Mössbauer Studies Of Fe-Pb-O Granular Films With Enhanced Tunneling Magnetoresistance Effect

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***ABSTRACT*-- From our previous studies, it has been found that the Fe-Pb-O granular films which have been adequately annealed exhibit an enhanced tunneling magnetoresistance effect(TMR). The TMR effect is about 10% at room temperature, which can be claimed as the maximum value ever detected so far. In this report the TMR effect of Fe-Pb-O granular films from different annealing time have been investigated. The Mössbauer spectrometer was used to collect the information of Fe magnetic microstructure. It has been found that the tunneling barrier from the magnetic compound formed between α-Fe_2O_3 and PbO plays an important role in obtaining large TMR effect. And the non-magnetic Fe-Pb-O compounds which exist on the surface of iron granules as a thin layer and grow with annealng time seem to decrease TMR effect.**

I. INTRODUCTION

The tunneling-type magneto-resistance effect (TMR) has attracted recent attention. It not only contains rich challenging research topics but also provides many potential applications. This effect can be used in magnetic field sensor and can also possibly be used in magnetic random access memory(MRAM) in the near future. It was first observed in Fe/Gd/Co junctions where conduction electrons tunnel through an insulating layer[1]. Later on this phenomenon has been found in several other junctions such as $Fe/Al_2O_3/Fe$ and $Fe/Al_2O_3/Co$[2]. The spin-dependent tunneling is believed to be responsible for the TMR phenomenon. More recently it has been realized that TMR is not limited to the trilayer junction structure. It can also be observed in the granular solids with the ultrafine magnetic particles in the insulating or semiconductor matrix[3, 4]. Essentially the granular films are much easier to prepare than the trilayer junctions and $\Delta\rho$ can be as large as 10^6 $\mu\Omega$-cm. If the saturation fields required to produce the large TMR for the granular films can be substantially reduced, the sensitivity of granular film might be an attractive alternative to that of sandwiched structures.

From our previous studies[5], it has been found that a proper amount of oxygen is required in the annealing process in order to obtain the Fe-Pb-O films with large TMR effect. As is well known, the shape of the tunneling barrier plays a major role in determining the TMR effect[6]. And the oxidation degree which can change the microstructure of the film will have a large impact on the tunneling barrier. In this report, we use *the annealing time with the same annealing* environment to control the oxidation degree in order to investigate the correlation of the Fe magnetic microstructures with the TMR effect.

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II. EXPERIMENT

The granular Fe-Pb-O films were prepared first by rf magnetron sputtering using homogeneously mixed composite target made from Fe and Pb powders. Kapton foils were used as the substrate. The substrates were cooled by liquid nitrogen during sputtering. The metastable Fe-Pb alloys are thus obtained from sputtering. Afterwords the films were annealed at 400°C. Various annealing times from 30 minutes to 5 hours were preset respectively. The Ar gas was flowing in the oven with some residual air during annealing. The detailed description of the preparation can be referred to ref. 5.

The film composition has been checked with the energy dispersive *X*-ray spectroscopy(EDS). The phases contained in the film were identified from powder *X*-ray diffraction. The conventional four-probe method was used to measure the resistivity of the samples in the temperature range of 5K and room temperature. The magneto-resistance effect(MR), defined as $TMR = \{\rho(O)-\rho(H)\}/\rho(0)$ was obtained at 300K with a maximum applied field of 0.9 Tesla. Under this field, the samples are not completely magnetically saturated. The Mössbauer measurements were carried out at room temperature in a

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transmission geometry with a constant acceleration.

III. RESULTS AND DISCUSSIONS

In Fig. 1 the representative *X*-ray diffraction patterns from Fe-Pb-O films are shown. It is evident that the pattern of as-made specimen contains peaks corresponding to the reflection planes of Pb which has a face-centered-cubic(fcc) structure. No diffraction peaks belong to α-Fe have been detected. This result confirms the formation of metastable Fe-Pb alloy after sputtering. After annealing, other phases except that of Pb start to appear. At least four phases can be identified. The major peaks are from PbO and α-Fe_2O_3. And a very small peak at $2\theta \approx 44.6°$ is due to the presence of α-Fe. Except those peaks, there are diffraction peaks at $2\theta \approx 28.3°$, 29.5°, 50.1° and 65.8° which grow rapidly with longer annealing time. Therefore, the last phase is believed to be the compound formed between PbO and Fe_2O_3[7].

In Fig. 2 the resistivity ρ at 300K and the absolute value of resistivity difference Δρ between zero field and 0.9Tesla are plotted in the logrithmic scale as a function of annealing time (t_A). The resistivity difference Δρ has been found to be negative and isotropic for all samples. It is shown in Fig. 2 that both ρ and Δρ are first increasing rapidly with t_A. Then ρ is slowly increasing and Δρ almost levels off with $t_A \geq 3$ hours. The above results lead to a maximum MR value of about 10% at t_A = 1.0 hours as shown in Fig. 3. It is noted that the magnitude of the resistivity ρ is extremely large for the sample with large MR value. Its value is in the order of 10 Ω-cm and the temperature dependence of resistivity follows the tunnel-type relation $\rho = A\exp(\alpha T^{-1/2})$[8]. Thus, it is apparent that the electron conduction is via a tunneling mechanism and the effect is indeed a TMR. However, a further increase of ρ will depress TMR effect. Compared with the results of other workers, the resistivity of Fe-Pb-O with a large TMR value is about one order of magnitude larger than those in other material systems[3-4,8].

The mössbauer spectra of Fe-Pb-O films at 300K are plotted in Fig. 4. The spectrum of as-made sample contains only a sextuplet which is identical to that of α-Fe. There is no isomer shift relative to α-Fe. This result indicates that the lead atoms in Fe-Pb alloys are simply acting to dilute the magnetism. There is no charge transfer between Fe and Pb atoms. Thus, the magnetic moment of Fe in Fe-Pb alloy is identical to that of α-Fe. After annealing, the spectrum of the annealed contains two sextuplets and a doublet in the central portion. The first sextuplet has

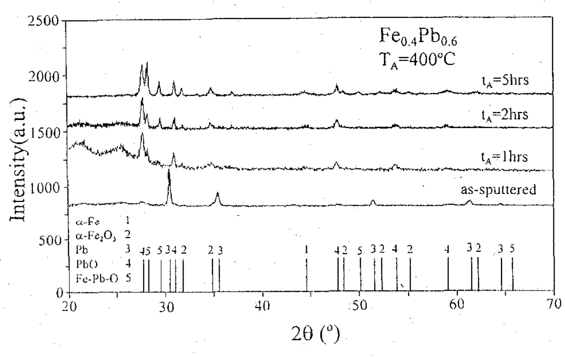

Fig. 1 Representative *X*-ray diffraction patterns for the Fe-Pb-O granular films. The films are annelaed at 400°C with different annealing time.

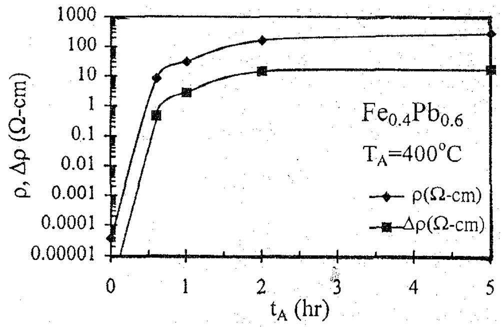

Fig. 2 Resistivity ρ at 300K and the absolute value of Δρ versus t_A for Fe-Pb-O granular films. The vertical axis is plotted in a logrithmic scale. The applied field is 0.9Tesla.

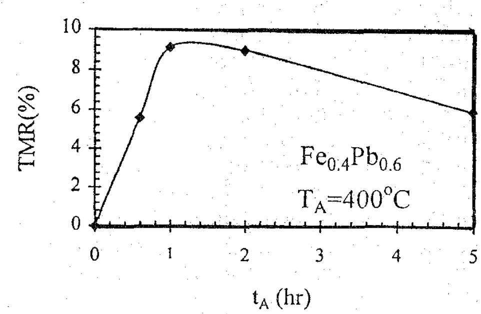

Fig. 3 Magnetoresistance effect(TMR) versus t_A for Fe-Pb-O granular films. The measurement temperature is 300K. The applied field is 0.9Tesla.

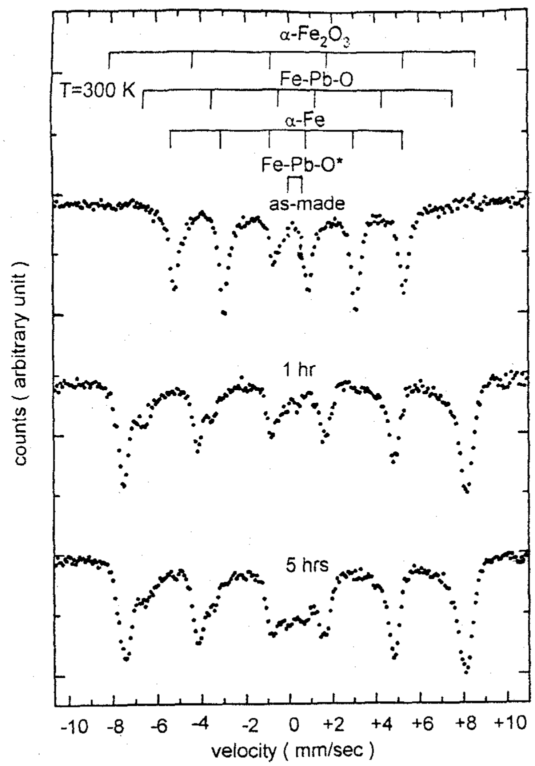

Fig. 4 Mössbauer spectra for the Fe-Pb-O granular films at 300K.

magnetic hyperfine field of 510KOe and isomer shift of 0.36 mm/sec relative to elemental iron. Thus, it can be concluded that it is from the contribution of α-Fe_2O_3. The second sextuplet has magnetic hyperfine field of 432 KOe and isomer shift of 0.41mm/sec. It is believed from the contribution of Fe-Pb-O compound. Besides, the relative intensities of two sextuplets are about the same with different annealing time. As to the doublet which becomes larger relative to others with longer annealing time, it has electric quadrupole interaction of 0.61mm/sec and isomer shift of 0.32mm/sec. The second sextuplet and the doublet have close values of isomer shft. Thus, they might be from the contribution of material with identical structure. The non-magnetic Fe-Pb-O compounds which exist at the boundary of iron granules and magnetic Fe-Pb-O compound consist of small crystallites. As a result, its magnetic ordering temperture is well below room temperature and a doublet has been observed at room temperature instead.

In our previous studies, it has been found that the films containing Fe granules in the PbO insulating matrix exhibit negligible TMR effect[5]. According to Moodera el. al., the electron spin polarization in tunnel junction can be amplified if the insulating matrix for the tunneling barrier is magnetic. Thus, we are tentatively propose that the magnetic tunneling barrier from the compounds formed between PbO and Fe_2O_3 has tendency to enhance TMR effect. A thin layer of non-magnetic Fe-Pb-O compound which exists as an interface layer between iron granules and magnetic Fe-Pb-O compounds and grows thicker at longer annealing time, however, will decrease TMR effect. This is because it will increase the width of the tunneling barrier. The understanding of film microstructure is required to verify above conclusion. The work of tranmission electron microscopy is underway.

In conclusion, we have successfully obtained Fe-Pb-O films with large TMR effect. The appearance of large TMR may be due to the presence of magnetic tunneling barrier from the compound formed between PbO and Fe_2O_3.

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REFERENCES

[1] M. Julliere, "Tunneling between ferromagnetic films", *Phys. Lett.* vol. 54A, pp225-226, September 1975.
[2] T. Miyazaki and N. Tezuka, "Giant magnetic tunneling effect in Fe/Al_2O_3/Fe junction", *J. Magn. Magn. Mater.* vol. 139, ppL231-234, 1995.
[3] H. Fujimori, S. Mitani, and S. Ohnuma, "Tunnel-type GMR in metal-nonmetal granular alloy thin films", *Mat. Sci. Eng. B.* vol. B31, pp219-223, 1995.
[4] T. Furubayashi and I. Nakatani, "Giant magneto-resistance in granular Fe-MgF_2 films", *J. Appl. Phys.*, vol. 79, pp6258-6260, 1995.
[5] J. H. Hsu and Y. H. Huang, summitted, to be published in *Appl. Phys. Lett.*.
[6] S. F. Alvarado "Spin-polarized electron tunneling: the importance of the potential shape", *Mat. Sci. Eng. B.* vol. B31, pp65-68, 1995.
[7] A. J. Mountvala, S. F. Ravitz, "Phase relations and structures in the system PbO-Fe2O3", *J. Am. Ceram. Soc.* vol. 45, pp285-288, 1962.
[8] P. Sheng, B. Abeles and Y. Arie, "Hopping conductivity in granular metals", *Phys. Rev. Lett.*, vol. 31, pp44-47, July 1973.
[9] H. Fujimori, S. Mitani, and S. Ohnuma, "Tunnel-type GMR in Co-Al-O insulated granular-Its oxygen-concentration dependence ", *J. Magn. Magn. Mater.* vol. 156, pp. 311-314, 1996.
[10] J. S. Moodera, X. Hao, G. A. Gibson, and R. Meservey, "Electron-spin polarization in tunnel junction in zero applied field with ferromagnetic EuS barrier", *Phys. Rev. Lett.*, vol 61, pp637-640, 1988.