Low-temperature growth of highly crystallized FeTiO$_3$-Fe$_2$O$_3$ solid solution thin films with smooth surface morphology

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Abstract. We report on the low-temperature growth of order-phased 0.8FeTiO$_3$·0.2Fe$_2$O$_3$ solid solution thin films on α-Al$_2$O$_3$ (0001) substrates by a pulsed laser deposition method. Order-phased thin films can be prepared in a range of substrate temperature ($T_S$) of 500 °C $\leq T_S \leq$ 700 °C. In this $T_S$ range, the crystallinity and surface smoothness of thin films are improved as $T_S$ is reduced from 700 °C, and highly (0001)-oriented films with a flat surface are obtained when $T_S = 500$ and 550 °C in spite of large lattice mismatch between the solid solution and the substrate (~ 7%). Magnetic and electric properties of thin films grown at $T_S = 500$ and 550 °C are comparable to those of bulk specimen.

1. Introduction

Spintronics is one of the hot topics in the current solid-state physics and electronics research. Integrating the degree of freedom in spin into semiconductors can lead to new classes of devices and circuits, including spin field effect transistors [1] and magnetic tunnel junctions [2]. Magnetic oxide semiconductors are promising materials for practical application because of their high Curie temperature ($T_C$) and stability in atmospheric environment.

Among various oxides, one candidate for practical magnetic semiconductor with $T_C$ around room temperature is solid solutions of ilmenite (FeTiO$_3$) and hematite (α-Fe$_2$O$_3$). Both FeTiO$_3$ and Fe$_2$O$_3$ have a corundum-based structure where oxide anions arrange into a distorted hexagonal close packed sublattice, and thus the system forms a complete solid solution $x$FeTiO$_3$·(1−$x$)Fe$_2$O$_3$ ($0 < x < 1$). For the FeTiO$_3$-rich compositions ($0.5 < x < 0.85$), preferential Ti substitution in the cation sublattice can bring about an ordered phase where alternating Ti-rich and Fe-only cation layers stack along [0001] direction, and antiparallel coupling of magnetic moments between adjacent cation layers results in ferrimagnetism although both endmembers are antiferromagnets [3]. $T_C$ can be above room temperature when $x < 0.73$. The conduction type can be controlled as either $p$- or $n$-type by simply changing the composition [4]. We recently reported the fabrication of epitaxial $x$FeTiO$_3$·(1−$x$)Fe$_2$O$_3$ ($x = 0.6, 0.7, \text{and } 0.8$) solid solution thin films on α-Al$_2$O$_3$ (0001) substrates by a pulsed laser deposition (PLD) method [5-8]. Although single-phased epitaxial films with ordered phase were obtained, their surfaces were rough with pits of 5 nm in depth, which is unfavorable in view of device application. Recently, many studies have been carried out on epitaxial growth of $x$FeTiO$_3$·(1−$x$)Fe$_2$O$_3$ thin films on α-Al$_2$O$_3$ substrate [9-11]; however, the relationship between the deposition condition and the surface

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morphology has not been investigated. The surface roughness is mainly caused by the lattice mismatch between solid solution and α-Al_2O_3 (as large as 7%) and relatively high growth temperature (typically 700 °C). When the thin films with a large lattice mismatch are fabricated at such a high growth temperature, atoms on the substrate are thermally-activated and readily diffuse. This diffusion leads to relaxation of the lattice strain, resulting in a surface roughness including random dislocations and cracks. One approach to solve this problem is a reduction in growth temperature to suppress the lattice relaxation.

In this study, we report on the low-temperature growth of epitaxial thin films composed of 0.8FeTiO_3·0.2Fe_2O_3 using a PLD method. The ordered-phase epitaxial thin films having a flat surface can be fabricated by optimising the growth temperature. Electric and magnetic properties of those films are discussed in comparison with those of bulk specimen.

2. Experimental

Films of 0.8FeTiO_3·0.2Fe_2O_3 composition were grown on α-Al_2O_3 (0001) substrates by a PLD method. The ceramic target used for the PLD was prepared by the conventional solid-state reaction between reagent-grade α-Fe_2O_3 (99.99%) and TiO_2 (99.9%). The high-density target and an atomically flat surface α-Al_2O_3 substrate were set in a vacuum chamber with a base pressure of 10^{-6} Pa. A KrF excimer laser (wavelength: 248 nm) was focused on the target with a fluence of 2 J/cm^2. The repetition frequency of laser was fixed at 2 Hz. The oxygen partial pressure (P_02) was kept at 1.0×10^{-3} Pa, and T_s was varied from 400 to 700 °C. The film thickness was evaluated to be about 70 nm using a surface profiler. The crystal structure was analyzed by X-ray diffraction (XRD) with Cu Kα radiation. The surface morphology of thin films was observed using an atomic force microscope (AFM). The measurements of magnetization were carried out using a superconducting quantum interference device (SQUID) magnetometer. The electric resistivity was measured by the van der Pauw method. Measurements of the Seebeck coefficient were carried out at room temperature.

3. Results and Discussion

Figure 1 (a) shows the out-of-plane XRD patterns of 0.8FeTiO_3·0.2Fe_2O_3 thin films. When T_s ≥ 500 °C, 0003 and 0009 reflections, which are absent in the case of disordered phase, are clearly observed in addition to 0006 and 00012 ones, indicating the formation of ordered phase of (0001)-oriented FeTiO_3·Fe_2O_3 solid solution. In contrast, when T_s = 400 and 450 °C, only 0006 and 00012 reflections ascribed to the disordered phase are detected. This is probably due to the insufficient heat supply which prevents atoms from diffusing on the film surface to arrange into the ordered phase. Figure 1 (b) represents a magnified image of 0006 peaks in figure 1 (a). For thin films grown at T_s = 500 and 550 °C, Pendellösung fringes are observed, indicating the high crystallinity and smooth surface morphology of these films. The 0006 reflection peaks are located at lower 2θ values relative to those of the other films. It is evident that thin films grown at T_s = 500 and 550 °C elongate along [0001] direction, due to the in-plane compressive strain imposed by the lattice mismatch (a axis lattice constant is 5.078 Å for bulk solid solution, and 4.763 Å for α-Al_2O_3). For films grown at higher T_s, the peak position is shifted to the higher 2θ values, which suggests the lattice relaxation. On the other hand, the peak position is also shifted to the higher 2θ values when T_s is decreased from 500 °C. This is not due to the strain relaxation but attributable to the presence of excess Fe^{3+}, since oxidation preferentially takes place at lower temperatures. Because of the smaller ionic radius of Fe^{3+} relative to that of Fe^{2+}, it is considered that the lattice constant becomes shorter for thin films grown at a lower T_s (< 500°C). In-plane XRD measurements (not shown) exhibit only 112 0 and 224 0 peaks, corresponding to α-plane reflections of the films. Namely, thin films are grown epitaxially on α-Al_2O_3 (0001) substrates. The orientation relationship is as follow; solid solution (0001)[1120]/α-Al_2O_3 (0001)[1120]. When T_s = 550 and 500 °C, the 1120 reflection peaks are located at higher 2θ values relative to the peak position of the thin film deposited at T_s = 700 °C, confirming the in-plane compression. Figure 1 (c) shows the rocking curves for the 0006 reflections. Obviously, a reduction in growth temperature also improves the mosaicness of thin films.
Figure 2 displays the AFM images of the films. In decreasing $T_S$ from 700 to 500 °C, the film surface tends to be smoother without any pits; the root-mean-squared (rms) roughness decreases with decreasing the growth temperature. This tendency agrees with the result of XRD patterns as shown in figure 1 (b), where Pendellösung fringe patterns appear for the films grown at $T_S = 550$ and 500 °C.

Figure 3 illustrates the temperature dependence of magnetization, $M(T)$, for the films. 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. The films with ordered phase grown at $T_S = 700, 550, \text{ and } 500$ °C exhibit an increase in $M$ with a decrease in $T$, indicating a ferrimagnetic ordering. Both of the films grown at $T_S = 500$ and 550 °C possess $T_C$ of about 245 K, comparable to the value of bulk specimen ($T_C = 234$ K) [3]. On the other hand, $T_C$ of the film grown at $T_S = 700$ °C is as high as 290 K. The $T_C$ higher than the bulk value may be ascribed to the excess amount of Fe$^{2+}$ ions caused by higher $T_S$, since Fe$^{2+}$ ions contribute to a net increase in $M$ for the solid solution. For the film with the disordered phase ($T_S = 400$ °C), $M$ is very small and shows no $T$-dependence, indicating that the film is antiferromagnetic. The in-plane $M$-$H$ curves at 100 K (see the inset of figure 3) also confirm the ferrimagnetic and antiferromagnetic properties of the ordered and disordered phases, respectively.

The temperature dependence of electric resistivity, $\rho(T)$, is shown in figure 4 for the films grown at $T_S = 500, 550, \text{ and } 700$ °C. The log $\rho$ vs. 1000/$T$ plot exhibits a linear relationship above 105 K and deviation from the linear relation below 105 K. The behavior above 105 K indicates an Arrhenius-type dependence of $\rho(T)$. On the other hand, the log $\rho$ vs. $T^{-1/4}$ plot (see the inset of figure 4) displays...
thermally-activated hopping to VRH at a critical temperature, suggesting that the charge carriers in the hopping (VRH) mechanism. Namely, the conduction behaviour is found to change from the linear relationship below 105 K, which means that the conduction occurs by the variable-range hopping mechanism. 

The solid solution thin films tend to localize at low temperatures. The Seebeck coefficients were +43, +75, and +31 $\mu$VK$^{-1}$ for the order phased thin films grown at $T_s$ = 500, 550, and 700 ºC, respectively. The positive Seebeck coefficients indicate the $p$-type conduction as expected from the composition [4].

4. Conclusion

0.8FeTiO$_3$·0.2Fe$_2$O$_3$ thin films were grown on $\alpha$-Al$_2$O$_3$ substrates at $T_s$ between 400 and 700 ºC ($P_{02}$ = 1.0×10$^{-9}$ Pa). The thin films with ordered phase can be fabricated in the $T_s$ range from 500 to 700 ºC. Especially, thin films with a smooth surface can be obtained at $T_s$ = 500 and 550 ºC. The result indicates that careful control of atomic diffusion process during the growth stabilizes the ordered phase of solid solution while minimizing dislocation formation through lattice relaxation, improving the crystallinity in the film. The solid solution thin films grown at $T_s$ = 500 and 550 ºC are expected to be more suitable for the device implementation because of their flat surfaces.

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