Magneto-resistance of Nano-Fe₃O₄/Ag Granular System

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Four kinds of Fe₃O₄/Ag granular systems were prepared from sintered mixtures of Fe₃O₄ and Ag or Ag₂O. Magneto-resistances (MRs) were measured at room temperature for samples with Ag volume fraction x between 0 and 0.4. Samples including relatively large Fe₃O₄ grains showed -1% to -1.4% room temperature MR ratios (MRR) at 1 T. On the other hand, samples including Fe₃O₄ nano-particles showed large negative room temperature MRR of about -4% to -5% at 1 T near the percolation threshold of $x_c \sim 0.2$. It was suggested that Fe₃O₄/Ag/Fe₃O₄ paths were effective for the large $|MRR|$ by the elastic conduction of spin-polarized electrons between Fe₃O₄ nano-particles. Possibility of spin accumulation in small Ag particles was also shown for this system.

Key words: half-metallic oxide, magnetically ordered materials, nano-granular system, magneto-resistance

1. Introduction

Half metallic magnetite (Fe₃O₄) junctions with -100 % spin polarization of conduction d electrons have been expected to realize the new oxide magnetic storage devices such as magnetic random access memory (MRAM) by large negative magneto-resistance (MR). In the thin films of Fe₃O₄, negative room temperature MR-ratios (MRR) of about -1% at 1 T have been reported for polycrystalline and single crystalline samples [1-8]. These MRR -results were interpreted as one of the intrinsic effects by the electron hopping between Fe²⁺ and Fe³⁺ ions. The large MR effect can be anticipated by the tunneling MR (TMR) through the thin insulating barriers between Fe₃O₄-grains. Relatively high $|MRR|$ -results about 5 % at 1 T have been reported for room temperature (RT) TMR in Fe₃O₄ films with oxide barriers such as MgO [9], γ -Fe₂O₃ [10-12] and ZnFe₂O₄ [13]. The MRR was defined here as $[\rho(H) - \rho_{\max}] / \rho_{\max}$, where ρ was the resistivity and $\rho_{\max}$ was the maximum one in low magnetic field region. In the bulk granular system, the Zn_{0.41}Fe_{2.59}O₄ with α -Fe₂O₃ grain boundaries [14] showed a largely negative RT- MRR of -61 % at 1 T, though it disappeared above 320 K. For nano-contacted Fe₃O₄ particles [15], the RT- MRR of -75 % at 8 mT was reported, but the nano-contacting parts were unstable against a small external turbulence.

In the present work, RT-MR effects in Fe₃O₄/Ag nano-granular systems were investigated, expecting the large RT- MRR with well reproducibility by physical and chemical stabilization of the conduction paths by the metallic Ag for the polarized conduction electrons among Fe₃O₄ nano-grains.

2. Sample preparation

Four kinds of samples with Fe₃O₄ nano-grains were prepared by the following procedures. First, the precursor of Fe₃O₄ nano-particles were precipitated by mixing aqueous solution of FeCl₂·4H₂O, 2FeCl₃·6H₂O and aqueous ammonia. Then the obtained Fe₃O₄ nano-particles were mixed with commercial Ag (samples I) or Ag₂O (samples II) powders. They were sintered at 473 K in the Ar atmosphere with 1.5% H₂ gas. The prepared samples had the Ag volume fraction of $x = V_{\text{Ag}} / (V_{\text{Fe}_3\text{O}_4} + V_{\text{Ag}})$ between 0 and 0.35. On the other hand, the samples III were directly precipitated by mixing the aqueous solution of FeCl₂·4H₂O, 2FeCl₃·6H₂O and the aqueous ammonium solution of Ag₂O, but solvable Ag volume fraction x was limited to 0.13. At x larger than 0.13, the Ag₂O powder particles partially deposited in the mixed solution. Therefore, for samples III, only the precipitates in $0 < x < 0.13$ were sintered under the same condition as former samples I and II. The samples C were obtained from the sintered powder mixtures of commercial Fe₃O₄ and Ag at 773 K in the atmosphere of H₂ : Ar = 0.02 : 0.98.

Fig. 1 XRD main peaks of (311) for Fe₃O₄ and (111) for Ag in samples II for values of x between 0 and 0.35.

The x-ray diffraction (XRD) patterns of samples II

were given in Fig. 1 for the (311) main peak of Fe_3O_4 and (111) one of Ag. From the half widths of diffraction peaks, the mean particle diameters d were estimated from Scherrer's formula for Fe_3O_4 ($d_{\text{Fe}_3\text{O}_4}$) and Ag (d_{Ag}). The x dependences of $d_{\text{Fe}_3\text{O}_4}$ and d_{Ag} were shown in Fig. 2.

In samples C, $d_{\text{Fe}_3\text{O}_4}$ and d_{Ag} were nearly constant at about 30 nm, which was the same order to the precursor of commercial powders, though the agglomeration of the grains can not be excluded in them. The $d_{\text{Fe}_3\text{O}_4}$ -values of samples I were 15 ~ 20 nm in $x < 0.1$ and about 30 nm in $x > 0.1$. The d_{Ag} -values were 20~25 nm in $x < 0.1$ and 30 ~ 35 nm in $x > 0.1$.

Fig. 2 x -dependences of the particle diameters of $d_{\text{Fe}_3\text{O}_4}$ and d_{Ag} , determined from XRD results.

The $d_{\text{Fe}_3\text{O}_4}$ -values of samples II were 10 ~ 15 nm, and the d_{Ag} -values were 15 ~ 25 nm in $x < 0.4$. These results mean that the samples II formed a good nano-particle system of Fe_3O_4 and Ag in whole x -region between 0 and 0.4, though the samples III included smaller Fe_3O_4 particles in $0 < x < 0.13$. Therefore we mainly paid attention to the MR-behaviors of samples II as one of the typical nano- Fe_3O_4 and Ag granular systems.

The transmission electron microscopy (TEM) images of sample II at $x = 0.05$ and 0.19 were shown in Figs. 3(a) and (b), where we used a crushing method to prepare the electron microscopy specimens. Some samples were ground under CCl_4 , then, dispersed on carbon coated micro-grids. Specimens were examined with Hitachi HF-3000S field-emission analytical TEM operating at 300 kV.

Since the very dense Debye rings were obtained, it was

very difficult to choose a ring of Ag- or Fe_3O_4 -phase by an objective aperture in dark-field imaging. TEM contrast might be affected also by crystal orientation and thickness. Therefore we judged that it was difficult to obtain a good image-formation by dark field, and qualitative analysis of the grain was performed by energy dispersive x-ray spectroscopy (EDX). The EDX spectrum showed that the most darkened parts corresponded to Ag-particles, and the other to Fe_3O_4 -particles. As shown in Fig. 3(a), the Ag-particles of $d \sim 20$ nm are isolated in the connected Fe_3O_4 -particles of $d = 10 \sim 20$ nm at $x = 0.05$. At $x = 0.19$, larger or agglomerated Ag-particles began to appear, as shown in Fig. 3(b). These results were not contradictory to the above XRD results.

(a)

(b)

Fig. 3 TEM images of samples II for $x = 0.05$ (a) and 0.19 (b).

3. Results and discussion

MR measurements were done by usual 4-terminals method in DC-field between -1 T and 1 T. To avoid the nonlinear effect between voltage V and current I , resistance R was measured at constant current I of 1 mA. Room temperature MRR -curves of samples II are partly shown in Fig. 4. They show slight hysteresis due to the small coercive force of H_c . The MRR absolute values

Fig. 4 Field dependences of the room-temperature MR ratios (MRR) of samples II.

Fig. 5 x -dependences of the MR ratios (MRR) at 300 K and 1 T for all of the samples.

Fig. 6 x -dependences of the 0-field resistivity ρ_0 at 300 K for all of the samples.

sharply increase in low field region and show no saturation at ± 1 T, which correspond to the magnetization curves up to 1 T by SQUID magnetometer.

In Fig. 5, MRR -values at 300 K and 1 T were plotted for all of the samples. It should be noted that the $|MRR|$ of samples I-III were commonly larger than the highest $|MRR|$ -value of 1.4 % in samples C. The $|MRR|$ of samples II reaches maximum value of 5.0 % at $x = 0.19$. For the samples I, largest $|MRR|$ of 3.9 % was also observed at $x = 0.19$. Both of maximum $|MRR|$ -values are larger than the $|MRR|$ of 3.5 % in the nano- Fe_3O_4 sample of $x = 0$. These results may show the physical and chemical stabilization of intermediate conduction paths between Fe_3O_4 nano-particles.

The ρ_0 of room temperature resistivity at 0 field were shown in Fig. 6 for all of the samples. ρ_0 is nearly equal to the maximum resistivity for each sample because of the very small hysteresis in the ρ - H curves. For samples II, $|MRR|$ and ρ_0 decreases and increases with increasing x in $x < 0.05$, and becomes minimum and maximum at $x = 0.05$, respectively. Above $x = 0.05$, $|MRR|$ increases and ρ_0 decreases with increasing of x , indicating visible peak at $x = 0.19$. Above $x = 0.19$, $|MRR|$ and ρ_0 decrease monotonously according to Ag-content. Samples I showed nearly the same behaviors with samples II. As for the samples III in $0 < x < 0.13$, minimum $|MRR|$ and maximum ρ_0 appeared at $x = 0.08$ and $x = 0.02$, respectively.

In the samples C, ρ_0 was nearly constant in $x < 0.2$, and rapidly decreases in $x > 0.2$. The $|MRR|$ decreases with increasing x below 0.2. At $x \sim 0.2$, $|MRR|$ had an weak peak value of 1.3 %, when ρ_0 also showed a broad peak. In $x > 0.2$, both of $|MRR|$ and ρ_0 began to decrease with increasing x . The weak peaks of $|MRR|$ near $x = 0.2$ are also found for samples I and II.

Since the linear relation between voltage V and current I was confirmed in the resistivity measurement for $x > 0.2$, the above experimental results around $x = 0.2$ can be interpreted as the percolation behavior of Ag conducting paths with the percolation threshold x_c of about 0.2. Similar results of peak in $|MRR|$ just below x_c were reported for the γ - Fe_2O_3 /Ag granular nano-composites [16]. Ordinary, the percolation problems were considered for the system including two kinds of conductive spheres with same diameter. Therefore it is not easy to apply the numerical results of percolation theory [17,18] to the present system with different diameters of $d_{Fe_3O_4}$ and d_{Ag} . However the x_c -value of 0.2 might reflect the theoretical percolation threshold of 0.198 obtained from the site model calculation for the closed packed fcc lattice [19].

Here we discuss the $|MRR|$ - and ρ_0 -behaviors of samples I, II and III at x around 0.05, where the $|MRR|$ and ρ_0 become minimum and maximum, respectively. One of the possibility to explain the above results is the spin injection [20] into the Ag nano-particles. In a low field region, the magnetic moments in Fe_3O_4 particles are randomly oriented and spin injection to Ag particles dose

not occur. However, in a high field, magnetic moments are aligned along the external field and the spin polarized electrons are injected into Ag nano-particles. If d_{Ag} is less than the spin diffusion length d_s , injected electron spins are accumulated in the Ag conducting paths. These non-equilibrium spins impede the spin current into Ag particles. Then resistivity increases by magnetic field, and the positive magneto-resistance effect appears. Actually, such an effect has been observed in Fe_3O_4 -Ag composite films [21] when d_{Ag} is nearly equal to d_s . If $d_{Ag} > d_s$, the orientation of injected spins are relaxed in the middle of the Ag path. When $d_{Ag} < d_s$, accumulated non-equilibrium magnetization in Ag particles would be fluctuated and diminished by thermal energy. Therefore, if the condition of $d_{Ag} \sim d_s$ is satisfied at $x \sim 0.05$, the absolute value of "negative" MRR may be partially reduced by the positive MRR by spin accumulation. The increasing of ρ_0 in 0-field might be also due to the spin injection from the Fe_3O_4 particles in the remanent magnetic state.

No anomalous behaviors of ρ_0 and $|MRR|$ of samples C near $x = 0.05$ can be explained by larger $d_{Fe_3O_4}$ than d_{Ag} which maintains directly conducting paths of Fe_3O_4/Fe_3O_4 . Even if the Ag content increases up to about $x=0.2$, small Ag particles may be incapable of connecting large Fe_3O_4 particles due to the large interstices. On the other hand, in samples I-III, the relation of $d_{Fe_3O_4} < d_{Ag}$ holds below $x = 0.4$, except for samples I above $x = 0.1$. Then the direct connection between Fe_3O_4 - and Ag-particles may be dominant due to the filling of interstices by large or agglomerated Ag particles as shown in Fig.3. Now the theoretical investigation of the site percolation problem may be important for the mixed system with different diameters of conductive particles to explain the MR- and ρ_0 -behaviors in detail.

4. Conclusion

Room temperature magneto-resistances were measured and discussed for the four kinds of Fe_3O_4/Ag granular systems. Most of the systems commonly showed weak peaks of magneto-resistance ratio $|MRR|$ and 0-field resistivity ρ_0 near the percolation threshold x_c of about 0.2. The maximum $|MRR|$ of about 5 %, which is fairly high value for the granular MR of Fe_3O_4 , was observed for nano- Fe_3O_4/Ag system prepared by sintering the mixture of Fe_3O_4 and Ag_2O (samples II). Meanwhile the possibilities of spin injection from Fe_3O_4 nano-particles and spin accumulation in Ag particles were suggested for the samples including Fe_3O_4 nano-particles (samples I, II and III) at x around 0.05.

It was also revealed that the site percolation problem for the mixed system, including two kinds of conductive particles with different diameters, is important to explain the MRR and ρ_0 behaviors in the present granular systems.

In the Fe_3O_4/Ag nano-particle system, the MR behavior near Verwey transition temperature $T_v \sim 120$ K is another interesting problem. The $|MRR|$ experiments near T_v are now in progress for the present system and shall be reported elsewhere.

Acknowledgment The present work was financially supported by Takahashi Industrial and Economic Research Foundation. The TEM research was also supported by Nano- technology Support Project from the Ministry of Education, Science, Sports and Culture, Japan.

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Received September 30, 2004 ; Accepted January 14, 2005