Room-temperature ferrimagnetic semiconductor $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ solid solution thin films

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The authors report on the fabrication of room-temperature ferrimagnetic semiconductor thin films composed of $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ solid solution on α-Al$_2$O$_3$ (0001) substrates using a pulsed laser deposition method. A single ordered phase ($R\bar{3}$ symmetry) is obtained under very limited deposition conditions including oxygen partial pressure of 2.0×10^{-3} Pa and substrate temperature of 700 °C. The thin film with the ordered phase is an *n*-type semiconductor and ferrimagnetic with the Curie temperature >400 K. The Hall effect measurements at room temperature suggest that the carrier spins are polarized. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2357547]

Magnetic semiconductors and diluted magnetic semiconductors with Curie temperature (T_C) above room temperature are some of the most promising materials for spin electronics,[1,2] where both charge and spin of electrons are exploited to realize multifunctional devices. Intensive studies have been also conducted on half-metallic ferromagnets such as Fe$_3$O$_4$,[3,4] CrO$_2$,[5,6] manganites,[7,8] and the double perovskite Sr$_2$FeMoO$_6$ (Ref. 9) because their fully polarized carriers are advantageous to spin injection in such devices. The development of ferromagnetic compounds with high spin polarization and high T_C is important from both scientific and technological points of view.

Although both FeTiO$_3$ and α-Fe$_2$O$_3$ are antiferromagnetic insulators,[10] interestingly their solid solutions exhibit both semiconducting and ferrimagnetic properties.[11,12] Furthermore, in this system the conduction type can be controlled as either *p* or *n* type by simply changing the composition.[12] For example, the $xFeTiO_3 \cdot (1-x)Fe_2O_3$ ($0 < x < 1$) bulk solid solutions exhibit *n*-type conduction in the compositional range of $0 < x < 0.73$, while the larger x yields *p*-type conduction. Recent theoretical work predicts the possibility of half-metallic character and high T_C in the solid solutions.[13] These properties make this system promising candidate for spin electronic applications.

α-Fe$_2$O$_3$ belongs to a family of corundum structure (space group: $R\bar{3}c$) and is composed of a distorted hcp closed packing of anions (O^{2-} ions). Fe ions occupy two-thirds of the available octahedral interstices, forming an alternate stack of Fe and O layers along the *c* axis. The crystalline structure of FeTiO$_3$ is a derivative of corundum α-Fe$_2$O$_3$, where Fe layers stacked along the *c* axis are alternately replaced by Ti layers. Due to this replacement, the crystal symmetry is reduced, and the space group changes from $R\bar{3}c$ to $R\bar{3}$. Consequently, the solid solutions of FeTiO$_3$ and α-Fe$_2$O$_3$ undergo order-disorder transition between $R\bar{3}$ and $R\bar{3}c$ symmetries. Ferrimagnetic properties are observed only when the crystalline phase is ordered with $R\bar{3}$ symmetry,

whereas the disordered phase with $R\bar{3}c$ symmetry shows antiferromagnetic properties or rather weak magnetization.[11]

We have recently reported the preparation of epitaxial $0.7FeTiO_3 \cdot 0.3Fe_2O_3$ ($x=0.7$) solid solution thin films by a pulsed laser deposition (PLD) method.[14] After appropriate annealing treatment the thin films with the ordered phase were ferrimagnetic semiconductors above room temperature. On the other hand, the Seebeck coefficient was almost zero because the composition of thin films was at the border between *p* and *n* types.[12] It is expected that the conduction type can be rendered either *p* or *n* type by changing the composition away from $x=0.7$.

In this letter, we report the preparation of $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ ($x=0.6$) thin films that have ordered-phase structure and exhibit *n*-type conduction as well as ferrimagnetism with T_C above 400 K. Furthermore, it is suggested that the carrier spins are polarized.

Thin films with $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ composition were grown on *c*-plane sapphire (0001) substrates by the PLD method. The sapphire substrates were annealed at 1000 °C in air to produce an atomically flat surface. The ceramic target for PLD was prepared by the conventional solid-state reaction between reagent-grade Fe$_2$O$_3$ and TiO$_2$ powders. The high-density target and the flat-surface sapphire substrate thus obtained were set in a vacuum chamber with a background pressure of 10^{-6} Pa. The distance between the substrate and the target was 3.5 cm. A thin film was grown on the substrate by focusing a KrF excimer laser at the wavelength of 248 nm on the rotating target. The deposition was performed at a repetition frequency of 2 Hz with a fluence of $2-3$ J/cm^2. The substrate temperature (T_S) was kept at 700 °C and the oxygen partial pressure (P_{O_2}) was varied from 1.0×10^{-4} to 1.0×10^{-2} Pa.

Rutherford backscattering spectroscopy was carried out using 2.0 MeV He^{2+} to determine the thickness and composition of the thin films. The analysis with simulation program SIMNRA revealed that the film thickness was about 70 nm and that the fraction of Fe and Ti was typically 0.28:0.13, meaning that the actual composition of the thin film was $0.63FeTiO_3 \cdot 0.37Fe_2O_3$. The crystal structure of the thin film was analyzed by x-ray diffraction measurement (XRD) with Cu $K\alpha$ radiation. Cross-sectional lattice images were obtained by a high-resolution transmission electron microscopy

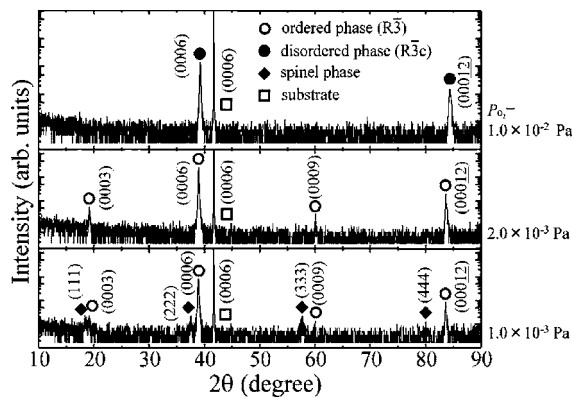a)Author to whom correspondence should be addressed; electronic mail: fujita@dipole7.kuic.kyoto-u.ac.jp

FIG. 1. Variation of XRD pattern with oxygen partial pressure for the thin films grown under $T_S = 700\ ^\circ$C. The open circles, closed circles, and closed diamonds denote the diffraction peaks due to the ordered phase, the disordered phase, and the spinel phase, respectively.

FIG. 3. Temperature dependence of magnetization for the thin films with the ordered phase (open circles) and the disordered phase (closed circles). The measurements were carried out with an applied field (H) of 8500 Oe along the in-plane direction. The inset shows the dependence of magnetization on the external magnetic field at 300 K.

(HRTEM). The measurements of magnetization (M) were carried out using a superconducting quantum interference device (SQUID) magnetometer. Photolithographically patterned Hall bars were used for transport measurements. The Seebeck coefficient was measured to identify the conduction type of the thin films.

Figure 1 shows the XRD patterns of $0.6\mathrm{FeTiO_3}\cdot0.4\mathrm{Fe_2O_3}$ thin films grown at $T_S = 700\ ^\circ$C under various $P_{\mathrm{O_2}}$. In ordinate of the figure, the logarithmic diffraction intensity is shown. The sample grown under $P_{\mathrm{O_2}} = 2.0 \times 10^{-3}$ Pa is composed of the single phase of (0001)-oriented $\mathrm{FeTiO_3}$–$\mathrm{Fe_2O_3}$ solid solution with the ordered structure of $R\bar{3}$ symmetry. When $P_{\mathrm{O_2}}$ is increased to 1.0×10^{-2} Pa, the (0003) and (0009) diffraction peaks from the thin film disappear. Evidently, the crystal structure of the thin film is changed to the disordered phase ($R\bar{3}c$ symmetry) because the disordered cation array with the $R\bar{3}c$ symmetry annihilates all (000*l*) reflections except the ones for which $l = 6n$. A close look at Fig. 1 reveals that the positions of diffraction peaks are at higher diffraction angle for the disordered phase than for the ordered phase. These observations are consistent with the results reported previously for the solid solution thin films with a composition of $x = 0.77$, for which the T_C is below room temperature.[15,16] On the con-

trary, when $P_{\mathrm{O_2}}$ is decreased to 1.0×10^{-3} Pa, a crystalline phase ascribed to spinel-type structure is observed as an impurity phase. Thus, $P_{\mathrm{O_2}}$ is a key factor in controlling the chemical composition including the valence state of Fe ions and specific phase.

Figure 2 depicts a cross-sectional HRTEM image and selected area electron diffraction (SAED) pattern for the solid solution thin film with the ordered phase. Highly epitaxial nature of the thin film is confirmed. The SAED pattern revealed in-plane and out-of-plane epitaxial growths of the thin film. The epitaxial relationship is as follows: solid solution thin film $(0001)[1\bar{1}00]//\mathrm{Al_2O_3}(0001)[1\bar{1}00]$. The $(01\bar{1}2)$ pole figure of the thin film (not shown) exhibits only three peaks similar to that of α-$\mathrm{Al_2O_3}$, confirming this epitaxial relationship.

Figure 3 compares the temperature dependence of M for the thin films with the ordered and disordered phases. The measurements were performed under a field-cooled condition while an external magnetic field (H) of 8500 Oe was applied parallel to the film surface. For the thin film with the ordered phase, M decreases almost linearly with increasing temperature, presumably up to the critical temperature (T_C) that is expected to be above 400 K. A similar behavior, which was observed in the bulk samples based on $\mathrm{FeTiO_3}$–$\mathrm{Fe_2O_3}$ solid solution, was ascribed to the R-type
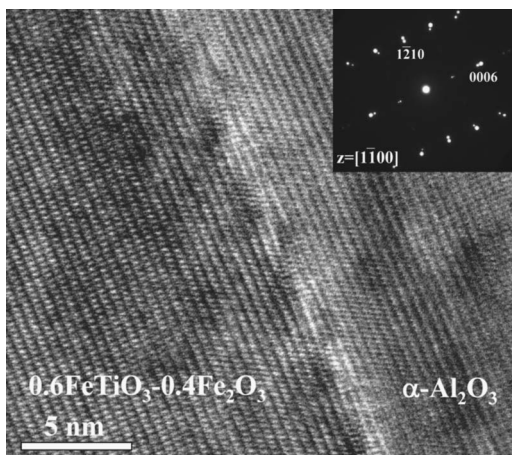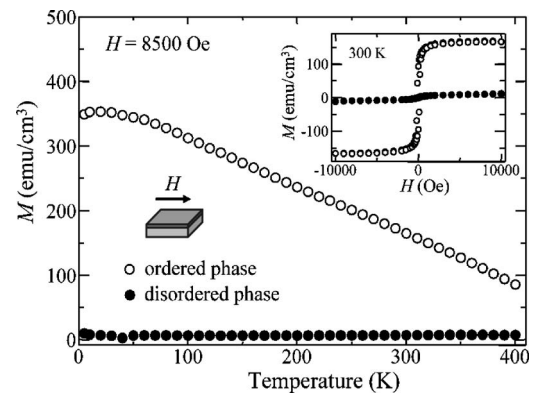

FIG. 2. Cross-sectional HRTEM image and the electron diffraction pattern of the solid solution thin film with the ordered phase. The direction of the incident electron is parallel to $[1\bar{1}00]$ direction of α-$\mathrm{Al_2O_3}$.
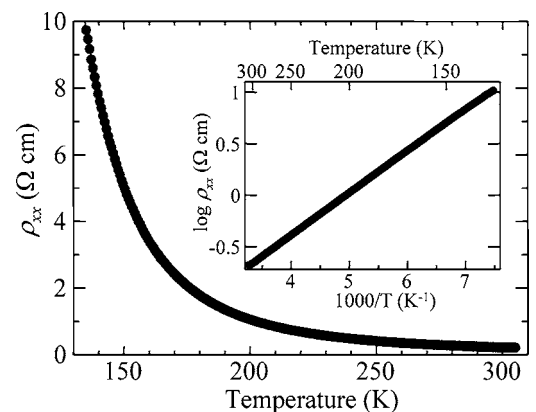

FIG. 4. Temperature dependence of electric resistivity for the thin films composed of the ordered phase. The activation energy of the thin film is determined from the slope of the figure in the inset.
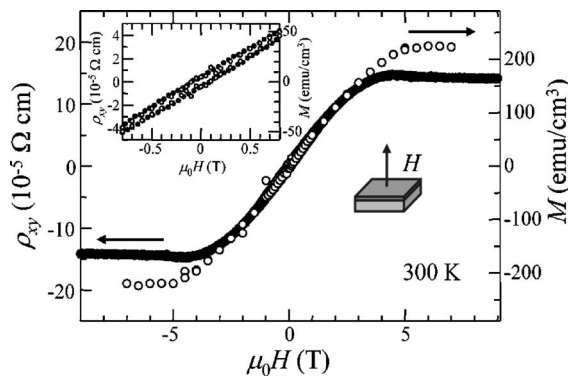
FIG. 5. Magnetic field dependence of ρ_{xy} (closed circles) and magnetization (open circles) for the thin films with the ordered phase. Both of the curves are shown on the expanded scale in the inset. The applied magnetic field is perpendicular to the film surface both for ρ_{xy} and magnetization measurements.

ferrimagnetism.[11] The inset of Fig. 3 displays plots of in-plane M-H curve at room temperature, which also confirm the ferromagnetic or ferrimagnetic behavior. The saturation magnetization at 2 K is about $3\mu_B$/mol, which is comparable to that expected for the solid solution with this composition, $2.52\mu_B$/mol. On the other hand, relatively small M for the disordered phase reflects the fact that magnetic moments on each layer in the disordered phase are canceled out partially. These results clearly indicate that the production of the ordered phase is responsible for the appearance of strong ferrimagnetism.

Temperature dependence of electric resistivity (ρ_{xx}) for the ordered phase is shown in Fig. 4. The thin film exhibits Arrhenius-type temperature dependence over a range between 130 and 300 K, with the activation energy of ~0.08 eV estimated from the slope. This value is comparable to those in bulk and thin film samples as reported previously.[12,17] The Seebeck coefficient of the thin film with the ordered phase is found to be -6 μV K^{-1}. The negative Seebeck coefficient is indicative of the n-type conduction of the specimen, as is expected from the composition.

The spin polarization of the mobile carriers is one of the critical properties relevant to the application of spin electronic devices. Figure 5 shows the H dependence of the Hall resistance (ρ_{xy}) measured for the thin film with the ordered phase at room temperature. The magnetic field was applied perpendicular to the film surface. The ρ_{xy} data were obtained by subtracting the magnetic field effect that is even function of field from the raw data. The plot of out-of-plane M-H curve is also shown in Fig. 5. The behavior of out-of-plane M-H curve differs from that of in-plane M-H curve shown in the inset of Fig. 3, suggesting the presence of magnetic anisotropy of the solid solution.[18] The Hall resistance for ferromagnets is generally expressed as $\rho_{xy} = R_0 B + R_S M$, where R_0, R_S, and B represent the ordinary Hall coefficient, anomalous Hall coefficient, and magnetic induction, respectively.[19] The first term denotes the ordinary Hall effect (OHE), and the second term the anomalous Hall effect (AHE). The AHE is proportional to M and conventionally originates from asymmetric scattering process involving a spin-orbit interaction. As shown in Fig. 5, ρ_{xy} exhibits a behavior similar to

that of out-of-plane M-H curve. Especially in the low magnetic fields, the coincidence between them is fairly good (see the inset of Fig. 5). This result demonstrates the presence of AHE and implies that the carrier spins of $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ thin films with the ordered phase are polarized at room temperature. The ρ_{xy} curve in the high magnetic field region has a negative slope due to the OHE, which again indicates n-type conduction. The Hall mobility and carrier concentration determined from the slope are 0.03 cm^2 V^{-1} s^{-1} and 1.0×10^{21} cm^{-3}, respectively. Small hump in ρ_{xy} around $\mu_0 H$ of 4 T may be attributed to the effect of H dependence of ρ_{xx}. Details of these results will be discussed elsewhere.

In conclusion, we have grown $0.6FeTiO_3 \cdot 0.4Fe_2O_3$ solid solution thin films on α-Al_2O_3 (0001) substrates using the PLD method to examine their electrical and magnetic properties. The growth of solid solution thin film consisting of the ordered phase ($R\bar{3}$ symmetry) is reproducibly achieved by precisely tuning the oxygen partial pressure. We also found that the ordered-phase thin films are ferrimagnetic with T_C above room temperature and show n-type conductivity. Moreover, spin polarization of the carriers was implied for the solid solution thin films with the ordered phase by the Hall effect measurements at room temperature.

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