pauw method. The major conduction type was determined through the measurement of Seebeck coefficient at room temperature.

3. Results and Discussion
Figure 1(A) shows the 2θ/ω (out-of-plane) XRD pattern of Fe$_3$O$_4$–Fe$_2$TiO$_4$ solid solution thin film. The diffraction peaks observed at around 2θ=42.4° and 92.5° are ascribed to the solid solution 400 and 800 reflections. The appearance of Pendellösung fringe patterns around the 400 and 800 reflections indicates the growth of a high-quality thin film. By analyzing the fringe pattern, the film thickness is...

![XRD 2θ/ω scan of the solid solution thin film grown on MgO(100) substrate. Inset shows the XRD 2θ/ϕ scan of the thin film. △: Fe$_3$O$_4$–Fe$_2$TiO$_4$ solid solution (F), ●: substrate (S). (B) Pole figures of the 222 reflection for solid solution film (left) and MgO(100) substrate (right). (C) AFM image (5×5 µm$^2$) for the solid solution film grown on MgO(100) substrate (left) and the cross-sectional profile along the solid line in the AFM image (right).](image-url)
evaluated to be about 60 nm. In the $2\theta/\phi$ (in-plane) XRD pattern [inset in Fig. 1 (A)], two diffraction peaks assigned to 220 and 440 reflections due to the solid solution are observed without any impurity phases. A tetragonal distortion is epitaxially induced on MgO substrates because the lattice constant of solid solution (0.8472 nm) [13] is just a little larger than twice the lattice constant of MgO (0.4213 nm $\times 2 = 0.8426$ nm). The in-plane lattice constant for solid solution film is shortened (0.8428 nm) to match twice the lattice constant of MgO, while the out-of-plane lattice constant is elongated to 0.8530 nm due to the compressive strain.

To evaluate the in-plane orientation relationship between the solid solution thin film and the MgO(100) substrate, the pole figure measurements were further performed using the 222 reflection [Fig. 1 (B)]. Both the pole figures of film and MgO substrate exhibit only four spots at every 90º corresponding to the fourfold symmetry. Namely, the atomic arrangement in the [111] direction exactly matches between the film and the substrate. This is due to the small lattice mismatch (0.68%) between the film and the substrate. In contrast to the case of using the $\alpha$-Al$_2$O$_3$(0001) substrate [10], the cube-on-cube epitaxy can be achieved by the use of MgO substrate; the solid solution thin film is epitaxially grown on MgO(100) without formation of twin domain boundaries. The orientation relationship between the film and the substrate is as follows; 0.4Fe$_3$O$_4$·0.6Fe$_2$TiO$_4$ solid solution(100)$[111] \parallel$ MgO(100)$[111]$.

Figure 1 (C) depicts a typical AFM image ($5 \times 5$ µm$^2$) for the solid solution thin film. The flat and smooth surface morphology can be observed without pits and islands (the root-mean-squared roughness is $\sim$0.07 nm). The generation of smooth surface strongly suggests the epitaxial growth in a layer-by-layer mode.

Figure 2 shows the temperature dependence of magnetization, $M(T)$, for the solid solution thin films. The measurements were performed under a field-cooling condition at an external magnetic field ($H$) of 15000 Oe applied along the in-plane direction of the film. Strong $M$ can be obtained in the temperature region below 400 K, indicating that the solid solution film is ferrimagnetic with a $T_C$ above 400 K. A close look at Fig. 2 reveals a maximum in the $M$–$T$ curve around 150 K. According to the Néel’s two sublattice model of ferrimagnetism [14], the observed behavior may be caused by a different $T$-dependence of $M$ between two sublattices (in the present case, the tetrahedral and octahedral sites in the spinel structure). The $M$–$H$ curve as depicted in the inset of Fig. 2 clearly displays the ferrimagnetic behavior at room temperature; the coercive force is 30 Oe, and the saturation magnetization is 160 emu/cm$^3$ ($1.3 \mu_B$/f.u.). It is worth noting that the saturation
magnetization for the films grown on MgO(100) is significantly increased compared to that for the films grown on α-Al₂O₃(0001) (0.8 µB/ f.u.) [10], presumably because the use of substrate with a smaller lattice mismatch leads to the improvement in crystallinity.

The temperature dependence of electric resistivity, ρ(T), for the solid solution thin film is shown in Fig. 3. The ρ–T curve exhibits a typical semiconducting behavior between 77 and 325 K. The ρ at 295 K is 0.52 Ωcm, comparable to that of bulk single crystal [8]. It should be noted that the ρ value for the films grown on MgO(100) is smaller than that for the film grown on α-Al₂O₃(0001) (0.87 Ωcm at 295 K) [10], which again confirms an improvement in the quality of films. The conduction behavior in a high temperature range obeys a thermal-activated hopping of the Arrhenius-type behavior, ρ=ρ₀exp(Eₐ/kB T), where ρ₀, Eₐ, and kB are the preexponential term, the activation energy, and the Boltzmann constant, respectively. The Eₐ estimated from the slope of the linear part is 0.045 eV [see the inset in Fig. 3]. The log ρ vs. T⁻¹ plot at low temperatures deviates from the linear relationship. Instead, the ρ curve follows the Mott formula, ρ=ρ₀exp(T₀/T)¹/₄, meaning a variable-range hopping (VRH). The change in the conduction behavior from the thermal-activated hopping to the VRH is due to the localization of electrons, which is also observed for the film grown on α-Al₂O₃(0001) as well as bulk single crystal. The Seebeck coefficient is evaluated to be –32 µV/K, indicating that the charge carrier is an electron (n-type).

4. Conclusion

We have fabricated spinel-type 0.4Fe₃O₄·0.6Fe₂TiO₄ solid solution thin films on MgO(100) substrates by a PLD technique. The solid solution thin films are epitaxially grown with cube-on-cube relationship on the MgO(100) substrate and possess the flat and smooth surface, due to the small lattice mismatch between the film and the substrate (0.5%). The crystallographic relationship is Fe₂O₃–Fe₂TiO₄ solid solution (100)[111] || MgO(100)[111]. We also have demonstrated that the solid solution thin film grown on MgO(100) substrates exhibits the ferrimagnetic behavior with Tc above 400 K and is an n-type semiconductor and that their physical properties are improved compared to that of films grown on α-Al₂O₃(0001). As temperature decreases, the conduction behavior was observed to change from the thermal-activated hopping to the VRH due to the localization of conduction carriers.

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