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Room Temperature Magneto-Resistance of Fe_3O_4/Ag Granular System

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Abstract

Magneto-resistances of sintered mixture of Fe_3O_4 and Ag or Ag_2O were measured at room temperature (RT). The samples including large Fe_3O_4 and Ag grains showed at most −1% of MR ratios, which had the tendency to disappear at larger Ag content than the percolation threshold of Ag. In the samples with small Fe_3O_4 and Ag grains, three times larger negative MR ratios were observed. For these series, we expected the large RT-MR ratio by physical and chemical stabilization of Fe_3O_4 nano-contacts and the spin-polarized conduction through thin metallic Ag at the intergrain parts between Fe_3O_4-grains. Consequently, Fe_3O_4/Ag/Fe_3O_4 paths were effective for the GMR by the conduction of spin polarized electrons from Fe_3O_4 grains.

Key Words : Fe_3O_4, Ag , Ag_2O, resistivity, magneto-resistance

INTRODUCTION

The magnetite (Fe_3O_4) has been known as the half metal with the spin polarized conduction electrons in the 3d minority spin bands [1,2]. In the recent years, the large negative magneto-resistance (MR) effect in low field was expected, and many experimental results were reported for the Fe_3O_4 thin films [3-10]. However only small negative MR ratio (*MRR*) of about −1% have been observed for polycrystalline and single crystal thin films at room temperature (RT) under the magnetic field of 1 T. As for the TMR effects, the RT-*MRR* of −0.5 % at 0.15 T and −7.4 ~ −6 % at 0.9 T were reported for the Fe_3O_4 films with the tunnel barriers of MgO [11] and γ-Fe_2O_3 [12-13], respectively. The Fe_3O_4 thin films in which γ-Fe_2O_3 grains were embedded [14] showed the RT-*MRR* of −1.5 % at 0.3 T. For the bulk granular magnetite system, the $Zn_{0.41}Fe_{2.59}O_4$ with α-Fe_2O_3 grain boundaries [15] had an extremely large −61 % of RT-*MRR* at 1 T, but it was disappeared above 320 K. On the other hand, the $ZnFe_2O_4$ tunnel barriers [16] gave −7 % of RT-*MRR* at 0.8 T. The RT-*MRR* of −75 % at 8 mT was a remarkable result for nano-contacted Fe_3O_4 particles [17], where the electron pressure to the pinned magnetic domain wall, namely, the *magnetic balloon effect*, was important. However it was difficult to keep and control the nano-contacted areas under variable disturbances.

In the present work, the RT-*MRR* effects by Ag grains at the boundaries of large or small Fe_3O_4 grains. We expected that the Ag grains made the contacts among Fe_3O_4 grains being stable mechanically and chemically, and supplied well conduction paths for the polarized electrons from Fe_3O_4 grains.

EXPERIMENTAL RESULTS

X-ray diffraction

The Fe_3O_4/Ag samples with large Fe_3O_4 grains were sintered from the powder mixtures of commercial Fe_3O_4 and Ag at 773 K in the atmosphere of H_2 : Ar = 0.02 : 0.98. Powder Cu$K\alpha$ x-ray diffraction patterns were depicted in Figure 1 for the (311) main peak of Fe_3O_4 and (111) one of Ag. Here x is defined as the Ag volume fraction of $V_{Ag}/(V_{Fe3O4}+V_{Ag})$. From the half widths of these peaks, the grain sizes of Fe_3O_4 and Ag were estimated as to be larger than 20 nm. These samples with x from 0.05 to 0.4 were called as the samples B.

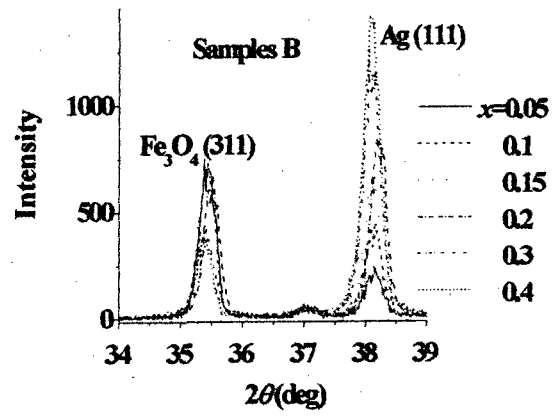

Figure 1: Main peaks of Fe_3O_4 and Ag in samples B.

In addition to the samples B, the three kinds of samples with small grains were prepared. The samples I and II were made from the powder mixtures of Fe_3O_4 and commercial Ag and Ag_2O, respectively, where the Fe_3O_4 precursor was precipitated by mixing $FeCl_2 \cdot 4H_2O$, $2FeCl_3 \cdot 6H_2O$ and $8NH_3$ aqueous solutions. On the other hand, samples III were directly precipitated by mixing of

the aqueous solutions of $FeCl_2 \cdot 4H_2O$ and $2FeCl_3 \cdot 6H_2O$, and NH_4OH solutions of Ag_2O, though the possible molar ratio of Ag was restricted below 0.4 (x=0.13). All of the samples I-III were sintered at 473 K in the Ar atmosphere with 1.5% H_2 gas.

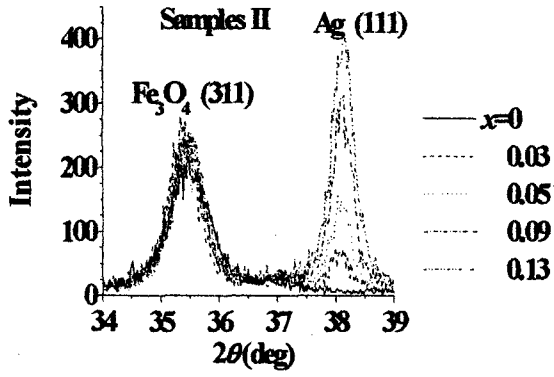

Figure 2: Main peaks of Fe_3O_4 and Ag in samples II.

The x-ray diffraction results of samples II were given in Figure 2. The x also means the volume fraction of Ag in each sample. The half widths of diffraction peaks showed that the grain sizes of Fe_3O_4 and Ag were about 10 nm and 20 nm, respectively. The samples I and III showed nearly same grain sizes of Fe_3O_4 and Ag as those in samples II. Roughly speaking, samples B have the bulk like natures of Fe_3O_4 in comparison to samples I-III with 10 nm-class Fe_3O_4 grains, though the precise grain sizes should be determined from TEM images.

Magneto-resistance

Samples B: The field dependences of electrical resistances $R(H)$ were measured by 4-terminals method under the field of $\mu_0 H$ from −1 T to 1 T at room temperature (RT) of 300 K. The magneto-resistance ratios (MRR) of samples B were given in Figure 3. Here the MRR was defined by $[R(H)-R_{max}]/R_{max}$, where R_{max} is the maximum resistance near 0 field. All of the samples showed no hysteretic MR with increasing and decreasing H due to the smallness of coercive force H_c. In the x-region below 0.15, the $|MRR|$ decreased with increasing x. The maximum $|MRR|$ at 1T was −1.4 % for x = 0.05. In x > 0.2, the $|MRR|$ began to decrease with increasing x and disappeared at x = 0.4.

The MRR at 1 T and the resistivity ρ_0 at 0 field were plotted in Figure 4 for samples B. The ρ_0 was nearly constant in x < 0.2, and the $|MRR|$ had an anomalous peak at about x = 0.2. Then the ρ_0 and $|MRR|$ rapidly decreased in x > 0.2. These results can be interpreted as the percolation behavior of conducting Ag paths with the percolation threshold x_c of about 0.2–0.3. The similar results were reported for the γ -Fe_2O_3/Ag granular nano-composites [18], where the field dependent electron hopping rate from Fe^{2+} to Fe^{3+} was discussed. Here we also assume that the intrinsic MR by electron hopping through the Fe_3O_4 grains should be dominant in the samples B at room temperature.

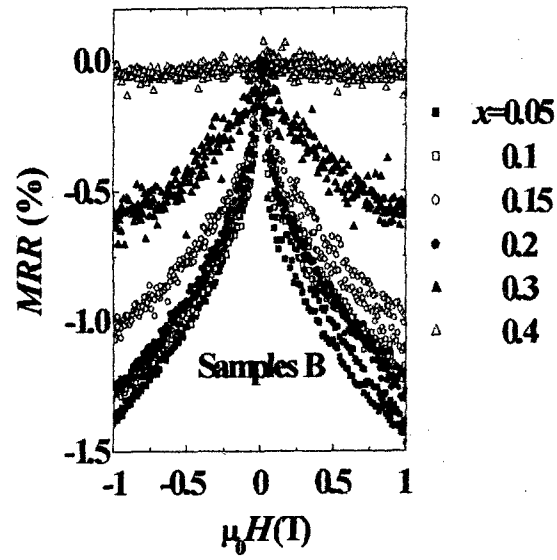

Figure 3: MR ratios at 300 K of samples B.

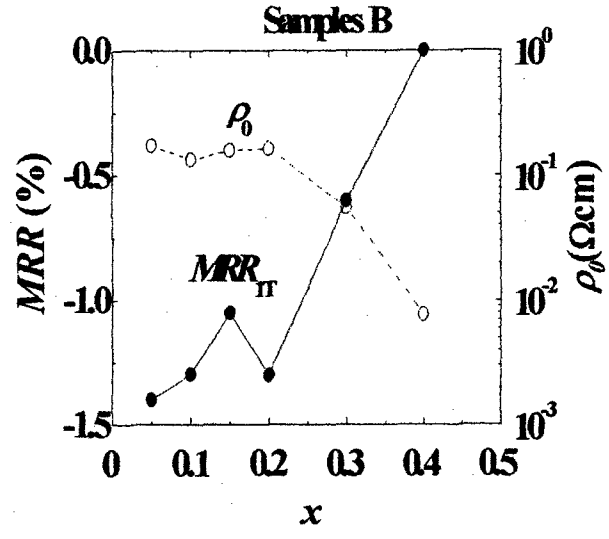

Figure 4: MR ratios at 1 T and resistivities ρ_0 at 0 field of samples B.

Samples I - III: For these samples, we expected the large RT-MR by the stabilization of Fe_3O_4 nano-contacts areas by metallic Ag nano-particle at the inter-grain parts between Fe_3O_4 nano-grains. The MRR at room temperature of samples II were given in Figure 5. It should be noted that samples II were prepared by sintering the mixture of Fe_3O_4 and Ag_2O powders. Since the precursor (x=0) Fe_3O_4 grains of present series have about 10 nm diameter, the nano- contacted areas between them have a possibility to induce relatively high MRR [17]. In 0<x<0.05, the $|MRR|$ decreased with Ag content. Then the $|MRR|$ began to increase with increasing x above

0.05 and reached 3.8 % at x = 0.13. This value of |*MRR*| is larger than that of precursor Fe_3O_4 of x = 0 and samples B. In samples B, we can assume that the contacted area between Fe_3O_4 grains is much larger than that in samples II. Therefore it was concluded that the stabilization of nano-contacted area is effective to realize the GMR effect in the Fe_3O_4 system.

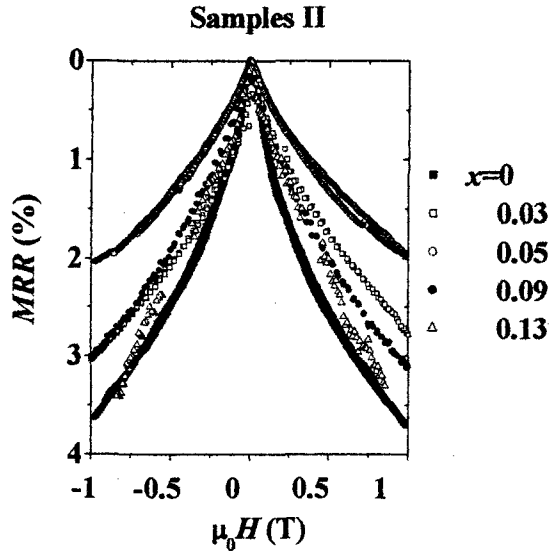

Figure 5: MR ratios at 1 T and 0-field resistivity ρ_0 of samples II.

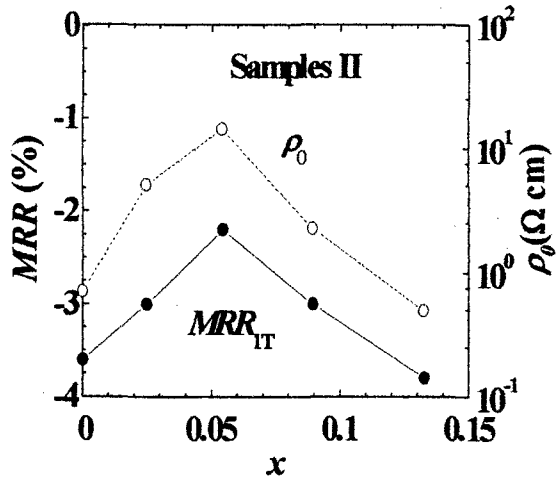

Figure 6: MR ratios at 1 T and 0-field resistivity ρ_0 of samples II.

The *MRR* at 1 T and the resistivity ρ_0 at 0 field were plotted in Figure 6 for samples II. The ρ_0 increased with increasing x in x < 0.05. At x = 0.05, the ρ_0 had a maximum value of about 16 Ω cm and |*MRR*| became minimum value of 2.2%. Then the ρ_0 decreased and the |*MRR*| increased with increasing x above 0.05. Though the x-value, at which the *MRR* has an anomaly, was different, the behaviors of *MRR* substantially agree with those of samples B as shown in Figures 7.

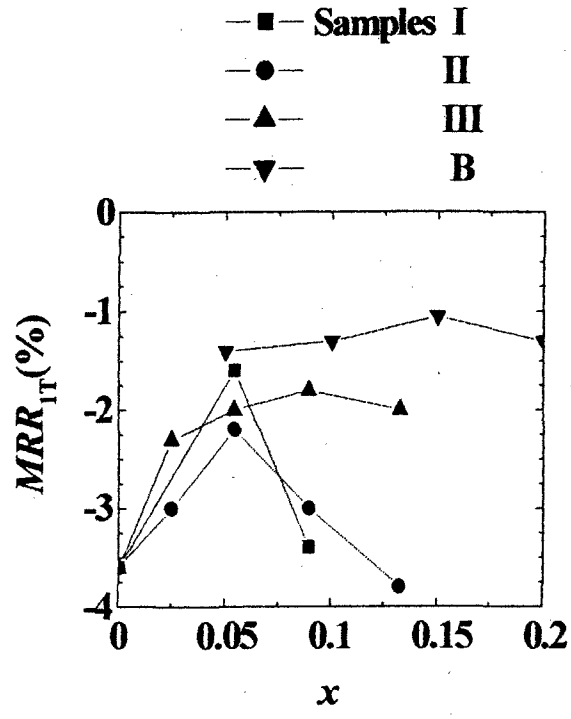

Figure 7: MR ratios at 1T of samples I-III and B.

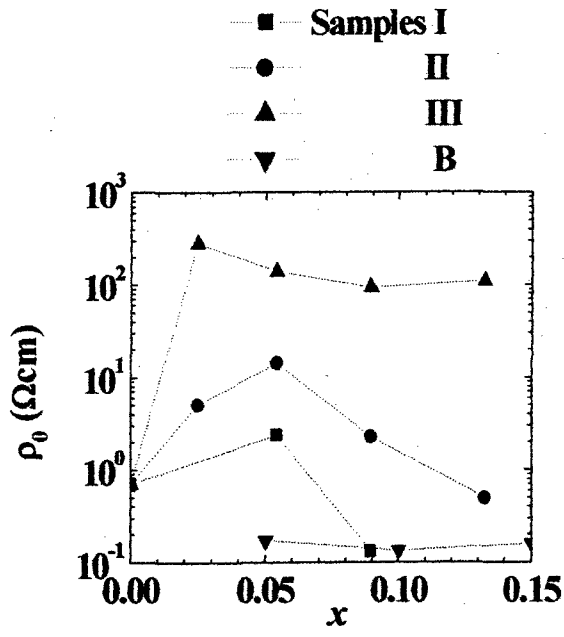

Figure 8 : 0-field resistivity ρ_0 of samples I-III and B.

There is a problem of increasing ρ_0 and decreasing $|MRR|$ in the region of $0 < x < 0.05$ as shown in Figure 6. In the sintering process, Ag_2O was reduced to Ag by hydrogen gas, and Fe_3O_4 might be partly oxidized to γ-Fe_2O_3 by residual oxygen from the reaction of $Ag_2O \rightarrow 2Ag+(1/2)O_2$. Instead of the spin polarized electron conduction, the hopping conduction of electrons from Fe^{2+} to Fe^{3+} ions are arose by the Fe_3O_4/γ-Fe_2O_3 /Ag/γ-Fe_2O_3/Fe_3O_4 paths, which give the relatively high resistivity and low $|MRR|$. However, the GMR like behaviors of decreasing ρ_0 and increasing $|MRR|$ in the high x region above 0.05, which looks like that the conduction of spin polarized electrons from Fe_3O_4 grains becomes dominant, can not be explained by the above consideration. The analogous situations also exist for samples I and III as shown in Figuress 7 and 8.

Here we consider that the increasing ρ_0 and decreasing $|MRR|$ in the region of $0 < x < 0.05$ of samples II, may be dominated by the contact resistance between Fe_3O_4 grains. In low Ag concentration region, the directly contacted area of Fe_3O_4 particles may be reduced by slight Ag-doping. When the x increases above 0.05, ρ_0 decreases and $|MRR|$ increases by the increasing number of Fe_3O_4/Ag/Fe_3O_4 connections, which induce the GMR behavior. The relatively high x-value of 0.15, at which the *MRR* has an anomaly in samples B, can be explained by the difference of the particle size of Fe_3O_4, because the large Fe_3O_4 particles have large contacted areas against the increasing of Ag concentration.

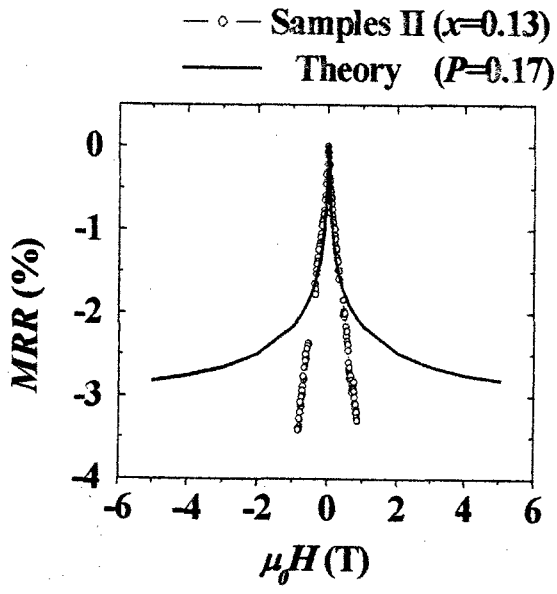

Figure 9 : *MRR* of samples II (x=0.13) and theoretical curve at polarization of P= 0.17.

In Figure 9, the theoretical curve of *MRR* was given for the conduction electrons with polarization P of 0.17. The theoretical *MRR*-values were estimated from $-P^2m^2/(1+P^2m^2)$, where $m=M(H)/M_s$ [8]. The $M(H)$ is the field dependent magnetization, and the M_s is the saturated one of samples II (x=0.13). The *MRR* of this sample showed the TMR like behavior in low field. But, even in the high field region, the *MRR* of this sample becomes linear in field. The investigation for higher x is interesting and now in progress.

ACKNOWLEDGEMENT

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