Ferrite-Plated Thin Films for Perpendicular Recording Media

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Abstract— Ferrite-plated films were studied for application as perpendicular recording media. Though the ferrite plating has a merit of low temperature process below 100 °C, the microstructure must be improved for the media application. Power ultrasound irradiation into reaction solutions had effects on the reduction of grain size and the improvement of crystallinity maybe due to the increase of the nucleation sites on substrates and the acceleration of the ion migration in reaction. Doping Co^{2+} ions into Fe_3O_4 films increased perpendicular coercivity $H_{c\perp}$. $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ plated films of 70 nm in thickness around at $x=0.5$ had $H_{c\perp}$ of 2.8 kOe, $H_{c\parallel}$ of 0.6 kOe, and M_s of 450 emu/cc. Mossbauer analyses showed the films have perpendicular anisotropy.

Key words: ferrite-plating, sonochemistry, power ultrasound, Co-ferrite, perpendicular recording media

I. INTRODUCTION

Ferrite thin film recording media have a good potential because of their low noise characteristics and good mechanical durability [1]. While physical vapor deposition methods, such as sputtering and evaporation, need high temperature over 300 °C for the ferrite film deposition and/or post-heating treatment, the “ferrite-plating” method facilitates to deposit polycrystalline spinel type of ferrite films at low temperature below 100 °C in aqueous solutions [2]. The ferrite-plated films in the former studies revealed columnar structure in the cross section and large grains near surface. Their structure will affect the recording performance in particular the noise characteristics. The structure is very similar to that of sputter-deposited films at high working gas pressures. This suggests that it is necessary to increase nucleation sites on substrates and to accelerate ion migration on growing films in order to deposit fine grained ferrite films. Thus, irradiation of power ultrasound during ferrite-plating was attempted. The power ultrasound enhancement in chemical reaction, called

“sonochemistry,” recently attracted considerable attention as a possible breakthrough in material science. A previous study on ultrasound enhanced ferrite-plating showed an improvement of Fe_3O_4 coatings on polyacrylate spheres of 0.25 μm in average diameter [3].

Soft magnetic ferrite films of several hundreds nanometers or over one micron in thickness were studied in most of the former studies on the ferrite-plating. For application to perpendicular magnetic recording media, ferrite films with high perpendicular coercivity over 1 kOe and the thickness below 100 nm are required. Thus addition of Co^{2+} ions was attempted to increase the coercivity and cause perpendicular anisotropy.

II. EXPERIMENTAL

As shown in Fig. 1, ultrasound waves (19.5 kHz, 600W) were applied by a horn (30 mm ϕ) into a reaction solution (300 ml) of FeCl_2 aqueous solution kept at 70 °C. A NaNO_2 solution was supplied to the solution to keep oxidation reduction potential (ORP) at -500 mV, and NH_4OH solution to keep the pH value at 7.0. For comparison, we also performed the ferrite plating without sonication, agitating the aqueous solution with a spinning stirrer which was replaced for the ultrasound horn and the spin-spray ferrite-plating [4]. Fe_3O_4 films were deposited on polyacrylate spheres, 4 μm in average diameter, and glass substrates.

$(\text{Co}, \text{Fe})_3\text{O}_4$ films were prepared by the spin-spray ferrite-plating on glass substrates at 90 °C using a reaction solution of $\text{FeCl}_2+\text{CoCl}_2$ and an oxidizing solution of $\text{NaNO}_2+\text{CH}_3\text{COONH}_4$ (pH = 5~7).

The surfaces of the ferrite coatings on the spheres were observed by a field emission type scanning electron microscope (FE-SEM). The cross sections of the plated particles were observed by a transmission electron microscope (TEM) on ultramicrotome-slices (60 nm in thickness) of an acrylate resin in which the particles were

embedded. The surfaces of the films on the glass substrates were observed by AFM. The crystallographic and magnetic characteristics of the films were investigated at room temperature, using a $\text{CuK}\alpha$ X-ray diffractometer, a Co^{57} -Mössbauer spectrometer, and a vibrating sample magnetometer (VSM).

Fig. 1 Schematic diagram of ultrasound enhanced ferrite-plating apparatus.

Fig. 2 Schematic diagram of spin-spray ferrite-plating apparatus.

III. RESULTS AND DISCUSSION

Figure 3 shows SEM photographs of Fe_3O_4 coated spheres after the reaction for 30 minutes. When plated with ultrasound irradiation, the spheres were encapsulated with Fe_3O_4 coating as shown in Fig.3(a). However, when plated without irradiation, the ferrite coating covered the surfaces only in part as shown in Fig.3(b). Figure 4 shows AFM images of the ferrite-plated films of 30 nm in thickness on glass substrates by (a) the ultrasound enhanced method and (b) the spin-spray method. Smaller and more uniform grains are observed in the Fig.4 (a) compared with (b). These results suggest that the number of nucleation sites on the substrates when plated with ultrasound irradiation is larger than that without the ultrasound. The power ultrasound generates in liquids localized "hot spots" of extremely high temperatures ($\sim 3,000\text{K}$) and high pressures ($\sim 1,000\text{K}$) due to collapse of cavitation bubbles, and the hot spots produce radicals such as $\text{OH}^\cdot$ and $\text{H}^\cdot$ in an aqueous solution [5]. The radicals may bring about OH groups, which works as the nucleation sites for the ferrite formation, on the substrates. In addition, the ultrasound irradiation should accelerate migration of ions in the solution and on the surfaces of the substrates. These two effects of the power ultrasound enhancement may help to produce the smaller and more uniform grains.

Fig. 3 SEM photographs of Fe_3O_4 coated spheres.

Figure 5 shows the dark field image of TEM cross sectional view for the ferrite-coated spheres with ultrasound irradiation. Parts, which are pointed out by arrows, are crystallites of the ferrite coating. The size is

about 30 nm. Figure 6 shows the electron diffraction patterns. The probe size is around one coated sphere. While spots, which reflect crystal orientation, are observed in Fig.6 (a) for the coated spheres with the ultrasound, the diffraction pattern of that without sonication is very close to rings as shown in Fig.6(b). These results suggest that crystallites of the ferrite coating by the sonicated plating are well oriented. Since the ultrasound irradiation accelerates the migration of ions, the ions should be trapped in the right sites to compose good crystallites.

(a) ultrasound enhanced ferrite-plating

(b) spin-spray ferrite-plating

Fig. 4 AFM images of Fe_3O_4 films prepared on glass substrates.

Fig. 5 TEM cross sectional view of Fe_3O_4 coated spheres prepared with ultrasound irradiation.

Fig. 6 Electron diffraction patterns of Fe_3O_4 films.

Doping of Co^{2+} ions into Fe_3O_4 films increased perpendicular coercivity $H_{c\perp}$. Figure 7 shows the typical M-H loops of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ plated films. $H_{c\perp}$ for 50 nm thick films was varied from 0.4 to 2.2 kOe with the ratio of Co/Fe in the reaction solution and took a maximum around at $x=0.5$, while $H_{c\parallel}$ remained around 0.2~0.8 kOe as shown in Fig. 8. The magnetic characteristics did not depend strongly on the thickness of the films, and $H_{c\perp}$ for the films of only 30 nm in thickness was 2.3 kOe. Figure 9 shows a Mossbauer spectrum of $\text{Co}_{0.43}\text{Fe}_{2.57}\text{O}_4$ films. In the case of perpendicular anisotropic films, the ratio of the peaks should be 3:0:1:1:0:3, and it should be 3:2:1:1:2:3 in the case of in-plane anisotropic ones. This spectrum is very similar to the perpendicular anisotropic ones. The results of X-ray diffractometry showed that these films did not have a specific preferential orientation. In this study, Co-ferrite films with $H_{c\perp}$ of 2.8 kOe, $H_{c\parallel}$ of 0.6 kOe, $(M_r/M_s)_{\perp}$ of 0.5 (without compensation of demagnetizing field), $(M_r/M_s)_{\parallel}$ of 0.24, and M_s of 450 emu/cc were deposited at the thickness of 70 nm. These values are very close to sputter-deposited Co-Cr alloy thin films.

Fig. 7 M-H loops of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ films.

Fig. 8 Dependence of coercivity on Co/Fe ratio in reaction solution.

Fig. 9 Mossbauer spectrum of $\text{Co}_{0.43}\text{Fe}_{2.57}\text{O}_4$ films.

IV. CONCLUSION

Aiming applications as perpendicular recording media, we investigated improvements of microstructure and magnetic characteristics of ferrite-plated films. Power ultrasound irradiation into reaction solutions has effects on the reduction of grain size and the improvement of crystallinity. The increase of the nucleation sites and the acceleration of the ion migration by the ultrasound enhancement are thought to cause the structural improvement. Doping Co^{2+} ions into Fe_3O_4 films increased $H_{c\perp}$ and caused perpendicular anisotropy. $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ plated films have the magnetic characteristics close to Co-Cr alloy films, and the magnetic characteristics of the films of 70 nm in thickness around at $x=0.5$ are as follows; $H_{c\perp}$ of 2.8 kOe, $H_{c\parallel}$ of 0.6 kOe, and M_s of 450 emu/cc.

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