Microstructure of electroless Co alloy films for perpendicular magnetic recording

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Abstract. The mechanism of columnar crystallite orientation in electroless Co–Ni–Mn–P films for perpendicular magnetic recording media was investigated using SEM, TEM and other methods. Micro-region analysis revealed that the Ni and P in the film is mainly distributed in the grain boundary. So it is suggested that the film has a segregated microstructure. The segregation of Ni–P alloy is the main cause which makes the c axis of α-Co orient along the film normal and the columnar grain become fine. Magnetic measurements also showed that the films had a good perpendicular property.

1. Introduction

Since Osaka [1] developed electroless-plated Co–Ni–Mn–P films (with an α-Co HCP structure) as perpendicular recording media, many investigations [2, 3] on these media have revealed that the $MnSO_4$ concentration in the bath is an important factor which controls the film microstructure and magnetic properties. This effect may be attributed to the adsorption of Mn complexing ions at the interface rather than to the codeposition of Mn in the film. In 1986 [4], the electroless Co–Ni–Mn–P film was developed and further research was carried out on its microstructure and magnetic properties [4, 5]. From dark field image observations [5], it was proposed that the film was composed of a ferromagnetic Co-rich phase inside a columnar particle which is surrounded by a non-magnetic Ni–P alloy phase, but there is no direct evidence about this. So far the mechanism of film growth with the c axis of α-Co normal to the plane is also not very clear.

In our previous paper [6], the results of XPS analysis revealed that there is a very close relation between P^0 (the zero valence state) content deposited and the degree $\Delta\theta_{50}$ of perpendicular orientation of the film. It is suggested the phosphorus (or its alloy) is an important factor, which directly concerns the columnar grain orientation. In this paper, we shall report some results obtained from SEM, TEM, etc, and the probable mechanism of the effect of the Ni–P alloy on the film microstructure will be discussed.

2. Experimental results

Electroless Co–Ni–Mn–P films were plated from the bath of composition given in table 1 and the basic compositions and operating conditions of the bath were selected according

Table 1. Basic compositions and operating conditions of the plating bath for Co alloy films. The pH value (adjusted by NH_4OH at room temperature) is 9.6. The operating temperature of the bath is $80 \pm 5\,°C$.

Chemical	Concentration (M)	Chemical	Concentration (M)
$(NH_4)_2SO_4$	0.5	NaH_2PO_2	0.2
$CoSO_4$	0.035	$CH_2(COONa)_2$	0.5
$NiSO_4$	0.01	$C_2H_3(OH)(COONa)_2$	0.05
$MnSO_4$	0.0–0.05		

to [1]. The concentration of $MnSO_4$ in the bath was adjusted in order to investigate its influence on the film microstructure. The substrates used in the experiment were polyimide, which were pre-treated as in our previous paper [7], i.e. degreased in ethanol, immersed in 10% HCl, roughened in 0.4 M NaOH, sensitized in $SnCl_2$–HCl and activated in a solution of $PdCl_2$–HCl. The plating time for all films is 10 min and all the samples used in each experiment were prepared under the same conditions except for the concentration of $MnSO_4$ in the plating bath. An x-ray diffractometer (D/MAX-RB, Rigaku, Cu $K\alpha$) was used to determine the film crystal structure. The orientation degree $\Delta\theta_{50}$ of the c axis of α-Co normal to the film plane was obtained from the Co(002) rocking curve. SEM observations on the films were carried out using a Hitachi S-450 scanning electron microscope and the mean composition deposited in film was measured with an electron probe (sensitivity, 0.5%). Cross sectioned samples were prepared by a simple method of tearing the film into two pieces. The film thickness can be also deduced from cross section SEM observations.

To perform TEM observations and micro-region analysis on film Z and film F (plated under 0.0 M and 0.04 M $MnSO_4$, respectively), the films were treated as follows: they were immersed in a 0.6 M NaOH solution for about 20 min to separate the films from their substrates, then attached to a double mesh and finally etched with a two-beam ion gun until suitable for the analyses. A Phillips EM-400T transmission electron microscope and its electron probe attachment (the diameter of the beam is 400 Å and the sensitivity is 0.5%) were used in the experiment. Finally, a vibrating-sample magnetometer and torque magnetometer were used to measure the magnetic properties of the films.

The results of x-ray diffraction revealed that all films have an HCP Co structure, with its c axis preferentially oriented normal to the film plane. Figure 1 shows the $MnSO_4$ concentration dependence of perpendicular orientation degree $\Delta\theta_{50}$ obtained from the Co(002) rocking curve. When the $MnSO_4$ concentration is 0.04 M, the value of $\Delta\theta_{50}$ reaches a minimum. This implies that the film has a good orientation. For $MnSO_4$ concentrations above 0.04 M, $\Delta\theta_{50}$ increases sharply.

Figure 2 shows some surface and cross section SEM photographs. It is very clear there are two features in figure 2(a).

(1) The grain size decreases gradually on increase in $MnSO_4$ concentration and the crystallites become more uniform when the $MnSO_4$ concentration is equal to 0.04 M.

(2) In figure 2(a) (4), the morphology of film surface is needle like, implying that maybe another preferential orientation of crystallites except the main texture of the c axis normal to the film plane exists. This is consistent with the results shown in figure 1, i.e. this film has a large $\Delta\theta_{50}$.
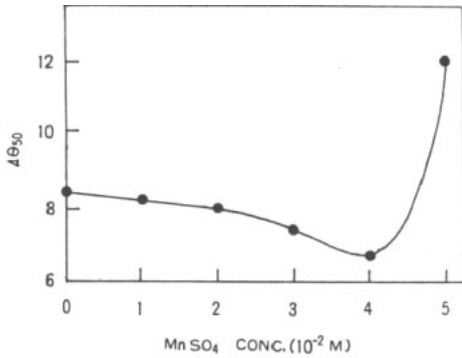
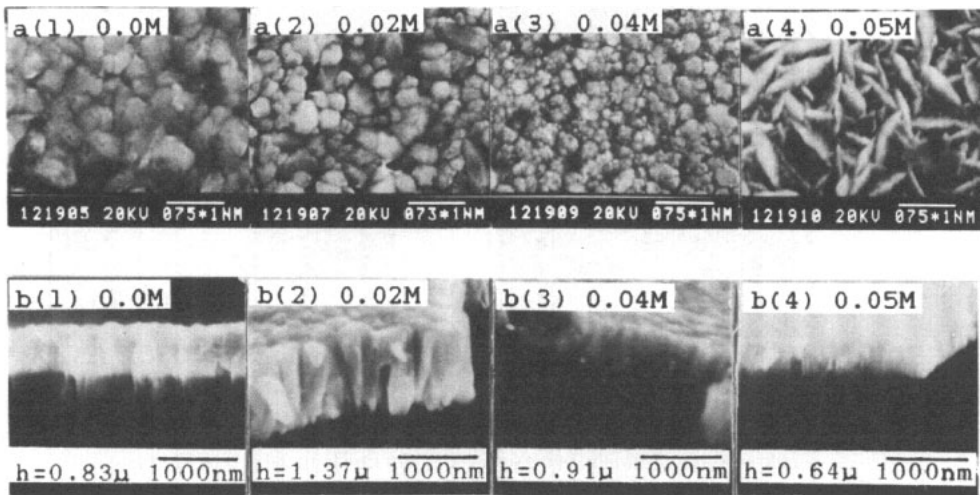**Figure 1.** The relationship between $\Delta\theta_{50}$ and $MnSO_4$ concentration.

Figure 2. SEM photograhs of (*a*) surface (*b*) cross-section for films plated under various $MnSO_4$ concentrations.

From figure 2(*b*), the columnar grains perpendicular to the film plane can be seen very clearly and the grain size decreaes with increasing $MnSO_4$ concentration. Although this feature is not very obvious in figure 2(*b*) (4), some inclined columnar grains can still be seen.

The mean composition deposited in the films was demonstrated in figure 3. On increase in $MnSO_4$ concentration, the Co and Ni contents almost remain constant; the Mn content increases slowly; only the P component increases notably. It varies from 2 to 6 at.%.

Figure 4 shows the typical bright-field image and electron diffraction pattern of a single grain in film F. The crystallites are in tight contact with each other. So the grain boundary is very narrow and vague in some regions. The features of the electron diffraction pattern demonstrate that the crystallite has an HCP Co structure and its ⟨001⟩ axis is almost parallel to the incident direction of the electron beam.
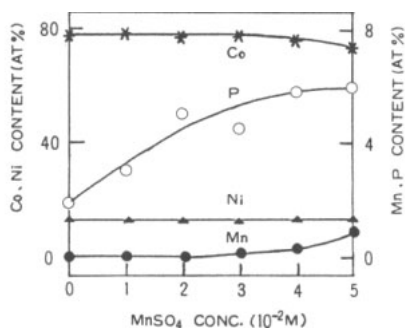
Figure 3. The dependence of composition deposited in the film on the $MnSO_4$ concentration in the bath. These data were obtained using the SEM attachment of the electron probe.
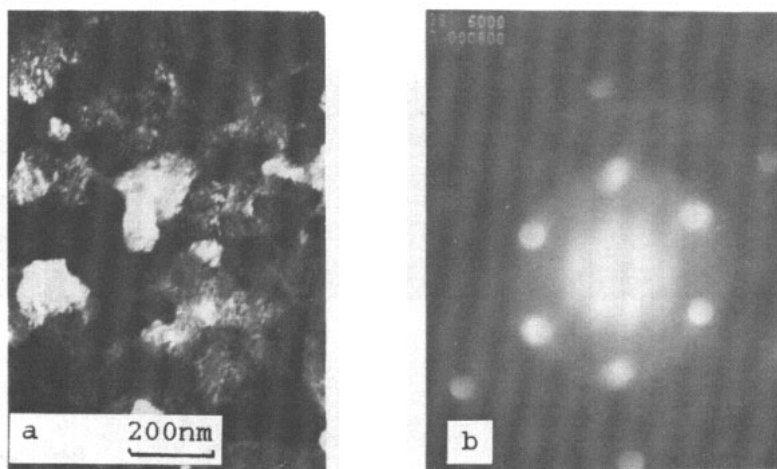

Figure 4. (*a*) The typical bright-field image of TEM and (*b*) electron diffraction pattern of single crystallite from the plane near (001)* for film F plated in 0.04 M $MnSO_4$.

The selected areas for point analysis of composition and the corresponding compositions are given in figure 5 and table 2, respectively. From table 2, several features in the component distribution can be found.

(1) The P content in the grain boundary is always higher than that in the region of related grains. On average, it is about 17% (film Z) or 36% (film F) higher than that in the region of related grains. Meanwhile the Ni content has the same trend.

(2) The distribution of Mn in film F is not uniform. In some regions (A1 and B1), its content is to low to detect but, in other regions (i.e. A2 and D2), this component can not be ignored. It can also be deduced from table 2 that the Mn is mainly distributed in grains.

(3) Because of segregation of elements in the micro-region, the average composition displayed in table 2 differs from that shown in figure 3 for the same film. The error of the measurement in table 2 is about 5%.

Figure 6 shows the hysteresis loops of film F, which is the same as that used in the SEM, TEM and x-ray diffraction experiments. In this figure, no calibration of the demagnetization factor was made and it seems that the perpendicular loop does not
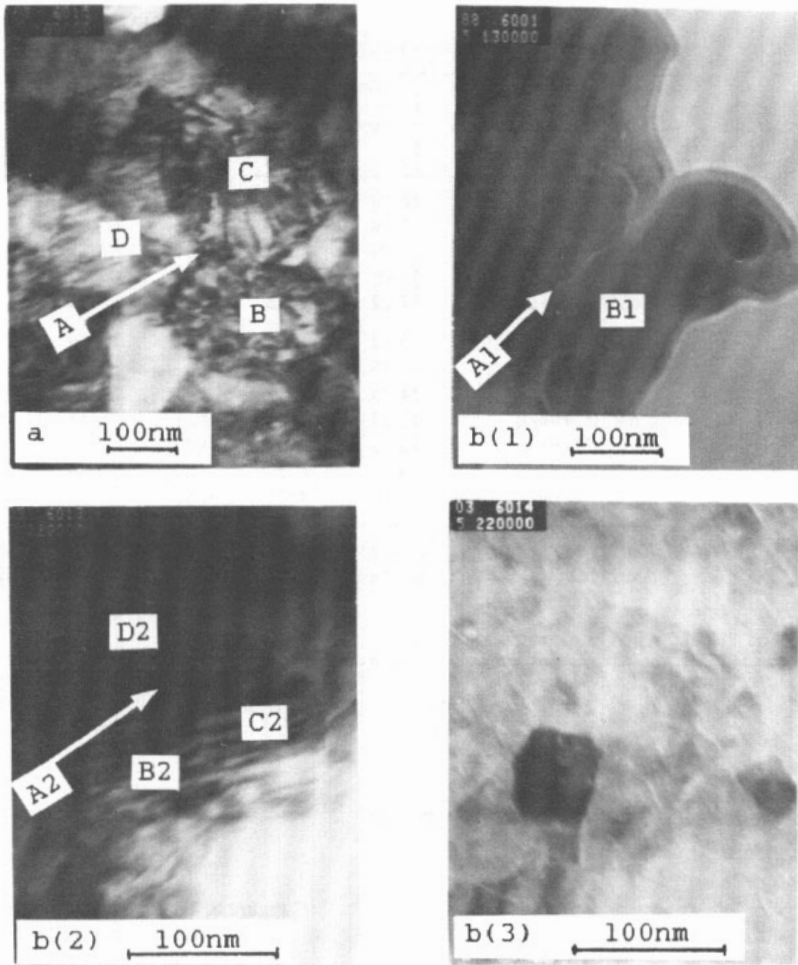
Figure 5. TEM photographs and indications of selected areas for point analysis of (*a*) film Z and (*b*) film F plated in 0.0 M and 0.04 M $MnSO_4$, respectively. Except for the grain size differences between the four images may be mainly caused by the differences between the morphology of surface and thickness of the TEM samples in the selected areas. They will produce a different contrast.

reach saturation. The reason for this may be that the applied field is not strong enough. The relative shapes of the curves imply that the film has a good perpendicular magnetic property. The values of some magnetic parameters are as follows: $H_k = 7.8$ kOe, $H_c(\perp) = 1.91$ kOe, $H_c(\|) = 1.43$ kOe, $SR(\perp) = 0.205$, $SR(\|) = 0.212$ and $K_u = -1.43 \times 10^6$ erg cm^{-3}.

3. Discussion

The concentration of $MnSO_4$ is a very important factor in the plating bath. It controls the orientation degree $\Delta\theta_{50}$ of the *c* axis of α-Co normal to the film plane. From figure

Table 2. Compositins in several selected areas. The error in the data is about 5%: GB, grain boundary; RRG, region of related grains.

Selected area	Content (at. %)			
	P	Ni	Mn	Co
Film Z, A (GB)	10.50	16.94	0.0	72.56
Film Z, B (RRG)	7.29	9.11	0.0	83.60
Film Z, C (RRG)	9.19	14.65	0.0	76.17
Film Z, D (RRG)	10.46	11.76	0.0	77.79
Film Z, Average[a]	7.02	13.52	0.0	79.46
Film F, A1 (GB)	9.04	8.70	0.0	82.26
Film F, B1 (RRG)	6.75	7.40	0.0	85.85
Film F, A2 (GB)	14.26	14.39	0.24	71.14
Film F, B2 (RRG)	12.03	12.29	0.21	75.47
Film F, C2 (RRG)	10.49	10.63	0.29	78.59
Film F, D2 (RRG)	8.51	10.13	1.00	80.36
Film F, Average[b]	9.14	10.74	0.60	79.52

[a] Average composition in the region around A shown in figure 5(a) (600 nm in diameter).
[b] Average composition in the region shown in figure 5(b) (3) (300 nm in diameter).
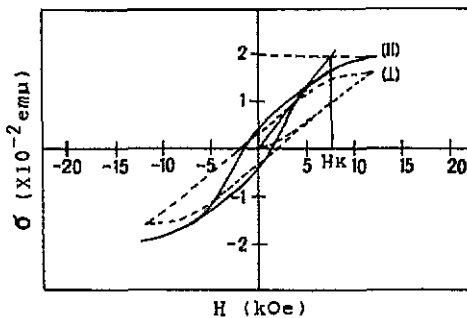

Figure 6. The hysteresis loops of film F plated in 0.04 M $MnSO_4$. No calibration of demagnetization factor was made in the figure.

3 and table 2, the Mn content is very low and increases slowly with increasing $MnSO_4$, concentration, implying that Mn is very difficult to codeposit into the film. This is the same as reported in [3]. The results shown in table 2 also reveal that the Mn deposited in the film is mainly distributed in the crystallites. Because of similarity between the electronegativities (ENs) and sizes of Co and Mn (EN(Co) = 1.8, R(Co) = 1.253 Å and EN(Mn) = 1.5, R(Mn) = 1.26 Å), the Mn atoms possibly replace some Co atoms, forming Co–Mn solid solution with an HCP Co structure. This suggestion is consistent with that reported in [7].

From the above analysis, the effect of $MnSO_4$ on the film microstructure should not be due to the Mn codeposition into the film. So we should focus on phosphorus or its alloy in the film. First of all, the P content in the film increases with increasing $MnSO_4$ concentration notably, and the grain size decreases. Next the P component segregates considerably at the grain boundary and the amount of segregation is enhanced from 17% for film Z to 36% for film F. Although the mean content of Ni in the film remains constant with $MnSO_4$ concentration, the results of the micro-region analysis given in

table 2 demonstrate that its segregation at the boundary is very high (about 30%). These facts enable us to draw the following conclusions or to make the following suggestions.

(a) Phosphorus is insoluble in the cobalt lattice [8] because of the large difference between the atomic radii of P and Co (1.10 Å for P, and 1.253 Å for Co). Phosphorus is mainly distributed in the boundary to reduce the free energy of the system caused by the lattice distortion.

(b) In general, nickel atoms can replace some Co, forming Co–Ni solid solution with an HCP structure [9]. However, in Co–Ni–Mn–P films, it may easily combine with P, forming Ni–P alloy in a crystalline or amorphous state.

(c) On the basis of (a) and (b), it is suggested that the electroless Co–Ni–Mn–P films have a segregated microstructure, i.e. the ferromagnetic columnar grain of the Co-rich phase is surrounded by the non-magnetic Ni–P alloy phase.

(d) The segregation of Ni–P alloy at the boundary may be the main factor in making the c axis of α-Co normal to the film plane. The higher the amount of Ni–P segregation is, the better orientation the crystallites can achieve. Meanwhile the Ni–P phase in the film has a function in making the columnar particles fine. This may be beneficial to the enhancement of recording density.

As in [3], the dependence of film properties on the concentration of $MnSO_4$ should be attributed to its influence on the chemical or electrochemical properties of complexing ions in the plating bath, which affects the characteristics of the film–solution interface and eventually leads to the formation and distribution of the Ni–P phase in the film depending on the $MnSO_4$ concentration.

Additionally, the coercive force, both $H_c(\perp)$ and $H_c(\parallel)$, has a large value and $SR(\perp)$ is slightly smaller than $SR(\parallel)$ for film F. These properties should be related not only to the orientation of columnar grain but also to the phase composition of the film, such as the segregation of Ni–P alloy. Furthermore, the low $SR(\perp)$ (relative to $SR(\parallel)$) may be due to the large demagnetization energy $2\pi M_s^2$ of film, which causes the effective anisotropy constant ($K_u = K_1 - 2\pi M_s^2 = -1.4 \times 10^6 \, erg \, cm^{-3}$) to be negative and makes M_s have a tendency to be oriented along the film plane.

It is worth mentioning that there exists a deviation between the data of some film properties (e.g. curves of $\Delta\theta_{50}$ against $MnSO_4$ concentration and of P content against $MnSO_4$ concentration) reported in [3] and presented here. This difference may be due to the following two facts. First, the substrate material has an effect on the film microstructure [2]. The substrate used in [3] is copper sheet and Ni–P alloy, but in this paper the film was plated on polyimide. Second, the substrate pre-treatment was done chemically. These processing and operating conditions should affect the film properties and the two above facts were noticed during our experiment.

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