phys. stat. sol. (c) **1**, No. 12, 3410–3413 (2004) / **DOI** 10.1002/pssc.200405467

Magnetoresistance and microstructure of the sintered ferrite of the mixture of Fe_3O_4 and Co-ferrite powder

C. Y. Chou[*, 1, 2], **P. C. Kuo**[1, 2], **Y. D. Yao**[3], **T. H. Wu**[1, 2], **S. C. Chen**[1, 2], **A. C. Sun**[1, 2], **C. H. Huang**[1], and **J. W. Chen**[4]

[1] Institute of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan
[2] Center for Nanostorage Research, National Taiwan University, Taipei 106, Taiwan
[3] Institute of Physics, Academia Sinica, Taipei 115, Taiwan
[4] Department of Physics, National Taiwan University, Taipei 106, Taiwan

Received 27 June 2004, accepted 14 October 2004
Published online 20 December 2004

PACS 72.25.-b, 75.47.-m

The Fe_3O_4 powder was mixed with Co-ferrite powder then sintering in argon atmosphere at temperatures between 1000 °C and 1250 °C for 4 hours. Effects of the sintering temperature, microstructure and Co-ferrite content on the magnetoresistance of the sintered ferrite of the mixture powder were investigated. The Co-ferrite content in the sintered ferrite was between 0 mol% and 32.28 mol%. It was found that the Co ions were dispersed uniformly in all sintered samples by the analysis of Co element mapping of the scanning electron microscopy. The maximum magnetoresistance ratio at room temperature is about 7.45% when Co-ferrite content was 4.26 mol% and sintering temperature was 1200 °C.

1 Introduction

Fe_3O_4 is one of the most common oxides which studied over past 50 years due to its unique and interesting magnetotransport properties [1–5]. Recent researchs were focused on the magnetotransport properties of the Fe_3O_4 due to its potential for applications in memory storage devices. The magnetotransport properties in the Fe_3O_4 of different forms including powder, films, and magnetic tunnel junctions with Fe_3O_4 electrodes had been intensively studied [6–8]. However, to get large MR ratio of Fe_3O_4 at room temperature was difficult. In this work, we mixed the Fe_3O_4 powder with Co-ferrite powder then sintering at various temperatures and investigated the effects of sintering temperature on the microstructure and MR ratio of the sintered ferrite.

2 Experimental procedure

The Fe_3O_4 powder was mixed with various amounts of Co-ferrite powder (0 ~ 30 mol%). The mixed powder was compressed into a 10 mm diameter, 1 mm thick pellet under a pressure of 3757 kg/cm^2, and then sintered in argon atmosphere at temperatures between 1000 °C and 1250 °C for 4 hours. Fe^{2+} and Fe^{3+} ions contents of the sintered sample were examined by the chemical titration method. Microstructure and elements mapping of the sintered sample were examined by the scanning electron microscopy. The MR ratio of the sintered sample was measured with the four-probe method at room temperature and the applied magnetic field was parallel to the direction of current. The maximum applied field was 8.8 kOe.

[*] Corresponding author: e-mail: a3150@ms3.hinet.net, Tel.: +886-2-23648881, Fax: +886-2-23634562

Table 1 Co-ferrite content in the mixed powder and sintered sample, and the Fe^{2+} and Fe^{3+} ion contents in the sintered sample.

Co-ferrite content in mixed powder (mol%)	content in sintered sample			
	Co-ferrite (mol%)	Fe_3O_4 (mol%)	Fe^{2+} (at%)	(Fe^{2+}/ $Fe^{2+} + Fe^{3+}$)
0	0	100	27.82	27.82%
2	1.84	98.16	21.60	21.73%
3	4.26	95.74	33.75	34.24%
5	6.06	93.94	18.53	18.91%
10	11.52	88.48	35.18	36.58%
20	19.98	80.02	29.64	31.75%
30	32.28	67.72	37.52	42.04%

3 Results and discussion

Table 1 shows the Co-ferrite content in the mixed powder and sintered sample, and the Fe^{2+} and Fe^{3+} ion contents in the sintered sample. The (Fe^{2+}/total Fe) value of pure Fe_3O_4 is 33 mol%. If the (Fe^{2+}/total Fe) value is lower than 33 mol%, some nonstoichiometric Fe_3O_{4+X} ferrite will form during sintering. This indicated that Fe_3O_4 and $CoFe_2O_4$ phases coexisted with Fe_2O_3 in the sintered sample. When the (Fe^{2+}/total Fe) value is higher than 33 mol%, some nonstoichiometric phase of $CoFe_2O_{4-X}$ ferrite will

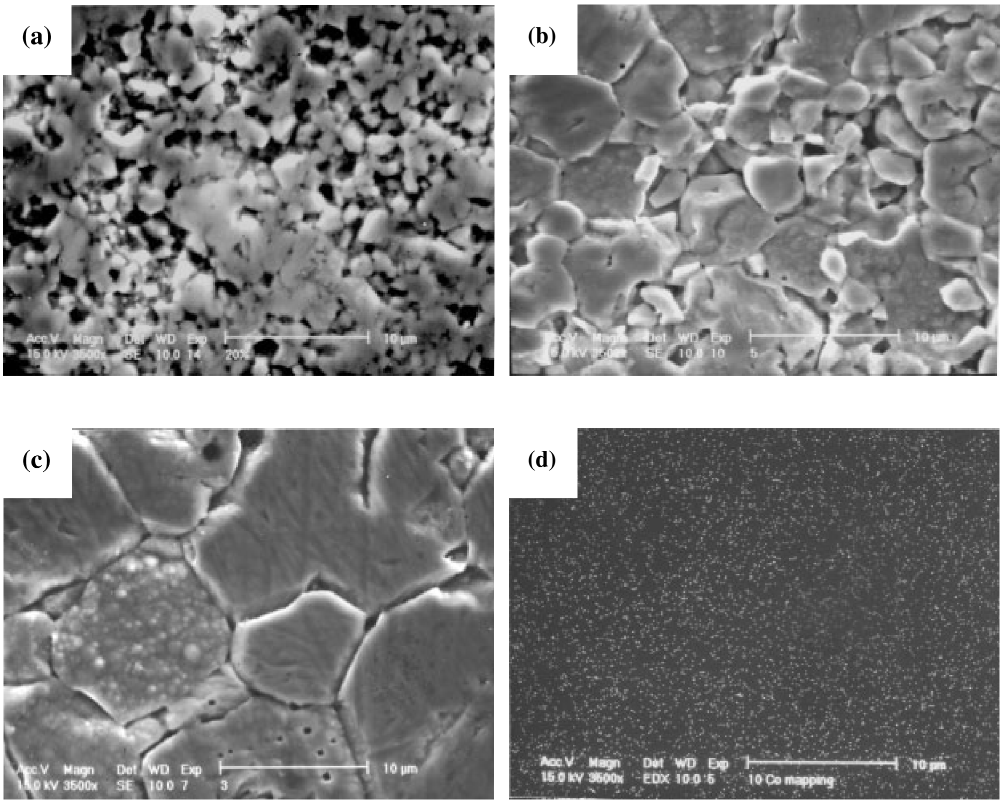

Fig. 1 SEM micrographs of the sintered samples with various sintering temperature at (a) 1000 °C, (b) 1100 °C and (c) 1200 °C, and (d) is the Co element mapping of (c).

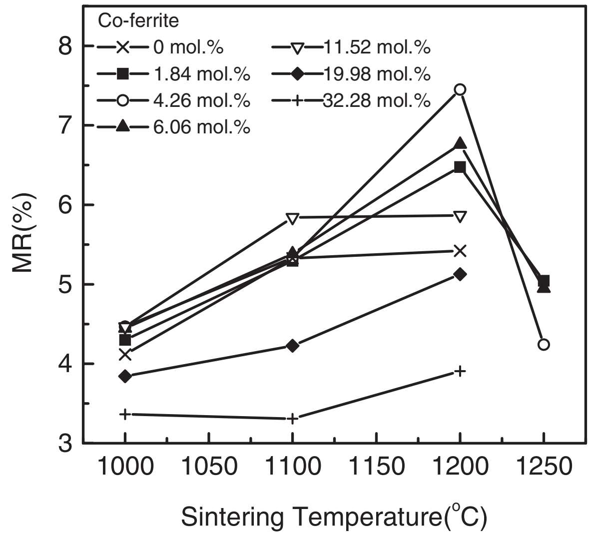

Fig. 2 Variation of the MR ratio with sintering temperature of sintered samples with various Co-ferrite contents.

form in the sintered sample. For pure Fe_3O_4, the (Fe^{2+}/total Fe) value is lower than 33 mol% after sintering, as shown in Table 1. This means that some Fe_3O_4 were oxidized to Fe_2O_3 during sintering.

Figure 1(a), 1(b), and 1(c) show the SEM micrographs of the sintered samples with different sintering temperatures and Fig. 1(d) is the Co element mapping of Fig. 1(c). The Co-ferrite content is 6.06 mol% for all samples. We can see that the average grain size and densification of the samples have been increasing with sintering temperature. The average grain sizes of Figs. 1(a), 1(b), and 1(c) are about 1.3 µm, 6.5 µm, and 12.5 µm respectively. From Fig. 1(d), it can be seen that the Co ions disperse uniformly in the sintered sample. This means that the Co-ferrite is uniformly dispersed in the sintered sample.

Figure 2 shows the variations of the MR ratio with sintering temperature of the sintered samples with different Co-ferrite contents at room temperature. We can see that the maximum MR ratio is obtained around 1200 °C for all samples. The maximum MR ratio of about 7.45% can be obtained after sintering at 1200 °C as the Co-ferrite content is 4.26 mol%. The MR curve of this sintered sample is shown in Fig. 3. Negative MR has been observed at 8.8 kOe.

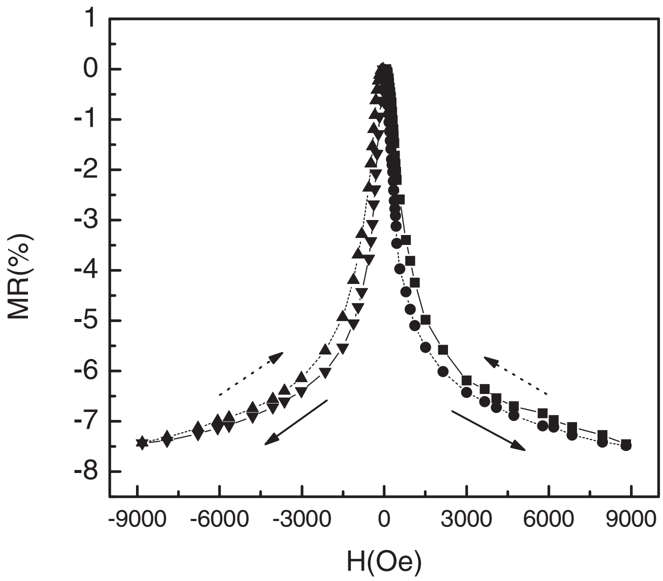

Fig. 3 MR curve of this sintered sample with 4.26 mol% Co-ferrite.

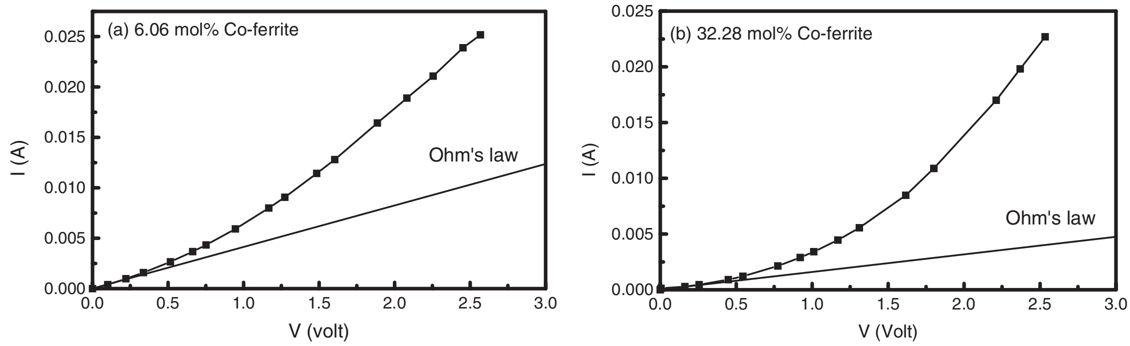

Fig. 4 *I–V* curves of the sintered samples with (a) 6.06 mol%, and (b) 32.28 mol% Co-ferrite.

In Fig. 2, the lower MR ratio of the sample sintered below 1200 °C is related to more pores in the sample, as shown in Fig. 1. As the sintering temperature is higher than 1200 °C, the decrease of MR ratio is due to the larger grain size. The sintered samples with more pores or larger grain sizes both will reduce the spin-dependent interfacial scattering and exhibit the lower MR ratio [9].

Figure 4(a) and (b) show the current (*I*) versus voltage (*V*) curves of the sintered samples with 6.06 mol% and 32.28 mol% Co ferrite respectively. These two *I–V* curves are deviated from Ohm's law as the voltage is higher than 0.3 Volt. Both of them show nonlinear relationship. This suggests that the magnetoresistance mechanisms in these sintered samples are the spin-polarized tunneling effect [10] where the electron flow through insulating barrier of Fe_2O_3, $CoFe_2O_4$, or $CoFe_2O_{4-X}$.

4 Conclusions

The effects of the Co-ferrite content and sintering temperature on the magnetoresistance of the sintered ferrite of the mixture of Fe_3O_4 and Co-ferrite powder were investigated. The grain size of sintered samples is increased but number of pores is decreased with increasing sintering temperature. The electron transport in the sintered samples is a spin-polarized tunneling effect. The maximum MR ratio is about 7.45% at room temperature.

Acknowledgments This work was supported by the National Science Council and Ministry of Economic Affairs of Taiwan through Grant No. NSC 91-2216-E 002-031 and 93-EC-17-A-08-S1-0006, respectively.

References

[1] C. A. Domenicall, Phys. Rev. **78**, 458 (1950).
[2] B. A. Calhoun, Phys. Rev. **94**, 1577 (1954).
[3] J. S.-Y. Feng, R. D. Pashley, and M. A. Nicolet, J. Phys. C **8**, 1010 (1975).
[4] V. V. Gridin, G. R. Hearne, and J. M. Honig, Phys. Rev. B **53**, 15518 (1996).
[5] T. Furubayashi, J. Appl. Phys. **93**, 8026 (2003).
[6] G. Q. Gong, A. Gupta, G. Xiao, W. Qian, and V. P. Dravit, Phys. Rev. B **56**, 5096 (1997).
[7] J. M. D. Coey, A. E. Berkowitz, L. Balcells, F. F. Putris, and F. T. Parker, Appl. Phys. Lett. **72**, 734 (1998).
[8] W. Kim, K. Kawaguchi, N. Koshizaki, M. Sohma, and T. Matsumoto, J. Appl. Phys. **93**, 8032 (2003).
[9] C. T. Lie, P. C. Kuo, A. C. Sun, C. Y. Chou, S. C. Chen, I. J. Chang, T. H. Wu, and J. W. Chen, IEEE Trans. Magn. **39**, 2800 (2003).
[10] C. L. Platt, B. Dieny, and A. E. Berkowitz, J. Appl. Phys. **81**, 5523 (1997).