Transport properties of $ZnFe_2O_{4-\delta}$ thin films

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This study presents an experimental investigation on the transport properties of $ZnFe_2O_{4-\delta}$ (ZFO) thin films to clarify the ambient atmosphere effects on the transport properties by varying the oxygen pressure and the substrate temperature. Previous investigations have demonstrated the significant role of Fe^{2+} ion concentration due to oxygen vacancies on the transport properties of ZFO. Our systematic investigation suggests that the electrical transport of ZFO thin films is also strongly influenced by structural disorders and vacancies. © *2007 American Institute of Physics.*
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INTRODUCTION

$ZnFe_2O_4$ (ZFO) is an insulating frustrated antiferromagnet with a spinel ferrite structure. The Zn ion is known to enter the tetrahedral "A" site of the spinel structure and the Fe ion occupies the octahedral "B" site. The origin of ZFO magnetic properties is the spin magnetic moment of the unpaired $3d$ electrons of the transition element, coupled by superexchange interaction via the oxygen ions separating them. As such, ZFO has been mostly investigated for the magnetic properties rather than the transport properties.[1–4]

Recent possible applications in spintronics renewed the interest in the transport properties of magnetic spinel ferrites.[5–7] The structure proved to be quite sensitive to vacancies and some other defects,[8] inferring also such structural effects on the transport properties. There are few reports on the transport properties of ZFO.[8–10] The conduction carriers were identified as "n" type[8] and the significant role of Fe^{2+} concentration was assumed. The assumptions are based on the electron hopping conduction mechanism between Fe^{2+} and Fe^{3+} ions,[10] quasi-similar with other spinel ferrites, including Fe_3O_4,[10–12] $ZnCoFe_2O_4$,[13] $MnZnFe_2O_4$,[14,15] $ZnNiFe_2O_42O_4$,[16] and so on. However, the knowledge as to the transport properties of ZFO thin films is still scarce. Thus, the objective of this study is to investigate the transport properties of ZFO thin films by varying the growth conditions including the oxygen pressure and the substrate temperature.

EXPERIMENTAL

ZFO thin films were deposited on MgO (001) and/or Al_2O_3 (0001) single crystal substrates using PLD (ArF excimer $\lambda = 193$ nm) in an oxygen atmosphere. The target was obtained by sintering mixed powders of ZnO and Fe_2O_3 (molar ratio 1:2) for 12 h at 1300 °C. The laser energy was set to be 40 mJ (~3 J/cm^2) with a frequency of 3 Hz. The film thickness was controlled to be 70–90 nm with the growth rate of 10–15 Å/min.[17] The oxygen pressure and the substrate temperature were varied from 10^{-3} Pa to 10^{-1} Pa and from 300 °C to 700 °C, respectively. After deposition, the thin films were cooled down to near room temperature in constant oxygen pressure. The crystal structures of the thin films were evaluated by x-ray diffraction (XRD) measurement. The transport measurements were performed using a four-probe method. The magnetic properties were measured by a superconducting quantum interference device (SQUID).

RESULTS AND DISCUSSION

Figure 1 shows the typical XRD data of the ZFO thin film deposited on Al_2O_3 substrate at 510 °C substrate temperature and 10^{-3} Pa oxygen pressure. (111) oriented ZFO film peaks were clearly seen, and, more importantly, there were no observable impurities on the XRD data. The absence of impurities was confirmed for all ZFO thin films deposited
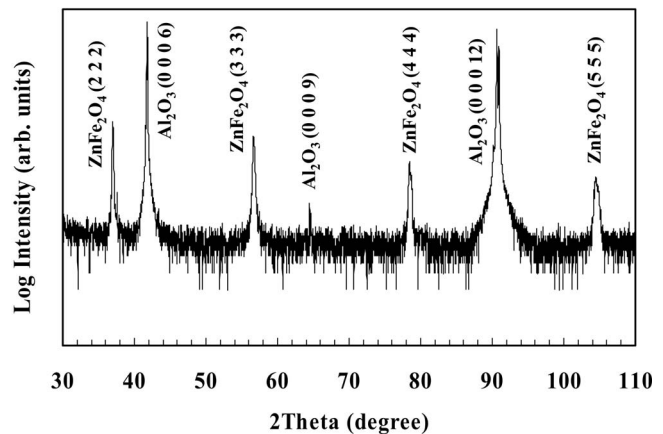

FIG. 1. XRD data of ZFO thin films deposited on Al_2O_3 (0001) substrate under 510 °C substrate temperature and 10^{-3} Pa oxygen pressure.

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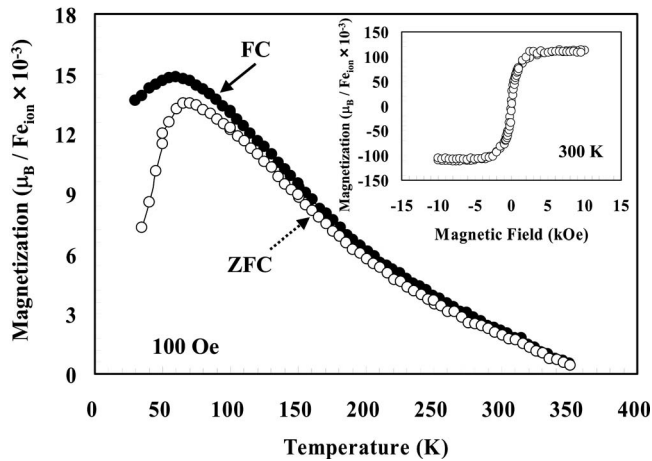
FIG. 2. Temperature dependences of magnetization measured under FC and ZFC at 100 Oe. The ZFO film was deposited under 610 °C substrate temperature and 10^{-1} Pa oxygen pressure. The inset shows the $M-H$ curve measured at 300 K.
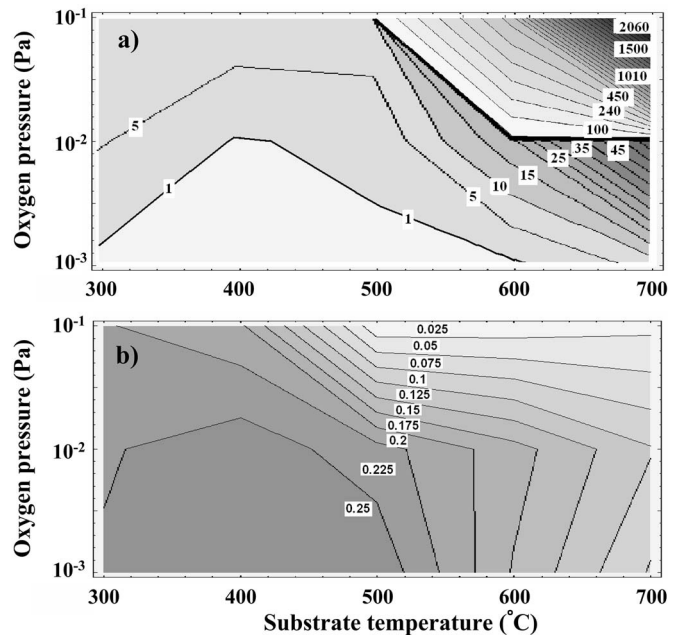

FIG. 3. (a) Variation of resistivity (Ω cm) measured at 300 K and (b) variation of saturated magnetization Ms (emu/mm^3) when varying the oxygen pressure and the substrate temperature.

onto MgO (001) substrate within the range of experimental conditions employed. Thus, the thin films fabricated herein were ZFO spinel structures. Figure 2(a) shows the $M-T$ curves under zero-field cooling (ZFC) and field cooling (FC) for the ZFO thin film deposited on MgO (001) substrate at 610 °C substrate temperature and 10^{-1} Pa oxygen pressure. The spin glass transition temperature Tg was found to be near 40 K, which is comparable to bulk Tg (20–30 K) and Neel temperature (10 K).[18] This trend was observed for films deposited in the temperature range of 400–650 °C. This is also consistent with previous report by Yamamoto *et al.*[17] when the deposition rate was less than 10–20 Å/min. The inset figure shows the $M-H$ data measured at 300 K. Weak ferromagnetism was observed, which is also consistent with previously reported trends.[1–4] Thus, the quality of ZFO thin films fabricated herein seems to be comparable with previous reports.

Figure 3(a) shows the resistivity variation of the ZFO thin films when varying the oxygen pressure and the substrate temperature during film growth. The resistivity was measured at 300 K. The figure has been obtained by interpolating resistivity data for 17 samples. It can be seen that decreasing both the substrate temperature and the oxygen pressure resulted in a decrease of the film resistivity. Figure 3(b) shows the variation of saturated magnetization Ms at $1T$ on the $M-H$ curves measured at 300 K. Ms tended to increase with decreasing both the substrate temperature and the oxygen pressure. It is noted that there is a good correlation between Ms and the resistivity in terms of the ambient atmosphere dependence. Since the resistivity showed three orders of magnitude variation when varying the ambient atmosphere, the transport mechanism might be altered. Figure 4 shows the temperature dependences of resistivity. All ZFO films showed insulating and/or semiconducting behavior. It can be seen that all data are reasonably fitted by a conventional thermal hopping formula as expressed by $-\rho(T) = \rho_0 \exp(\Delta E/k_B T)$, where ρ_0 is a material parameter that does not strongly depend on the temperature, k_B is the Boltzmann constant, T is the temperature, and ΔE is the thermal activa-

tion energy. Thus, thermally activated electron hopping seems to govern the electrical transport in all ZFO films within the investigated range. ΔE decreased from 0.13 to 0.07 eV with decreasing substrate temperature and oxygen pressure, as shown in the inset.

There seem to be several possible mechanisms to interpret the experimental trends. In several previous reports[8,9] the primary transport mechanism in ZFO thin films was assumed to be the electron hopping between Fe^{3+} and Fe^{2+} ions in the same manner as Fe_3O_4. The presence of Fe^{2+} ions is induced by oxygen vacancies in reducing atmosphere, and also the amount of Fe^{2+} ions might enhance Ms via ferrimagnetism. Thus, one can expect a quasi-proportional dependence of film resistivity on the Fe^{2+} variation. Based on this scenario, thermodynamic equilibrium Fe^{2+} lines should correlate with the resistivity variation lines. Figure 5 shows several thermodynamic equilibrium lines between $ZnFe_2O_4$,

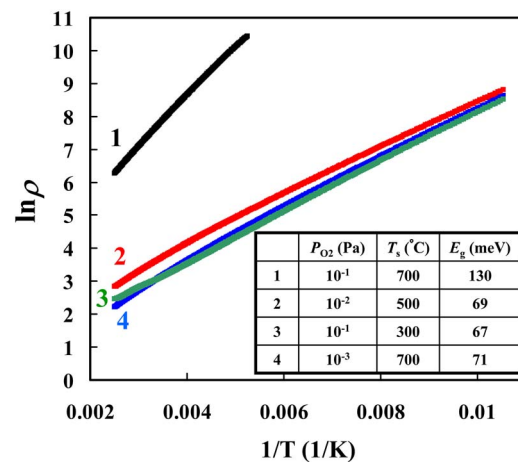|	P_{O_2} (Pa)	T_s (°C)	E_g (meV)
1	10^{-1}	700	130
2	10^{-2}	500	69
3	10^{-1}	300	67
4	10^{-3}	700	71

FIG. 4. Temperature dependences of resistivity for ZFO thin films. The inset shows the variation of thermal activation energies.
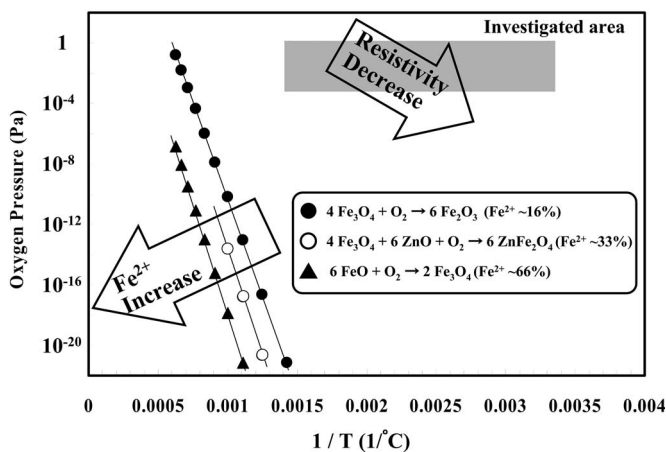
FIG. 5. Comparison between thermodynamic equilibrium lines (the amount of Fe^{2+}) and our experimental trend of resistivity variation.

Fe_2O_3, Fe_3O_4, and ZnO calculated by $\ln(P/P_0) = \Delta G/(RT)$. R is a gas constant, T is the temperature, and ΔG is the standard Gibbs' formation free energy.[19] Within our experimental range, it should be noted that the Fe^{2+} variation tendency is directed toward almost perpendicular direction compared with the observed experimental trend of the resistivity. In other words, the scenario based on the amount of Fe^{2+} alone cannot explain the experimental trend of resistivity, especially the trend when decreasing the substrate temperature. Even considering some other neglected influences of grain boundary or measurement errors, it is quite unlikely to justify almost 90° misalignment of the variation tendency. For example, even considering the grain boundary influences, previous results suggest that the grain boundaries should mainly be responsible for increasing the resistivity.[8,16] Since the grain size should actually decrease with decreasing the temperature,[3] the grain boundary scenario cannot explain our experimental trends.

Since the transport mechanism based on the presence of Fe^{2+} alone cannot explain the observed experimental trend when decreasing the substrate temperature, a different origin should be considered. The other possible scenario is based on that the resistivity and magnetic properties are also influenced by structural disorders and vacancies. In fact, the full-width at half maximum (FWHM) in (222) peak increased from 0.09 to 0.15 as the substrate temperature decreased from 700 °C to 300 °C, indicating the degradation of crystallinity. The FWHM data were estimated from normal θ -2θ scans. Usually, structural disorders and vacancies in oxide thin films tend to be generated as decreasing the substrate temperature and the oxygen pressure. When decreasing the oxygen pressure, the amount of Fe^{2+} increases via oxygen vacancies. This might enhance the electrical conduction of ZFO by the electron hopping between Fe^{3+} and Fe^{2+} ions. Note that the contribution of Fe^{2+} on the transport should differ from the conventional hopping regime in Fe_3O_4. The saturated magnetizations of ZFO in Fig. 3 are far below those of Fe_3O_4. Therefore, the presence of the antiparallel spin alignment of Fe ions at the B site in ZFO is assumed, which obviously differs from Fe_3O_4. In addition, when varying the oxygen pressure at low temperature 300 °C, the tem-

perature dependence of resistivity was found to be rather insensitive to the variation of oxygen pressure. This indicates the dominance of structural effects on the electrical conduction of ZFO at low temperature range. Thus, the resistivity trend when decreasing the substrate temperature is consistent with the scenario based on structural effects. These experimental results highlight that the electrical transport in ZFO is strongly enhanced not only by the presence of Fe^{2+} but also by structural disorders and vacancies. As to the structural effects on the transport properties of spinel oxides, Manendez-Proupin and Gutierrez theoretically reported that structural vacancies induce impurity level and/or mid-gap state due to the crystal disorder in γ-Al_2O_3.[20] Such defect states by structural disorders and vacancies might be related to the enhancement of electrical conduction of ZFO. However, the details of such structural effects on the transport properties of ZFO, including oxygen vacancies, cation vacancies, and others, were not identified in this study. Further investigations by measuring the valence state of Fe ions, the microstructures, and the electronic structures near the Fermi level using XPS, EXAFS, and others would contribute to further understanding of the structural effects on the transport properties of ZFO.

CONCLUSION

In conclusion, the transport properties of ZFO thin films were investigated to clarify the ambient atmosphere effects on the electrical transport by varying the oxygen pressure and the substrate temperature. Previous investigations have demonstrated the significant role of Fe^{2+} due to oxygen vacancies on the electrical transport in ZFO thin films. Our systematic investigation suggests that the electrical transport in ZFO thin films is also strongly influenced by structural disorders and vacancies. Although the electronic structures including the valence state of Fe ions and the density of state near the Fermi level were not identified herein, these experimental findings will contribute to further understanding of the transport properties in ZFO thin films.

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