Transactions of the Materials Research Society of Japan 25 [4] 1151-1154 (2000)

Electrical and magnetic properties of magnetite films prepared by ferrite plating

Y. NAKAYAMA, T.ISHIKAWA, Y. KITAMOTO, and M. ABE

Department of Physical Electronics, Tokyo Institute of Technology

2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552

Fax: 81-03-5734-2906, e-mail: ynaka@pe.titech.ac.jp

This paper describes the magnetoresistanace (MR) effect of magnetite (Fe_3O_4) films prepared by the ferrite plating. We investigated the dependence of magnetic and electrical properties on the concentration of the oxidizing agent C_{ox}. While saturation magnetization M_s decreased, resistivity and MR ratio increased with increasing C_{ox}. The MR ratio reached 5.5%. The ratio of Fe^{2+} ions to Fe^{3+} ions in the films decreased with increasing C_{ox} resulting in the increase in the resistivity and the MR ratio. The electrical transport was attributed to spin-dependent tunneling between Fe_3O_4 grains through insulating regions in the grain boundaries.

Key words: magnetoresistance, magnetite, ferrite plating

1. INTRODUCTION

Magnetoresistance (MR) has been attracting many researchers' interests, in particular, regarding applications to reproducing heads for hard disk drives and memories.[1] While physical vapor deposition methods such as sputtering have been used in almost all of studies about magnetoresistance of magnetite films, there are no studies on magnetite fabricated by plating. Since the ferrite plating enables us to synthesize spinel ferrite films at low temperature below 100 °C from aqueous solutions,[2-4] the ferrite-plated films are easy to apply magnetic devices even using plastic substrates with flexibility and low cost. Thus, we investigated the MR effect of magnetite films prepared by the ferrite plating. The magnetite films synthesized by the ferrite plating were actually composed of Fe_3O_4 and γ-Fe_2O_3.[4] The ratio in the films was changed by the degree of oxidation. In this paper, we investigated the dependence of magnetic and electrical properties of $Fe_{3-x}O_4$ films on a concentration of an oxidizing solution that influences the oxidation.

2. EXPERIMENTAL

Figure 1 shows the ultrasound-enhanced ferrite-plating apparatus. The volume of the apparatus was 15 ml. Ultrasound waves (19.5 kHz , 600W) were applied by a horn (30mmϕ) to an aqueous reaction solution. The conditions of the solutions are listed in Table I. Both reaction and oxidizing solutions were supplied at the flow rate of 6.0 ml/min. The reaction temperature was 85°C. $Fe_{3-x}O_4$ films with thickness of 0.09~0.28 μm were deposited on glass substrates. The thickness of the films was determined by a scanning electron microscope. Crystallographic and magnetic properties were analyzed by a X-ray diffractometer (XRD) and a vibrating sample magnetometer (VSM), respectively. The ratio of Fe^{2+} ions to Fe^{3+} ions was evaluated by a Co^{57}-Mössbauer spectrometer. Current-in-plane (CIP) electrical properties were investigated by a four-probe method. MR measurements were performed in the maximum magnetic field of 2.5 kOe.

Table I Conditions for magnetite thin film

Reaction solution	**$FeCl_2$**	**0.025mol/l**
Oxidizing solution	**$NaNO_2$**	**0.0014 ~ 0.0579mol/l**
	CH_3COONH_4	**0.13 mol/l**

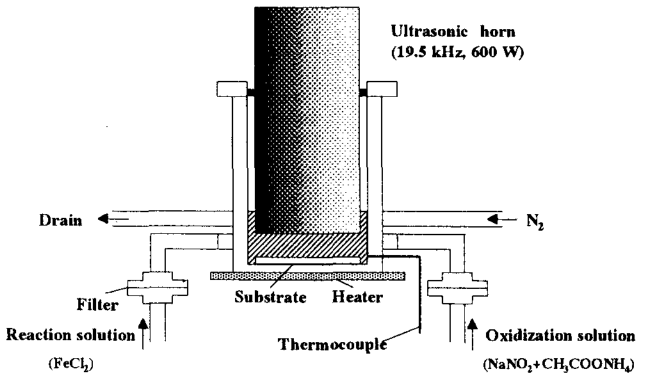


Fig.1 Ultrasound-enhanced ferrite plating apparatus

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the $Fe_{3-x}O_4$ films fabricated at various concentrations of $NaNO_2$. The thickness at the concentration of $NaNO_2$ of 0.0217 mol/l was 0.28 μm, and the others were about 0.1 μm. These results indicate that crystallinity did not change much when C_{ox} increased up to 0.0217 mol/l.

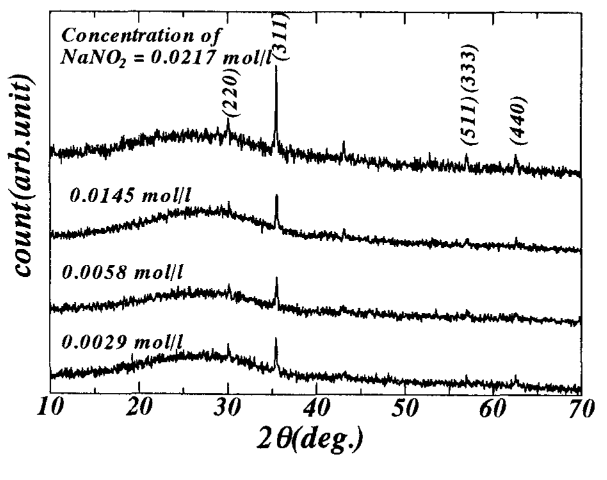


Fig.2 XRD patterns of $Fe_{3-x}O_4$ films fabricated at various concentrations of $NaNO_2$ in oxidizing solution C_{ox}

Figure 3 shows the dependence of the saturation magnetization M_s on the concentration of $NaNO_2$. M_s was almost constant at 550 emu/cc when C_{ox} was 0.0029 - 0.0168 mol/l, and then decreased gradually with increasing C_{ox}.

Figure 4 shows the dependence of the electrical resistivity on C_{ox}. The electrical resistivity increased from 2.5 to 490 Ωcm with increasing C_{ox}. These values were 100 –1000 times higher than that of bulk Fe_3O_4.

Figure 5 shows the dependence of MR ratio on the concentration of $NaNO_2$. The MR ratio increased with increasing C_{ox}, reaching 5.5% at C_{ox} of 0.055 mol/l. The field where resistance took the maximum was extremely close to the coercivity. This suggests that MR of these plated films is associated with spin-dependent intergranular transport. Since the state that magnetic vectors of grains are anti-parallel is strongly dominant at the coercive field, the resistance is thought to take the maximum.

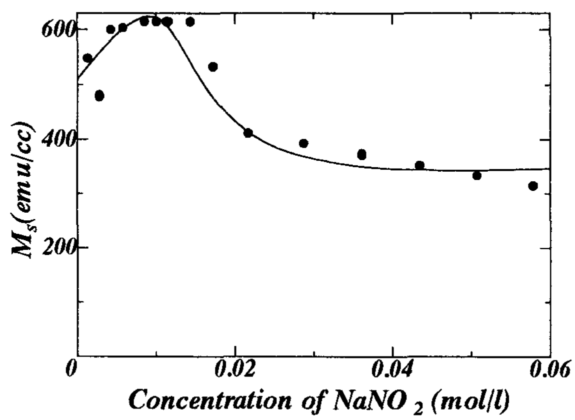


Fig.3 Dependence of saturation magnetization on concentration of $NaNO_2$ in oxidizing solution C_{ox}

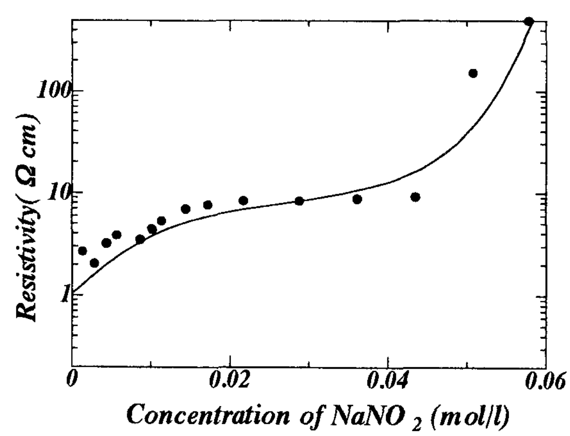


Fig.4 Dependence of electrical resistivity on concentration of $NaNO_2$ in oxidizing solution C_{ox}

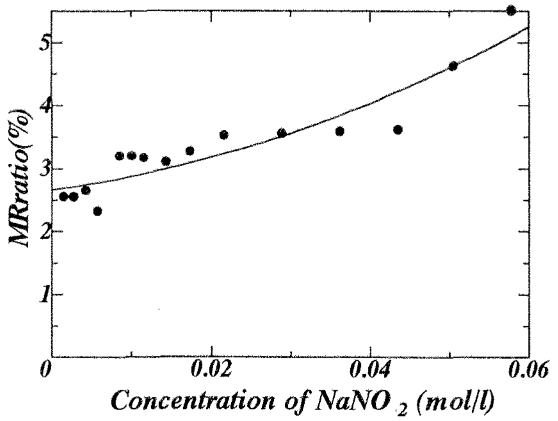
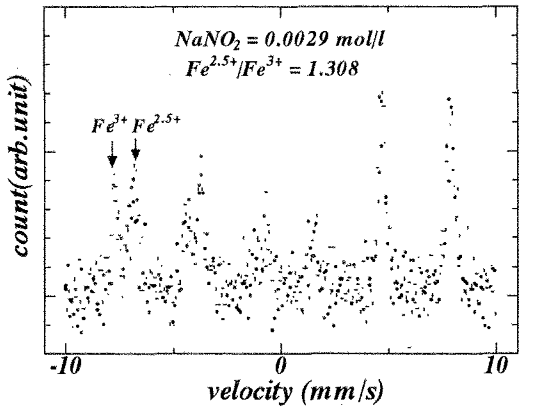
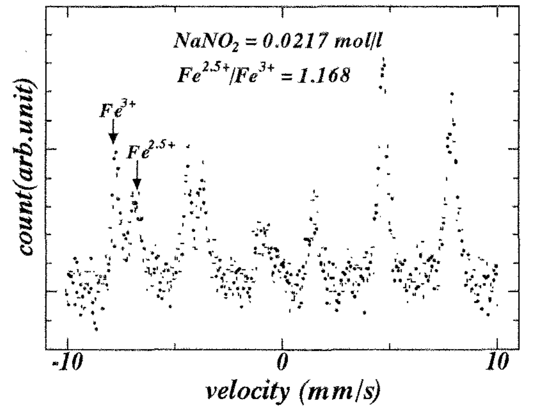


Fig.5 Dependence of MR ratio on concentration of $NaNO_2$ in oxidizing solution C_{ox}



(a) Concentration of $NaNO_2$ = 0.0029 mol/l



(b) Concentration of $NaNO_2$ = 0.0217 mol/l

Fig.6 Mössbauer spectra

Figure 6 shows the Mössbauer spectra of the $Fe_{3-x}O_4$ films deposited at the concentration of $NaNO_2$ of (a) 0.0029mol/l and (b) 0.0217 mol/l. The ratio $Fe^{2.5+}$ in A site to Fe^{3+} in B site decreased from 1.308 to 1.168 when C_{ox} increased from 0.0029 to 0.0217 mol/l. From the theory of the hopping-conduction of electrons between Fe^{2+} ions and Fe^{3+} ions in magnetite films, the electrical resistivity increases with the increase of Fe^{3+} ions. The Mössbauer results agree with the increase in the resistivity with increasing C_{ox} because regions of γ-Fe_2O_3 that is an electrical insulator increased in the films.

Figure 7 shows a SEM cross section of the $Fe_{3-x}O_4$ films. The film exhibits columnar structure.

Taking the dependence of the MR ratio in Fig.5 and this columnar structure into account, the γ-Fe_2O_3 regions with no electrical conductivity existed in the grain boundaries, and the electrical transport and the MR effect were caused by spin-dependent tunneling through these insulating regions between Fe_3O_4 grains.

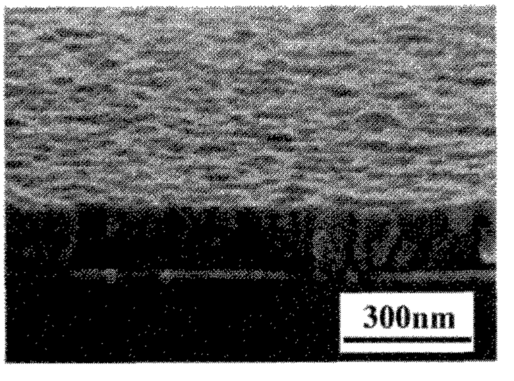


Fig.7 SEM image

4. CONCLUSION

The dependence of magnetic and electrical properties of $Fe_{3-x}O_4$ plated films on the concentration of the oxidizing agent was investigated. While saturation magnetization M_s decreased, the electrical resistivity of magnetite films increased from 2.5 to 490 Ω with increasing the concentration of $NaNO_2$. The maximum value of the MR ratio was 5.5 %. The ratio of $Fe^{2.5+}$ ions in A site to Fe^{3+} ions in B site decreased from 1.308 to 1.168 when the concentration of $NaNO_2$ increased from 0.0029 to 0.0217 mol/l, indicated the increase in insulating regions in the $Fe_{3-x}O_4$ films. Since the films exhibited columnar structure, the magnetoresistance of magnetite films fabricated by the ferrite plating was attributed to spin-dependent tunneling between Fe_3O_4 grains through insulating regions such as, γ-Fe_2O_3, in the grain boundaries.

5. ACKNOWLEGEMENTS

This study has been financially supported by the "Research for the Future" Program, #JSPS-RFTF96R06901, from the Japan Society for the Promotion of Science, and by Kanagawa Academy of Science and Technology Research Grants.

6. REFERENCE

[1]W. J. Gallagher, S.S. P. Parkin, Yu Lu, X. P. Bian, A. Marley, and K. P. Roche, J. Appl. Phys. **81**(8), 3741(1997)

[2]M.Abe, T.Itoh and Y.Tamaura, Thin Solid Films., **216**, 155 (1992)

[3]Y.Kitamoto, M.Zhang, S.Haijima, K.Matsumoto, and M.Abe, J.Phys.Ⅳ., **7**, C1-581(1997)(Proc. ICF 7,1996)

[4]M.Abe,Y.Kitamoto, K.Matsumoto,M.Zhang, and P.Li, IEEETrans.Magn., **33**, 3649 (1997)

(Received December 16, 1999; Accepted May 27, 2000)