Proposal of a Suitable Antiferromagnetic Film for Pinning Fe₃O₄ Film: CrMnPt

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Exchange coupling between half-metallic Fe₃O₄ and antiferromagnetic PtMn, MnIr, and CrMnPt films was investigated, with the goal of inducing unidirectional anisotropy in the Fe₃O₄ film, which has hard magnetic properties. The Fe₃O₄–CrMnPt system exhibited superior exchange coupling properties: a large unidirectional anisotropy constant (K_e) of $\sim 0.15\text{--}0.18\text{ erg/cm}^2$, a high blocking temperature (T_B) of $\sim 320^\circ\text{C}$, and a nearly unidirectionally shifted M – H curve. In the Fe₃O₄–PtMn system, the K_e value degraded to around zero. The oxygen in the Fe₃O₄ film diffused into the adjacent films through thermal annealing to produce PtMn-phase transition, resulting in considerable K_e degradation. In the Fe₃O₄–MnIr system, the K_e and T_B values were a little too low for practical application. From these results, it is reasonable to suppose that the most suitable antiferromagnetic material for pinning Fe₃O₄ film in spintronics devices is CrMnPt.

Key words: exchange coupling, half-metallic, hard-magnetic, Fe₃O₄, antiferromagnetic, PtMn, MnIr, CrMnPt, unidirectional anisotropy, spintronics devices

1. Introduction

Spintronics devices: tunneling magnetoresistance (TMR) devices, giant magnetoresistance (GMR) devices, magnetic random-access memory, etc., are currently active areas of research. In these devices, the magnetoresistance (MR) ratio is related to the spin polarization (P) of the electrons in the ferromagnetic electrodes of the tunnel junctions (TMR)¹⁾ or intermediate layers (GMR)²⁾. The most attractive materials for high P are the so-called half-metallic ferromagnets, which are metallic for one spin direction and insulating for the other³⁾. Among the many half-metallic ferromagnetic materials, Fe₃O₄ film will be one candidate for practical use in terms of a sufficiently high Curie temperature (T_C , 858K)³⁾. (The other candidates include Heusler alloys, i.e., Co₂MnSi, Co₂MnSi, etc.⁴⁾) The band calculation predicts half-metallic ferromagnetic material ($P=1$) for Fe₃O₄⁵⁾. Also, Dedkov et al. provide evidence for the half-metallic ferromagnetic state of ultra-thin Fe₃O₄ film ($\sim 41\text{ \AA}$) by spin-resolved photoelectron spectroscopy, where $P\sim 0.8$ ⁶⁾. Then, our group has previously succeeded in fabricating a high-quality ultra-thin Fe₃O₄ film⁷⁾, and is now developing a current-perpendicular-to-plane (CPP)-GMR device using this Fe₃O₄ film⁸⁾.

The use of this Fe₃O₄ film in a spintronics device requires a technique for pinning the Fe₃O₄ film by using an antiferromagnetic layer, together with a technique for obtaining a high MR ratio. However, until now there have

been few studies on the pinning of Fe₃O₄ film by using antiferromagnetic layers. A large exchange coupling field (H_{ex}) [a large unidirectional anisotropy constant (K_e), $K_e \geq 0.15\text{ erg/cm}^2$], a high blocking temperature (T_B , $T_B \geq 300^\circ\text{C}$), and a perfectly unidirectional-shifted M – H curve are needed. We define H_{ex} and T_B as the shift in the easy-axis magnetic hysteresis loop and the temperature at which H_{ex} disappears. A perfectly unidirectional-shifted M – H curve is defined as an M – H curve that satisfies $H_{ex} > H_C$ (H_C : coercive force). Since Fe₃O₄ film has hard magnetic properties [anisotropy field (H_k) of Fe₃O₄ film $> 70\text{ kOe}$, i.e., K_F of Fe₃O₄ film $> \sim 1.4 \times 10^7\text{ erg/cm}^3$ ^{9, 10)}. The large H_k (K_F) of Fe₃O₄ film is caused by defects and antiphase boundaries in the film, which lead to a canting spin structure, i.e., a spin frustration⁹⁾], pinning it has been difficult. This is largely because, at the very least, $K_F V_F < K_{AF} V_{AF}$ must be satisfied to pin it¹⁰⁾. Here, K_F and K_{AF} are the ferromagnetic (Fe₃O₄) and antiferromagnetic magnetocrystalline anisotropy constants, and V_F and V_{AF} are the volumes of the ferromagnetic (Fe₃O₄) and antiferromagnetic grains. However, there are very few antiferromagnetic films with a K_{AF} large enough to satisfy this relationship. So, the crucial point in pinning Fe₃O₄ film is to use an antiferromagnetic film with a large K_{AF} .

Candidate antiferromagnetic materials include ordered-Pt₅₀Mn₅₀ (in atomic %) ¹¹⁾, disordered-Mn₈₀Ir₂₀ ¹²⁾, disordered-Cr_{45.5}Mn_{45.5}Pt₉ ¹³⁾, and disordered-Cr_{45.5}Mn_{45.5}Pt₉ with stress-induced anisotropy¹⁴⁾. These materials have been successfully used in current-in-plane (CIP)-GMR and TMR devices as exchange-biased layers. (The PtMn, MnIr, and CrMnPt films have been successfully used with $K_e \geq \sim 0.15\text{ erg/cm}^2$ and $T_B \sim 300^\circ\text{C}$. That is the reason why the aforementioned $K_e \geq 0.15\text{ erg/cm}^2$ and $T_B \geq 300^\circ\text{C}$ are needed for practical use.)

Then, we have evaluated the exchange coupling properties of Fe₃O₄–PtMn, Fe₃O₄–MnIr, Fe₃O₄–CrMnPt, and Fe₃O₄–CrMnPt with stress-induced anisotropy and have identified the most suitable antiferromagnetic material for pinning half-metallic and hard-magnetic Fe₃O₄ film. Here, we have already reported the detailed exchange coupling in the Fe₃O₄–CrMnPt system¹⁰⁾. So, in this article, we leave out the detailed description of the Fe₃O₄–CrMnPt system and concentrate on the identification of the most suitable antiferromagnetic material.

2. Experiment

Imitating one portion of an actual CPP-GMR film, we prepared four kinds of samples onto a MgO(001) substrate (size: 10 mm $\times$ 10 mm square, thickness: 0.5 mm), as

Table 1 Film structure of samples and thermal annealing conditions.

Sample	Film structure	Conditions
A	Cu(1000 Å, bottom)/Fe ₃ O ₄ (50 Å)/Ni ₈₁ Fe ₁₉ (30 Å)/Pt ₅₀ Mn ₅₀ (150 Å)/Ru(10 Å, top)	250°C for 3 h
B	Cu(1000 Å)/Fe ₃ O ₄ (50 Å)/Ni ₈₁ Fe ₁₉ (30 Å)/Mn ₈₀ Ir ₂₀ (150 Å)/Ta(50 Å)	230°C for 3 h
C	Cu(1000 Å)/Fe ₃ O ₄ (50 Å)/Co(30 Å)/Cr _{45.5} Mn _{45.5} Pt ₉ (300 Å)	230°C for 3 h
D	Cu(1000 Å)/Fe ₃ O ₄ (50 Å)/Co(30 Å)/Cr _{45.5} Mn _{45.5} Pt ₉ (300 Å)/NiO(500 Å)	230°C for 3 h

shown in Table 1. One reason why we selected a film structure of Cu/Fe₃O₄/NiFe or Co/antiferromagnetic layer, not Cu/antiferromagnetic layer/NiFe or Co/Fe₃O₄, is that the antiferromagnetic layer in CPP-GMR device we are now developing is placed on the (Fe₃O₄/NiFe or Co) films. Another reason is that a surface-roughness of CrMnPt film deposited on a metallic film with an fcc structure is a little large¹⁵⁾, and as it turned out large H_{ex} (K_e) can not be induced in the ferromagnetic film deposited on CrMnPt film. The Cu film acted as the lower electrode layer in the CPP-GMR device. The NiFe or Co film was inserted between the Fe₃O₄ and antiferromagnetic PtMn, MnIr, or CrMnPt film to prevent oxygen diffusion from the Fe₃O₄ into the antiferromagnetic film. To protect the PtMn and MnIr films from oxidation during annealing, Ru and Ta films were deposited onto their films. To promote stress-induced anisotropy in the CrMnPt film, NiO film was deposited onto the film. Details of the method used to obtain stress-induced anisotropy in CrMnPt film [and the mechanism of subsequent H_{ex} (K_e) enhancement] are described elsewhere^{10, 14)}. The thickness of the Fe₃O₄ film was set to 50 Å for the following reasons. The Fe₃O₄ film we previously developed exhibited a stable saturation magnetization (M_s) of ~ 440 emu/cm³ when the thickness was above ~ 100 Å (The M_s value of the bulk was ~ 477 emu/cm³)^{7, 8)}. However, the Fe₃O₄ film should be as thin as possible. Because it has a resistivity of ~ 10000 $\mu\Omega\text{cm}$ ⁷⁾, while a CPP-GMR device requires low electrical resistance. For 50-Å-thick Fe₃O₄ film, the M_s is ~ 400 emu/cm³^{7, 8)}. Judging from this M_s value, we believe that the half-metallic properties are maintained with a thickness of 50 Å.

The films were deposited using rf magnetron sputtering in argon gas. During the sputtering, a dc magnetic field of ~ 100 Oe was applied in-plane to induce unidirectional anisotropy in the ferromagnetic (Fe₃O₄/NiFe) or (Fe₃O₄/Co) film. The films were prepared under optimum sputtering conditions for obtaining large H_{ex} (K_e). After evacuating below 4×10^{-7} Torr, film deposition was performed at an argon pressure of 3×10^{-3} Torr for the Cu film, 13×10^{-3} Torr for the Fe₃O₄ film^{7, 8)}, 3×10^{-3} Torr for the NiFe and Co films, 3×10^{-3} Torr for the PtMn and MnIr films, 15×10^{-3} Torr for the CrMnPt film^{10, 13, 14)}, 3×10^{-3} Torr for the Ru and Ta films, and 0.6×10^{-3} Torr for the NiO film^{10, 14)}. The sputtering rates were 1.17 Å/s

for the Cu film, 0.11 Å/s for the Fe₃O₄ film, 2.68 Å/s for the NiFe film, 1.22 Å/s for the Co film, 2.51 Å/s for the PtMn film, 2.84 Å/s for the MnIr film, 6.93 Å/s for the CrMnPt film, 2.62 Å/s for the Ru film, 2.70 Å/s for the Ta film, and 1.30 Å/s for the NiO film. The deposition was performed at room temperature, except in the case of the Fe₃O₄ film, which was deposited at 250 °C^{7, 8)}. After deposition, the samples were annealed in vacuum and then cooled to room temperature under a static magnetic field of 3 kOe. The thermal annealing was done at 230 °C for 3 h, except in the case of sample A, which was annealed at 250 °C for 3 h. This is because, at the very least, thermal annealing at or above 250 °C is needed to produce PtMn-phase transition from a disordered phase to an ordered phase¹¹⁾. The direction of the applied magnetic field was parallel to the direction in which H_{ex} (K_e) was induced. The H_{ex} was measured using a vibrating-sample magnetometer. The K_e at room temperature and the T_B were measured using a torque magnetometer. The crystallographic microstructure was analyzed using the $\theta - 2\theta$ scanning method of x-ray diffractometry (XRD, Cu $K\alpha$).

3. Results and discussion

Figure 1 shows $M-H$ loops for exchange-coupled films: (a) sample A, (b) sample B, (c) sample C, and (d) sample D. The maximum applied field in measurement was ± 1 kOe. As shown in Fig.1, the H_{ex} value for sample A was ~ 20 Oe, which is too small for practical application. Sample B exhibited a relatively large H_{ex} value of ~ 160 Oe. However, a perfectly unidirectional-shifted $M-H$ curve could not be obtained. Additionally, the square hysteresis of the $M-H$ curve collapsed. In contrast, samples C and D exhibited large H_{ex} values, ~ 250 and ~ 300 Oe, respectively, and nearly unidirectional-shifted $M-H$ curve. Figure 2 shows temperature dependence of K_e for exchange-coupled films: (a) sample A, (b) sample B, (c) sample C, and (d) sample D. As shown in Fig.2, we were unable to measure the temperature dependence of K_e for sample A because the K_e values were too small to measure the torque curve. Sample B exhibited a relatively large K_e of ~ 0.07 erg/cm² at room temperature, and had a relatively high T_B value of ~ 260 °C. However, these K_e and T_B values may be a little low for practical application. In contrast, samples C and D

Fig. 1 $M-H$ loops for exchange-coupled films: (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

Fig. 2 Temperature dependence of the unidirectional anisotropy constant (K_e) for exchange-coupled films: (a) sample A, (b) sample B, (c) sample C, and (d) sample D.

exhibited very large K_e values of ~ 0.15 and 0.18 erg/cm², respectively, at room temperature, and both had a high T_B value of ~ 320 °C. We therefore see that the Fe_3O_4 —CrMnPt system exhibits the best exchange coupling properties: a large K_e of ~ 0.15 – 0.18 erg/cm², a high T_B of ~ 320 °C, and a nearly unidirectional-shifted $M-H$ curve. As we have discussed in Ref. 10, these superior exchange coupling properties in the Fe_3O_4 —CrMnPt system originate in a K_{AF} of the CrMnPt film ($\sim 10^7$ erg/cm³)¹⁵ large enough to satisfy $K_F V_F < K_{AF} V_{AF}$ and to pin the hard-magnetic Fe_3O_4 film⁹). The larger K_e value for

Fig. 3 XRD profiles of sample A obtained by using the $\theta - 2\theta$ scanning method: (a) $10 \text{ deg} \leq 2\theta \leq 100 \text{ deg}$ and (b) $36 \text{ deg} \leq 2\theta \leq 46 \text{ deg}$. Here, Fe and FeO peaks were not detected.

sample D (~ 0.18 erg/cm²) than for sample C (~ 0.15 erg/cm²) is attributed to stress-induced anisotropy in the CrMnPt film of sample D¹⁰.

The question we have to ask here is why the H_{ex} value for sample A was too small [$H_{ex} = \sim 20$ Oe, Fig.1(a)]. This finding contradicts the general recognition until now that among the antiferromagnetic materials PtMn induces the largest H_{ex} (K_e) value in ferromagnetic material. The center of gravity for (Fe_3O_4 /NiFe)-films' M_S value within sample A decreased from theoretical ~ 548 emu/cm³ to experimental ~ 496 emu/cm³ (See Fig.1). Here, the theoretical value was estimated assuming $M_S = 796$ emu/cm³ for NiFe film and $M_S = 400$ emu/cm³ for Fe_3O_4 film. To the contrary, the theoretical values in the samples B, C, and D well corresponded to the experimental ones: ~ 540 – 548 , ~ 780 – 787 , and ~ 787 – 788 emu/cm³ for samples B, C, and D. Then, we measured the XRD profiles for sample A using the $\theta - 2\theta$ scanning method. As shown in Fig.3, the Cu film preferentially exhibited (111) and (200) crystalline orientations on the MgO(001) substrate, the Fe_3O_4 film exhibited (111) crystalline orientation on the Cu film, and a $L1_0$ -PtMn phase (ordered phase)¹¹ was adequately formed through thermal annealing. The most important finding here is that many manganese oxides and $\alpha - \text{Fe}_2\text{O}_3$ peaks were detected [Fig.3(b)]. The respective peak positions of manganese and iron oxides indexed in Fig.3(b) well corresponded to those described in ASTM cards. Additionally, the peaks of manganese alloys such as MnNi and MnFe were not detected, suggesting that Mn atoms in PtMn film does not diffuse into Fe_3O_4 film. Therefore, as to why we could not obtain large H_{ex} (K_e) in the Fe_3O_4 —

Fig. 4 XRD profiles of sample B obtained by using the $\theta - 2\theta$ scanning method: (a) $10 \text{ deg} \leq 2\theta \leq 100 \text{ deg}$ and (b) $36 \text{ deg} \leq 2\theta \leq 46 \text{ deg}$. The peak around $2\theta = 38.5 \text{ deg}$ was an inherent peak in our XRD apparatus. In Fig.3(b), this peak may be superimposed on $\text{Mn}_3\text{O}_4(040)$.

PtMn system, we think this is caused by the fact that the oxygen in the Fe_3O_4 film diffuses into the adjacent films through thermal annealing to produce PtMn-phase transition¹¹⁾ and as a result manganese oxides and $\alpha - \text{Fe}_2\text{O}_3$ are formed around the ferromagnetic/antiferromagnetic interface, resulting in considerable reduction in interfacial exchange paths. Standard free energies of formation (ΔG°) of NiFe-oxide and Co-oxide are the same degree¹⁶⁾. So, even when we change an inserted layer (between the Fe_3O_4 and PtMn films) from the NiFe to Co film, we will not be able to prevent the above-stated oxygen diffusion. Also, it is quite likely that an interdiffusion of Pt and Mn atoms in the PtMn film for transforming into an ordered phase induces the oxygen diffusion. So, granted that we succeed in reducing the annealing temperature of PtMn-phase transition down to 230°C , the oxygen diffusion will occur.

A high-quality MnIr film was obtained for sample B as shown in Fig.4. Manganese oxides or $\alpha - \text{Fe}_2\text{O}_3$ peaks were not be detected, indicating that the undesirable $M-H$ curve in the Fe_3O_4 –MnIr system [Fig.1(b)] is due to the intrinsic magnetic properties of MnIr. From the face-centered-cubic symmetry of MnIr¹²⁾, we can expect its K_{AF} to be too small to satisfy $K_{\text{F}}V_{\text{F}} < K_{\text{AF}}V_{\text{AF}}$ and to pin hard-magnetic Fe_3O_4 film. Such a small K_{AF} must therefore result in an undesirable $M-H$ curve. (The XRD profiles of samples C and D are described elsewhere¹⁰⁾.)

4. Conclusion

In summary, we investigated the exchange coupling between half-metallic Fe_3O_4 and antiferromagnetic PtMn,

MnIr, CrMnPt, and CrMnPt with stress-induced anisotropy. The Fe_3O_4 –CrMnPt system exhibited the best exchange coupling properties: a large K_{e} of $\sim 0.15 - 0.18 \text{ erg/cm}^2$, a high T_{B} of $\sim 320^\circ\text{C}$, and a nearly unidirectional-shifted $M-H$ curve. These properties meet the requirements for using antiferromagnetic layers to pin Fe_3O_4 films in spintronics devices. In the Fe_3O_4 –PtMn system, the H_{ex} (K_{e}) value was too small for practical application. The oxygen in the Fe_3O_4 film diffused into the adjacent films through thermal annealing to produce PtMn-phase transition, resulting in considerable degradation in the H_{ex} (K_{e}) value. In the Fe_3O_4 –MnIr system, the K_{e} and T_{B} values were a little too low for practical application. From these results, the most suitable antiferromagnetic material for pinning the half-metallic Fe_3O_4 film in spintronics devices may be CrMnPt. The sole weakness of CrMnPt will be a critical thickness of CrMnPt film being a little thick ($250 \text{ \AA}$)¹⁴⁾. Further investigation to thin it may be needed for practical use.

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