PAPER *Special Issue on Recent Progress in Information Storage Technology*

Magnetic Properties and Recording Characteristics of Co-containing Ferrite Thin-Film Media Prepared by ECR Sputtering

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SUMMARY Co-containing ferrite thin-film media deposited by a reactive-ECR-sputtering at a low substrate temperature of 150 degree Celsius were oxidized by ECR plasma. The magnetic properties and recording characteristics of the media were improved by the oxidation with maintaining a smooth surface. The media showed high D_{50} of 203 kFRPI in MIG head recording and reproduction. The Co-containing ferrite thin-film is feasible to be used as a protective overcoat layer.

key words: *ECR sputtering, ferrite thin-film, perpendicular magnetic recording, recording media, post-oxidation, overcoat*

1. Introduction

At the beginning of research and development of Co-containing ferrite thin-film media for perpendicular recording, we have proposed the following preparation method [1]–[5]. At first, a NiO underlayer which played a role to control the crystal orientation of a subsequently deposited ferrite thin-film was reactive-sputter-deposited on a glass substrate. Then, a CoO-Fe_3O_4 thin-film was reactive-sputter deposited using an Fe-Co alloy sputtering target at a substrate temperature of about 200–300 degree Celsius. In thin-film deposition, conventional diode or magnetron sputtering apparatuses were used. The CoO-Fe_3O_4 thin-film was transformed to Co-γFe_2O_3 thin-film with high coercivity over 2000 Oe by a post-oxidization because the coercivity of the CoO-Fe_3O_4 thin-film deposited using conventional sputtering method was too low to utilize as a recording medium.

Recently, we have reported the Co-containing ferrite thin-film media prepared by a reactive sputtering method utilizing an electron-cyclotron-resonance (ECR) microwave plasma (reactive-ECR-sputtering) [6]–[9]. An interesting and useful point of this novel preparation method is that the Co-containing ferrite thin-film with high coercivity over 2500 Oe and perpendicular magnetic anisotropy can be obtained at low substrate temperatures from room temperature to 150 degree Celsius without any underlayers and post-oxidation.

In this paper, post-oxidation effects of the reactive-ECR-sputtered Co-containing ferrite thin-films are described focusing on morphology, magnetic and recording properties. The feasibility of the Co-containing ferrite thin-film used as a protective overcoat layer of the metallic thin-film media was also described.

2. Experimental

An ECR sputtering apparatus (AFTI Corp.: AFTEX-3400U) was employed to deposit Co-containing ferrite thin-films. Reactive sputtering was performed using a cylindrical Fe-Co alloy target with a Co content of 6 at.% in the mixture gas of argon and oxygen. Total sputter gas pressure and O_2 partial pressure were 0.080 Pa and 0.011 Pa, respectively. Microwave input power, target voltage and substrate temperature were set at 300 W, 250 V and 150 degree Celsius, respectively. In fabrication of the recording media, the Co-containing ferrite thin-film was directly deposited onto 2.5-in. glass disk substrate (OHARA Corp., TS-10ST) without depositing any underlayers and overcoat layers.

In the investigation of feasibility of Co-containing thin-film as the protective overcoat layer, a 20 nm thick Co-containing ferrite layer was reactive-ECR-deposited onto a 40 nm thick Co-Cr layer.

Measurement of magnetic properties and surface morphology of the media were performed using a vibrating sample magnetometer (VSM) and an atomic forced microscopy (AFM), respectively. Electric resistivity of the Co-containing ferrite thin-film was measured by putting two electrodes of resistivity meter on the film surface with a spacing of 7 mm. Recording characteristics was measured by using a flying type IND/AMR merged head and a contact-sliding type MIG head designed for 8 mm VCR.

Manuscript received January 22, 2002.
Manuscript revised April 8, 2002.

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Table 1 Magnetic properties and electrical resistivity, R of Co-containing ferrite thin-films.

	$H_{c\perp}$ [Oe]	$H_{c//}$ [Oe]	$S_{\perp}$	M_s [emu/cc]	$M_r t$ [memu/cm^2]	R [MΩ]
As-deposited ferrite thin-film	3110	820	0.56	234	0.52	0.020
Ferrite thin-film oxidized by ECR plasma	3180	1150	0.75	235	0.70	0.48
Ferrite thin-film annealed in air	3220	1240	0.82	225	0.74	480

3. Results and Discussions

3.1 Post-Oxidation Effects

The as-deposited Co-containing ferrite thin-film prepared by the reactive-ECR-sputtering method showed an electric resistivity of 20 kΩ which was almost same as that of an as-deposited $CoO\text{-}Fe_3O_4$ thin-film prepared by the conventional sputtering method and which was considerably low as compared with that of the $Co\text{-}\gamma Fe_2O_3$ thin-film prepared by the combination of conventional-sputter-deposition and post-oxidation performed by annealing in air, which typical electric resistivity is in the range from 100 MΩ to 1000 MΩ. For this reason, it was suspected that the as-deposited Co-containing ferrite thin-films prepared by reactive-ECR-sputtering method were insufficiently oxidized.

To investigate the oxidation effects, two kinds of post-oxidation were carried out for the 40 nm thick Co-containing ferrite thin-films prepared by the reactive-ECR-sputtering. One oxidation method is *annealing in air*, that is, samples are heated up and kept at 300 degree Celsius for one hour with applying a 1000 Oe magnetic field in perpendicularly to the film surface. Another oxidation method is *ECR plasma oxidation*: the samples are exposed to an oxygen plasma stream generated utilizing an ECR phenomena and a penning ionization effect of helium [4]. An ECR ion shower apparatus (ELIONICS Corp.: EIS-200ER) was used in the latter oxidation experiment. A microwave input power and an ion acceleration voltage and processing temperature were set at 150 W, 150 V and 150 degree Celsius, respectively. The ECR plasma oxidation time was 150 second and a magnetic field of about 350 Oe was applied perpendicularly to the film surface.

Table 1 shows the magnetic properties and electric resistivity (R) of the three Co-containing ferrite thin-films: as-deposited film, film oxidized by ECR plasma, and film annealed in air. Perpendicular squareness and coercivity of the as-deposited film were 0.56 and 3110 Oe, respectively. The ferrite thin-film oxidized by ECR plasma increased the perpendicular squareness from 0.56 to 0.75. The ferrite thin-film annealed in air increased perpendicular squraeness to 0.82 and the perpendicular coercivity to 3220 Oe.

Table 2 Grain size, R_a and $R_{\max}$ of Co-containing ferrite thin-films.

	Grain size [nm]	R_a [nm]	R_{max} [nm]
As-deposited ferrite thin-film	14.9	0.60	3.61
Ferrite thin-film oxidized by ECR plasma	18.4	0.64	3.44
Ferrite thin-film annealed in air	39.4	1.40	8.31

These fractional increase in perpendicular squareness and coercivity is supposed to be due to the increased magnetic anisotropy induced by application of magnetic field during oxidation and/or due to stress induced magnetic anisotropy. To clarify their reason, further experiment is necessary.

The ferrite thin-film oxidized by ECR plasma and annealed in air shows the increase in the electric resistivity of the film by 20 times and 20000 times as compared with the as-deposited film, respectively. This shows that these two oxidation methods are effective to promote the oxidation of the films.

Table 2 shows the surface morphology of the three kinds Co-containing ferrite thin-film media. The as-deposited Co-containing ferrite thin-film has a small grain size of 14.9 nm and a smooth surface R_a of 0.6 nm. The Co-containing ferrite thin-film oxidized by ECR plasma had a grain size of 18.4 nm and R_a of 0.64 nm, and remarkable changes in grain size and R_a were not observed. On the other hand, the film annealed in air had a grain size of 39.4 nm and R_a of 1.4 nm. In annealing, grains become large resulting in rough surface because of long time exposure in high temperature. It was proved that the ECR plasma oxidation was effective to improve magnetic properties as a recording layer with maintaining smooth surface and fine grains of the film.

3.2 Recording Characteristics of Co-containing Ferrite Thin-Film Media

The recording characteristics of the Co-containing ferrite thin-film media were measured and compared among the three samples: one was the as-deposited media by reactive-ECR-sputtering without post-oxidation. The other two media were ones post-oxidized by the ECR plasma for 150 second and by annealed in air. The characteristics of these Co-containing ferrite thin-film media were shown in Table 1 and Table 2.

The roll-off curves measured with a flying type IND/AMR merged head and a contact-sliding type MIG head are in Fig. 1 and Fig. 2, respectively. The specifications of using heads are shown in Table 3.

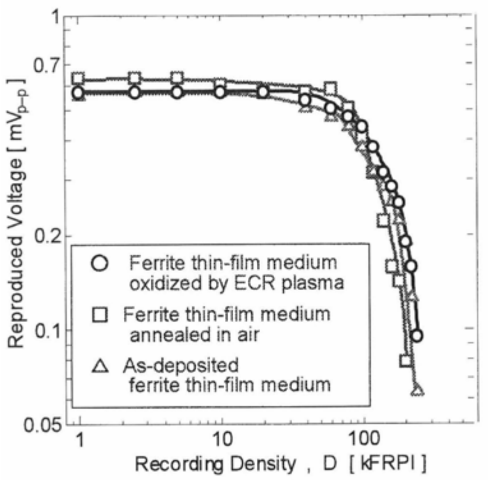

Fig. 1 Roll-off curves obtained in flying type IND/AMR head recording and reproduction.

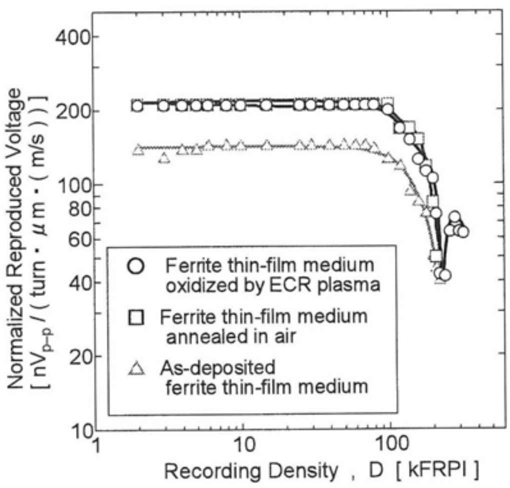

Fig. 2 Roll-off curves obtained in contact-sliding type MIG head recording and reproduction.

Table 3 The specifications of the IND/AMR head and MIG head.

	Gap length [μm] (IND/MR)	Track width [μm] (IND/MR)	Flying height [nm]
IND/AMR head	0.28/0.20	1.45/0.90	30
MIG head	0.20/—	20/—	—

In recording and reproduction using the flying type IND/AMR merged head, the substantial differences in reproduced voltage at lower recording density were not observed among these three media. The D_{50} for the post-oxidized media by ECR plasma, and post-oxidized media by annealing in air and as-deposited media were 160 kFRPI, 120 kFRPI and 138 kFRPI, respectively. The medium oxidized by ECR plasma showed the highest D_{50} because it had a small grains, small surface roughness and high perpendicular coercivity.

On the contrary, in recording and reproduction using the contact-sliding type MIG head, the reproduced voltage for post-oxidized media was higher than that of the as-deposited media approximately by 20%. The contact sliding type MIG head recording could magnetically saturate the media sufficiently as compared with the flying type IND/AMR merged head recording as described above. It is supposed that the increase in reproduced voltage was due to the increase in perpendicular coercivity and squareness of the media derived by post-oxidation. The D_{50} for the post-oxidized medium by ECR plasma was 203 kFRPI, which was slightly higher than that of the post-oxidized medium by annealing in air, 195 kFRPI. This might be caused by the influence of spacing loss caused by the different surface roughness.

The high value of D_{50} obtained in the contact sliding MIG head recording showed the fact that the coercivity of these media was too high to be magnetically saturated with the flying type IND/AMR merged head.

Figure 3 shows the noise spectra at 200 kFRPI, and Fig. 4 shows the signal to noise ratio of Co-containing ferrite thin-film medium measured with a flying type IND/AMR merged head.

The medium noise level for the media post-oxidized by annealing in air was higher than the other two media: as-deposited medium and ECR plasma oxidized medium. This high medium noise for the medium annealed in air was attributed to large grains of the media.

The ferrite thin-film medium oxidized by ECR

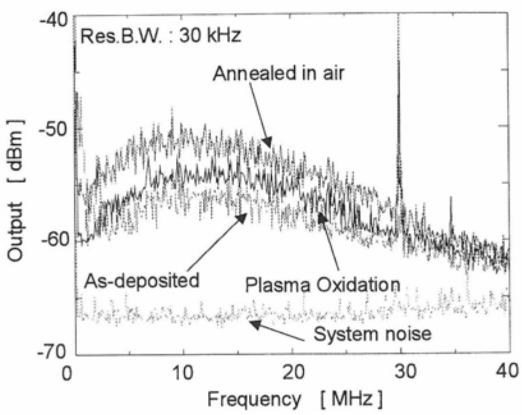

Fig. 3 Noise spectra at 200 kFRPI for three media.

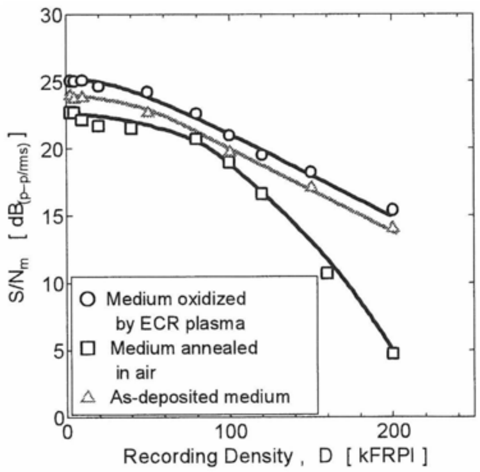

Fig. 4 Recording density dependence of signal-to-noise ratio of Co-containing ferrite thin-film medium obtained in flying type IND/AMR head recording and reproduction.

plasma shows a higher signal to noise ratio than the as-deposited medium and the medium oxidized by annealing in air as shown Fig. 4. This is because the ferrite thin film medium oxidized by ECR plasma had higher coercivity, larger squareness than the as-deposited medium, and also had minute grain and smooth surface as compared with the medium oxidized by annealing in air.

Therefore, it can be concluded that the combination of reactive-ECR-sputtering deposition and post-oxidation with ECR oxygen plasma is the most desirable preparation method of the Co-containing ferrite thin-film media.

3.3 Application of Ferrite Thin-Film to Protective Overcoat Layer

The fact, the ferrite film is extremely hard and can be deposited at a low temperature by ECR-sputtering, brought us expectation to use the ferrite film as a *magnetic protective overcoat layer* of the metallic recording layer.

Figure 5 shows the configuration of three kinds media prepared for this feasibility study. (a) is the ferrite thin-film medium with a 40 nm thick ferrite layer deposited directly on a glass substrate by reactive ECR sputtering without post-oxidation. (b) is the medium with a 20 nm thick ferrite thin-film protective layer on a Co-Cr layer. And (c) is the medium with a 20 nm thick SiO_2 protective layer on a Co-Cr layer. Samples (b) and (c) were prepared for comparison.

Evaluation of the tolerance to head scratching was carried out with a scanning type scratch tester (SIMADZU Corporation, SST). For comparison, the test was also performed on the commercial longitudinal hard disk with a diamond like carbon overcoat layer. The results of the scratch test are listed in Table 4.

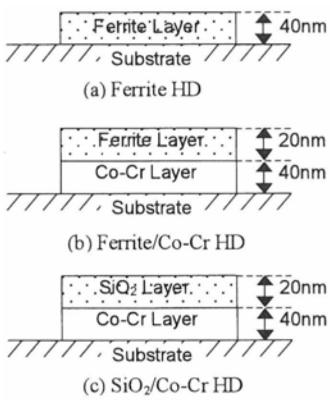

Fig. 5 Structure of Ferrite HD, Ferrite/Co-Cr HD and SiO_2/Co-Cr HD.

Table 4 Scratch test results for Ferrite HD, Ferrite/Co-Cr HD, SiO_2/Co-Cr HD and commercial HD with DLC protective overcoat layer.

	Scratch load [mN]
(a) Ferrite HD	558
(b) Ferrite/Co-Cr HD	550
(c) SiO_2/Co-Cr HD	521
Commercial hard disk with DLC layer	552

The scratch load is defined as the loading force at the moment of peeling off or destruction of the film. The scratch load of the ferrite thin-film medium and the Co-Cr medium with a ferrite thin-film were approximately 550 mN. This value was larger than that of the Co-Cr medium with the SiO_2 protective layer, and was almost same as that of the commercial hard disk.

As the ferrite thin-film has an extremely high tolerance to scratching which is almost same as a diamond like carbon overcoat, contact sliding recording with a MIG head was tried on the Co-Cr medium with the ferrite thin-film and SiO_2 protective overcoat layer. Figure 6 and Table 5 shows the roll-off curves and magnetic properties of two kind media, respectively. It was confirmed that the both media did not damage in this contact sliding operation. The reproduced voltage of the medium with a ferrite thin-film protective overcoat layer was higher than that of the media with the SiO_2 overcoat layer. Therefore, the ferrite protective overcoat layer acts as not only a protective layer but also a recording layer.

4. Conclusions

The following results were obtained in this study.

(1) Post-oxidation of reactive-ECR-sputtered Co- con-

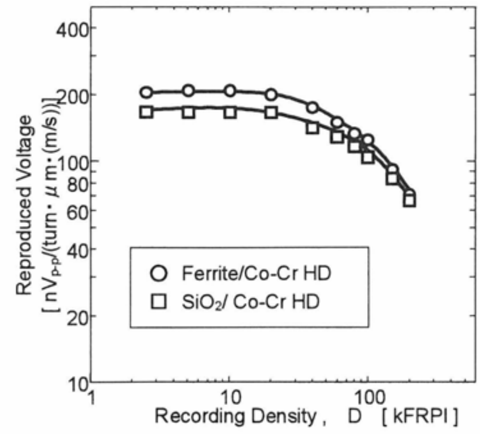

Fig. 6 Roll-off curves of Ferrite/Co-Cr HD and SiO_2/Co-Cr HD obtained in contact-sliding type MIG head recording and reproduction.

Table 5 Magnetic properties of Ferrite/Co-Cr HD and SiO_2/Co-Cr HD.

	$H_{c\perp}$ [Oe]	$S_\perp$
(b) Ferrite/Co-Cr HD	2712	0.61
(c) SiO_2/Co-Cr HD	1975	0.36

taining ferrite thin-films in magnetic field increased perpendicular coercivity and perpendicular squareness. ECR plasma oxidation method is preferable to oxidation method by annealing because smooth surface and fine grains were maintained even after oxidation.

(2) Superior recording characteristics was obtained when the Co-containing ferrite thin-film media were employed combining with the contact sliding type MIG head. The medium oxidized by ECR plasma showed low medium noise and high D_{50} than the media annealed in air.

(3) Reactive-ECR-sputtered ferrite thin-film is applicable to a protective overcoat layer of the magnetic recording disk because it has extremely high tolerance to scratching.

Thus, it is concluded that the combination of the reactive-ECR-sputter deposition and post-oxidation with ECR plasma is the best preparation method of Co-containing ferrite thin-film, and that the Co-containing ferrite thin film can be used as an overcoat protective overcoat layer.

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