Metal-insulator Type Nano-granular Magnetic Thin Films

-Sof Magnetic Properties, TMR Effect and Their Applications-

S Ohnuma, N Kobayashi, H Fujimori and T Masumoto
Research Institute for Electric and Magnetic Materials,
2-1-1, Yagiyama-minami, Taihaku-ku, Sendai, Miyagi, 982-0807, Japan
Email address: s.ohnuma@denjiken.ne.jp

Abstract. Metal-Insulator type nano-granular magnetic (NGM) thin films have been noteworthily developed as several functional magnetic materials. The formation of nano-granular structure is strongly related to the magnitude of heat formation ($\Delta H$) of intergranule materials. Forming a larger $\Delta H$ allows a clearer granular structure to be obtained. Soft magnetic properties and TMR effect of NGM films are reviewed in this article, including their applications. The HRTEM observation reveals that average distance among neighboring granules mainly controls magnetic properties in NGM films. Co-O based NGM film where granules contact each other has soft magnetism and exhibits an excellent frequency response of permeability, while the film with isolated granules is superparamagnetic state and shows giant magnetostriction effect. Both large electromagnetic noise suppression and low field magnetic sensing effects are demonstrated as their applications.

1. Introduction
The preparation of a soft magnetic film with a nano-granular structure by sputtering method was first reported in 1985[1]. This soft magnetic film, Fe-B-N, was composed of a nano-granular structure of two amorphous phases of Fe-B and B-N, and possessed both large saturation magnetization, $B_s$ (10 kG) and high specific electrical resistivity, $\rho$ (1000 $\mu\Omega$cm). This study suggested the possibility of developing a new class of material with good soft magnetic properties in the high frequencies [2]. Since then, extensive studies on several types of nano-granular soft magnetic films Fe-ME-(O, N, F) have been reported in literature [3, 4] (ME=Al, Si, Zr, Hf, Ti, Mg). These films consist of nano-sized Fe granules and an insulative matrix of ME-(O, N, F) with well under 1 nm thickness. We have firstly realized high frequency soft magnetic films with large $B_s$, magnetic anisotropy field, $H_k$, and $\rho$, by adopting nano-granular Co-ME-O films[5], and also found the films demonstrating a tunneling type magnetoresistance effect (TMR) in the course of the development of Co based soft magnetic films [6]. Magnetic properties of these films change according to the chemical composition, showing a strong correlation with the transport properties. For example, Co-Al-O films for Co concentration below 60 at.% are superparamagnetic, and show a higher $\rho$ than $10^4$ $\mu\Omega$cm with giant magnetoresistance (GMR) arising from spin dependent tunneling [6].

The purpose of this report is selectively review the work of metal-insulator type nano-granular magnetic (NGM) films, performed at Research Institute for Electric and Magnetic Materials on the soft magnetic properties and TMR effect. Particular emphasis will be paid on the material design suitable for their applications. A noise suppressor at semi-microwave frequency and low field magnetic sensor are demonstrated as the example of their applications.

2. Preparation and Microstructure
Nano-granular films were prepared by a reactive sputtering under Ar+(O or N) plasma using (Fe, Co)-(M=Al, B, Mg, Si, Zr, RE) alloy targets (RE=Gd, Sm, Y), and by co-sputtering or tandem
sputtering under Ar plasma using Fe, Co or alloy target and M-oxide or -fluoride target (M=Al, Mg). The films obtained are in the nano-granular state, consisting of the magnetic nano-granules of Fe, Co or their alloy, and the intergranules of insulating oxide, nitride or fluoride. The intergranular phase of M-oxide in the film was induced by preferential oxidation of M element during deposition. Such a reactive sputtering method using alloy target was useful for controlling accurately the concentration of gas element and for obtaining films with homogenous composition. On the other hand, films showing the TMR effect were mainly prepared on a rotating substrate by tandem sputtering. The key in order to find more suitable M-elements which give good nano-granular structure is the difference of the heat of formation ($\Delta H$) between (Fe, Co)-(O, N or F) and M-(O, N or F) compounds. For example, The $H_c$ and $B_s$ of Co-M-O films decreases and increases monotonically with increasing $\Delta H$ of the intergranule M-oxide phase, respectively [5,7].

To clarify the nano-granular structure, TEM observations were made on Co-ME-O films. Two micrographs of the structure of Co-Al-O films deposited from a Co$_{85}$Al$_{15}$ and Co$_{75}$Al$_{25}$ targets are shown in Fig.1. There can be seen a fairly narrow size distribution of granules around several nm. The morphology of Fig. 1(a) shows dark warped granules (magnetic Co) and bright intergranules (Al-oxide). Co granules are in the crystalline fcc/hcp state and coupled ferromagnetically, so that the film has $B_s$ of about 1 T and soft magnetic properties due to nano-structural effect [8]. The $\rho$ is large as 300 $\mu \Omega \text{cm}$, because of Al-oxide as intergranules, which structure is in the amorphous state. In addition, the film has a large $H_k$. These large $B_s$, $\rho$ and $H_k$ give rise to remarkable frequency response of magnetic permeabilities, $\mu$. The experimental results will be presented in the next section 3.

On the other hand, Fig. 1(b) shows that Co granules are well separated and are embedded in Al-oxide matrix. The shape of each granule is likely spherical[6]. Because of this structure, the film becomes superparamagnetic and exhibits large tunnel electric resistance $\rho=8x10^4$ $\mu \Omega \text{cm}$, accompanying with large MR effect. The recent results on the larger TMR materials will be presented in Section 4.

Considerable interest for us is the compositional difference between the granule phase and the intergranules phase in the film. The composition analysis at nano-scale portion in the film examined by means of nm-focused EDX and EELS, using a beam spot diameter of around 1nm[9]. By comparing the results for the granules and intergranule regions, a clear difference between the two compositions was detected. We found the amount of Al element was extremely low in the granules but high in the intergranule region, while the amount of O element was high in the intergranule region and low in the granules. On the other hand, the Co element concentration was fairly high in the granules. These results on the partial composition analysis were in agreement with our previous expectation on the formation of an Al-O glass close to the Al$_2$O$_3$ compound as an intergranule phase [5].

3. High frequency soft magnetic properties:

Recent improvements of electromagnetic devices have led to demand for further miniaturization and higher operation of magnetic devices. An important property of magnetic materials required for such applications is frequency response of permeability, which is limited by both eddy current loss and ferromagnetic resonance, $f_r$. According to the modified Landau-Lifshitz equation[10], which predicts the $\mu_f$ response, large values of $B_s$, $\rho$ and $H_k$ are required simultaneously for excellent high frequency soft magnetic materials. In order to realize a soft magnetic film with larger $M_s$, $H_k$
and ρ simultaneously, we have paid attention to Co-based films. Our basic idea arises from the fact that generally Co-based alloys exhibit small magnetostriction and high induced magnetic anisotropy. Therefore, if the granule size and the distance between granules (intergranule region) in the Co-based nano-granular films can be controlled, it may be possible to prepare high frequency soft magnetic films. We have already succeeded for preparing several alloy type of nano-granular soft magnetic films [4]. For example, soft magnetic Co-Zr-O system films with large Hk more than 100 Oe can be obtained in wider compositional range than one of Co-Al-O system films [11]. And we have found that the Ni family elements such as Pt, Pd and Ni certainly improve the properties of the Co-Based nano-granular films, by causing them to be magnetically soft and also enhancing the Hk [7]. Fig.2 shows the magnetization curves and μ-f response of Co-Pd-Si-O films, as one of the examples.

Both Increments of Bs and ρ in nano-granular soft magnetic (NGSM) film can be readily explained by the formation process of granular structure as mentioned before. However, the great Hk value can not be explained by the same reason as Bs and ρ. As the excellent frequency characteristics are mainly attributed to the extraordinarily large Hk in the Co based NGSM film, our next particular concern is the reason why Hk, which is induced by magnetic field [13], is so large. We have carried out systematic investigations on the field induced magnetic anisotropy. Measurements were made of the magnetization curves along and across to the magnetic easy direction and the torque curve[12]. Then, Hk and Ku were estimated. Ku is the uniaxial magnetic anisotropy constant and related to Hk as Ku=(Bs/Hk)/8π. The following properties were found. 1) Torque curve is highly of two-fold symmetry. 2) Easy direction of magnetization is along the field direction applied during the sputtering or annealing. 3) Ku can be induced reversibly by the successive re-annealing in field. 4) Ku depends on the magnetic elements, being large according to the sequence of Fe based < Co based < Co+Pd based.

In order to reveal the origin of Ku in NGSM films, the change in Ku vs. x, where x=Co/(Fe+Co) in (Fe1-x,Co)x(Al-O)18 films were investigated [13]. Ku is 10^5 erg/cc in the order of magnitude on the Fe-rich side but it increases with increasing x, taking a maximum of about 4x10^6 erg/cc in the Co-rich region. The Ku vs. x curve is quite different from the relation Ku=αx^2(1-x)^2 driven from the model for ferromagnetic binary alloys, in which Ku must take maximum just at x=0.5, because Ku in the model is induced by directional ordering of atom pairs [14]. From the above, it is considered that large Ku may originate in the nm scale variation of Co base nano-granular structures. In order to clarify this speculation, structural investigations have been performed by means of TEM and small angle X-ray or neutron scattering, now.

The excellent μ-f response, therefore, promise that nano-granular soft magnetic thin films are strong candidate for magnetic cores, such as inductor and magnetic recording head at GHz frequency. Co85B15-Pd-O NGSM films, e.g., have ρ around 10^6 μΩcm, Bs around 8-9 kG, and Hk around 100-150 Oe. The large ρ leads to little eddy current loss, when the film thickness is less than 1 μm, whereas, both large Bs and Hk result in a considerably high μ'×(60-90) and μ"×(200-600) near fr, and their fr is around 3GHz. These data are worthy of not only for the applications using high μ' and quality factor (Q), but also for the devices using large μ". Since Co85B15-Pd-O NGSM films have large electrical loss and magnetic loss near fr, e.g., they are expected to be usefull as an excellent noise suppressor in

Figure 2. Magnetic properties of soft magnetic Co-Pd-Si-O film (a: magnetization curve, b: μ-f response)
semi-micro wave frequency range. A micro strip line, MSL, of Zc=50 Ω, whose both ends were connected to network analyzer, was used to evaluate the noise suppression effect [15].

Fig. 3 shows the frequency dependence of noise suppression effect ($\Delta P_{\text{loss}}/P_{\text{in}}$) up to 6 GHz for several kinds of Co$_{85}$B$_{15}$-Pd-O films. $\Delta P_{\text{loss}}$ indicates the real power loss of magnetic films with the size of 15x15 mm, which has been taken by subtracting part by MSL from the total power loss [16]. The result of Film Impedor (NEC-Tokin Co. Japan, 50 μm thickness), which is well known as an electromagnetic noise suppression material at high frequency, is also shown in the figure as a comparison. The $\Delta P_{\text{loss}}/P_{\text{in}}$ of films increases with increasing frequency up to 3 GHz and keeps constant (around 0.6) in frequencies higher than 3 GHz. It is noted that $\Delta P_{\text{loss}}/P_{\text{in}}$ of the NGMS films are about 6 times larger than that of the Film Impedor, nevertheless the thickness of Film Impedor is 50 times thicker than those of the NGMS films. An excellent noise suppressing effect in soft magnetic Co$_{85}$B$_{15}$-Pd-O films is attributed to a large electric loss due to a sheet resistance around 100 Ω, and a magnetic loss or $\mu''$ near $f_r$ [17]. We have deposited NGSM film directly on the LSI, which top cover was removed, and found that NGSM film reduced noise level from LSI more than 50 %, In some applications for noise suppression, the thinness of the films is advantageous for heat removal from electric devices.

4. TMR effect:

When the volume fraction of intergranule increases beyond the percolation limit, the electrical conductance obeys a thermal hopping tunnel conductance, and then $\rho$ becomes large. Coincidentally, large TMR appears [6]. The tunnelling conductance has been evident by the temperature ($T$) variation of $\rho$ according to $\rho=AT^2$, and by the weak temperature dependence of TMR excepting for its anomalous increase at very low temperatures [18]. Further evidences have been obtained by the fact that the current vs. bias voltage curve is parabolic, accompanying Coulomb staircase. The Coulomb staircase implies the existence of the charging effect (Coulomb blockade effect) of Co nanogranules in the tunnelling process.

TMR values obtained in Co-(Al-O) films [6] are in the level of 8 % at room temperature, as shown in Fig.4, which is similar in magnetic field dependence of multilayered Fe/Cr and granular Co-Cu films, characterized by the same negative value irrespective of the longitudinal and transverse cases. We have confirmed that the magnetization curve of Co-Al-O films can be fitted to a Langevin function, implying that these films are superparamagnetic. Nevertheless, in the granular films it is prominent to take useful values of TMR coincident to various $\rho$ values that are larger and smaller than those of multilayers and junctions, respectively. This is quite important merit for applications. We have searched more desirable granular TMR materials. The results are also shown in Fig.5. TMR values up to about 14% can be obtained in the range of $10^3<\rho<10^9$ μΩcm. (Fe-Co)-AlF$_3$ [19] and (Fe-Co)-
MgF$_2$ [20] films have larger values of TMR and $\rho$, compared with Co-(Al-O) films [6]. This may be attributed to the crystalline structure of intergranules, AlF$_3$ or MgF$_2$, which is different from the amorphous structure of Al-oxide intergranules.

We have tried to construct a lateral hetero-structure with a soft magnetic film to improve the field sensitivity of TMR, named as GIG sensor [21]. In GIG sensor, it is expected that the large stray field from the soft magnetic film may easily magnetize the nano-granular piece. Fig. 6 shows the schematic structure of GIG sensor developed by us. The field response obtained in the GIG devices suitably designed is about 7% of $\Delta$MR per 1 Oe of $\Delta$H with good linearity. The mechanism of the enhancement of the low field response in the GIG sensor is considered as follows: As the soft magnetic film is magnetized in a low external magnetic field, then a large stray magnetic flux from the gap edge of the soft magnetic films passes through the TMR film located in the gap. Then, even at a low external field the TMR film is well magnetized. The magnitude and field dependence of the MR ratio of GIG sensor are considered to depend on the characteristics of both soft magnetic films and TMR materials, as well as GIG structure geometry, such as width and form of the gap and arrangement of the electrodes. The GIG devices are more improved and useful for various kinds of low field sensors, if the structure is optimized. And we are developing the sensor with several companies.

5. Closing remarks

Our recent results on nano-granular magnetic thin films are introduced and discussed from the standpoint of high frequency soft magnetic properties and a giant magnetoresistance. We have tried not only high frequency noise suppression effect and low field magnetic sensor, but also several other magnetic devices as their applications. Nano-granular magnetic films also show excellent properties in the areas of magnetic recording media, Hall effect [22], and magneto-optical effect [23]. These remarks are expected to be important for “information technology” in the new generation.

6. Acknowledgement:

This work reported here has been performed in collaboration with M. Ohnuma, H. Mamiya and K. Hono of National Institute for Material Science, and M. Yamaguchi, Y. Shimada and S. Mitani of Tohoku University, and T. Iwasa, H. J. Lee and K. Nagura of Research Institute for Electric and Magnetic Materials. The research was mainly supported by a grant from The Japan Society for the Promotion of Science (JSPS).

7. References

[1]  H. Karamon, T. Masumoto and Y. Makino 1985 J. Appl. Phys. 57 3527
[2]  H. Karamon 1988 J. Appl. Phys. 63 4306, H. Matsuyama, H. Eguchi and H. Karamon 1990 J. Appl. Phys. 67 5123
[3]  A. Makino and Y. Hayakawa 1994 Materials Science and Engineering A181/A182 1020
[4] S. Ohnuma, H. Fujimori, F. Matsumoto and T. Masumoto 1994 *Materials Science and Engineering* A182 892
[5] S. Ohnuma, H. Fujimori, S. Mitani, and T. Masumoto 1996 *J. Appl. Phys.*, 79 5130
[6] H. Fujimori, S. Mitani and S. Ohnuma 1995 *Materials Science and Engineering* B31 219
[7] S. Ohnuma, N. Kobayashi, T. Masumoto, S. Mitani and H. Fujimori 1999 *J. Magn. Soc. Japan* 23 23
[8] G. Herzer 1990 *IEEE Trans. Magn.* 26 1397
[9] M. Ohnuma, K. Hono, H. Onodera, S. Ohnuma, H. Fujimori, and J. S. Pedersen 2000 *J. Appl. Phys.* 85 817
[10] A. Hosono and Y. Shimada 2000 *J. Magn. Soc. Jpn.* 12 295
[11] S. Ohnuma, H. J. Lee, N. Kobayashi, H. Fujimori and T. Masumoto 2001 *IEEE Trans. Magn.* 37 2251
[12] H. J. Lee, S. Ohnuma, H. Fujimori and T. Masumoto 2000 *J. Magn. Soc. Jpn.* 24 687
[13] S. Ohnuma, N. Kobayashi, and T. Masumoto 1999 *J. Appl. Phys.* 85 4574
[14] H. Fujimori 1983 *Amorphous Metallic Alloys*, ed F.E. Luborsky (Butterworths Stoneham MA) Chapter 16 pp 300-316
[15] S. Yoshida, H. Ono, S. Ando, F. Tsuda, T. Itoh, Y. Shimada, M. Yamaguchi, K. I. Arai, S. Ohnuma and T. Masumoto 2001 *IEEE Trans. on Mag.* 37 2401
[16] S. Ohnuma, H. Nagura, H. Fujimori and T. Masumoto 2004 *IEEE Trans. on Mag.* 40 2712
[17] S. Ohnuma, T. Iwasa, H. Ono, M. Yamaguchi and T. Masumoto 2005 *Diegest of Intermag*. CE-02
[18] S. Mitani, H. Fujimori and S. Ohnuma 1998 *J. Magn. Magn. Mater.* 177-181 919
[19] N. Kobayashi, *unpublished data*
[20] N. Kobayashi, S. Ohnuma, T. Masumoto and H. Fujimori 2001 *J. Appl. Phys.* 90 4159
[21] N. Kobayashi, S. Ohnuma, S. Murakami, T. Masumoto, S. Mitani and H. Fujimori 1998 *J. Magn. Magn. Mater.* 188 30
[22] A. B. Pakhomov, X. Yan and B. Zhao 1995 *Appl. Phys. Lett.* 67, 3497
[23] E. J. Gan’shina, A. Granovsky, V. Guschin, N. Perov and B. Dieny 1997 *J. Magn. And Magn. Mater.* 165 320