Complete Magnetic Anisotropy Films for Perpendicular Recording Prepared by an Electroless Plating Method

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A complete magnetic anisotropy film was formed by an electroless plating method for a high-density perpendicular recording medium. The Co alloy plating bath, using ammoniacal malonate-tartrate-succinate mixed complexing agents was studied mainly by varying three main metal ion factors in the bath: *i.e.*, the concentrations of $NiSO_4$, NH_4ReO_4, and $MnSO_4$. The fine columnar structure of magnetic film in a cross section was confirmed by SEM observation. Three different kinds of eight-inch disks A, B, and C, were prepared under selected conditions with magnetic film thickness of 0.50, 0.25, and 0.20 μm respectively. The recording performance was evaluated with a Winchester ring head with a 0.33 μm gap length under various head-medium spacings. A perpendicular recording mode was confirmed, and the following recording densities were obtained: D_{50}=54 and 58 kFRPI for disk A, and 57 and 63 kFRPI for disk B when using 0.20 and 0.15 μm practical usable spacing respectively, and D_{50}=68 kFRPI for disk C when using the more advanced 0.12 μm spacing. It was suggested that the electroless cobalt alloy plating has a high potential as a process for producing perpendicular recording media.

Since the proposal of a perpendicular recording system by the Iwasaki school,[1,2] interest in it has exploded as a high potential technology to extend the limit of the present longitudinal recording system. Many workers have reported on perpendicular recording media, such as sputtered Co–Cr,[3] sputtered Ba ferrite,[4] evaporated Co–Cr[5] and coated Ba ferrite.[6] Recently, many extensive studies have been reported, not only of the medium but also of the perpendicular recording system, such as the spacing effect of the read/write conditions,[7] a comparison of the read/write characteristics between using a ring head and using a perpendicular head,[8] and the evaluation of the whole system for a perpendicular recording floppy disk drive.[9]

However, only a few attempts[10–13] have been made to use the electroless plating method to produce a medium which has higher productivity and cost performance. If the perpendicular medium could be obtained by means of an electroless plating method, as well as the longitudinal-recording-mode disk developed by NEC Corporation,[14] the realization of the system, with its merits of mass production and wear durability, would be accelerated.

With such considerations in view, the present authors attempted to prepare perpendicular recording media by means of an electroless plating. It was first reported by the present authors[10] that the perpendicular oriented c-axis of the cobalt hcp structure can be easily obtained by means of manganese codeposition into Co–Ni–P films; nevertheless, a very small amount of manganese is codeposited.[13] Moreover, the decrease in the saturation magnetization, which produces the completely magnetic anisotropy film, was performed by the rhenium codeposition into Co–Ni–Mn–P film.[15–18]

This communication reports the preparation of a new stable electroless bath for completely magnetic anisotropy films and their recording performance.

Experimental

Electroless cobalt alloy films were plated from an ammoniacal malonate-tartrate-succinate complexing-agent bath, whose composition and conditions were listed in Table 1. A polished electroless plated Ni–P film, composed of amorphous states, was usually used as a substrate, and an activated copper sheet was used only for the compositional analysis. The film composition of Co, Ni, Re, Mn, and P was determined 0.5 μm thick films by EPMA and X-ray fluorescence methods. The X-ray diffraction patterns and rocking curves for the plated films were measured by means of X-ray diffractometer with an Fe target. The magnetic properties were measured in 0.5μm thick films by the use of a vibrating sample magnetometer and a torgue magnetometer in a 10 kOe maximum applied field. Coercivities $Hc(\perp)$ and $Hc(//)$ were evaluated from the M–H hysteresis loops measured in perpendicular($\perp$) and parallel(//) magnetic fields. The anisotropy field, Hk, was evaluated from the in-plane M–H hysteresis loop. SEM photographs for a cross section of the magnetic film were obtained by means of an Hitachi S-700 field emission SEM with a magnification of

TABLE 1. ELECTROLESS PLATING BATH COMPOSITION AND CONDITIONS

Chemicals	Concentration/mol dm^{-3}
$NaH_2PO_2 \cdot H_2O$	0.30
$(NH_4)_2SO_4$	0.50
$CH_2(COONa)_2 \cdot H_2O$	0.30
$C_2H_2(OH)_2(COONa)_2 \cdot 2H_2O$	0.20
$C_2H_4(COONa)_2$	0.30
$CoSO_4 \cdot 7H_2O$	0.06
$NiSO_4 \cdot 7H_2O$	0.06—0.16
NH_4ReO_4	0—0.009
$MnSO_4 \cdot 4$—$6H_2O$	0—0.09
Bath temperature	80 °C
pH adjusted by NH_4OH	9.2

20000 and 50000. Eight inch disks were prepared with the bath conditions selected. The disk structure was the same as that reported in a previous paper.[12] The protective SiO_2 overcoat was formed by means of a spin-coat method.

Results and Discussion

Electroless Plating Bath for Perpendicular Recording Media. On the basis of various investigations for complexing agents, the ammoniacal malonate-tartrate-succinate mixed system was first selected, considering that sodium malonate and sodium tartrate tend to be favorable complexing agents for cobalt and perrhenate ions respectively, and further that sodium succinate tends to improve the $\Delta\theta_{50}$ value of the c-axis orientation. Moreover, the bath stability was improved by using a mixture of the three complexing agents.

Since the bath pH hardly affected the perpendicular orientation of the hcp structure and the magnetic anisotropy properties in the region between pH 8.8 and 9.4 in a manner dissimilar to that reported in the previous research,[13] the bath pH of 9.2, showing relatively favorable conditions, was chosen in this research.

The metal ion concentrations are a very important factor, like the complexing agents, in controlling magnetic properties. The cobalt sulfate was first fixed at 0.06 mol dm^{-3} in order to obtain optimum conditions for the other metal ion concentrations on the basis of the experimental results regarding the effect of the ratio of cobalt and phosphinate ions on the magnetic properties. Under the conditions at a fixed 0.06 mol dm^{-3} $CoSO_4$, the effects of the other metal ion concentrations of $NiSO_4$, NH_4ReO_4, and $MnSO_4$ on film properties were also investigated, as shown later.

The effects of the $NiSO_4$ concentration on the magnetic properties and the half width for the rocking curves of the (002) plane, $\Delta\theta_{50}$, have already been indicated in previous papers.[16,17] It was also reported there[16,17] that the optimum conditions for perpendicular magnetic anisotropy film were obtained in the $NiSO_4$ concentration region between 0.12 and 0.16 mol dm^{-3} at the fixed concentrations of 0.005 mol dm^{-3} NH_4ReO_4 and 0.05 mol dm^{-3} $MnSO_4$. In the above region, the magnetic anisotropy energy, *Ku*, became positive and reached its maximum value (1.6×10^5 erg cc^{-1}) at 0.12 mol dm^{-3} $NiSO_4$. The saturation magnetization, *Ms*, was also reported to gradually decrease with an increase in the $NiSO_4$ concentration.

From the effect of the $NiSO_4$ concentration on the compositional analysis for plated films, shown in a previous paper,[18] it was concluded that the increase in the $NiSO_4$ concentration caused the cobalt content to decrease and the nickel content to increase with constant values of 6 at% Re, 0.2 at% Mn, and 11 at% P.

The effect of the ammonium perrhenate concentration on the magnetic properties and the $\Delta\theta_{50}$ at the fixed concentrations of 0.12 mol dm^{-3} $NiSO_4$ and 0.05 mol dm^{-3} $MnSO_4$ is shown in Fig. 1. Since the Co–Ni–Mn–P films previously reported[12] did not become a complete magnetic anisotropy film, because of their higher *Ms* value, the rhenium codeposition into Co alloy film was intended to produce the *Ms* decrease in films. The demagnetized field, $Hd=4\pi Ms$, decreases with the decrease in Ms; therefore, a proper decrease in the *Ms* values could realize complete magnetic films with positive *Ku* values. Since it was very difficult to codeposit chromium into Co alloy film by means of an electroless plating method, whose codeposition could be easily deduced as a candidate from a sputtered Co–Cr film, the codeposition of rhenium, instead of chromium, was attempted in an effort to make the *Ms* decrease. The very small amount of NH_4ReO_4 into the bath made the Ms value decrease as shown in Fig. 1(b). Consequently, it produced a change in the *Ku* value from negative to positive, as may be seen in Fig. 1 (a). The other magnetic factors of *Hk* and ΔHc $(=Hc(\perp)-Hc(//))$ also showed optimum values in the concentration region between 0.003 and

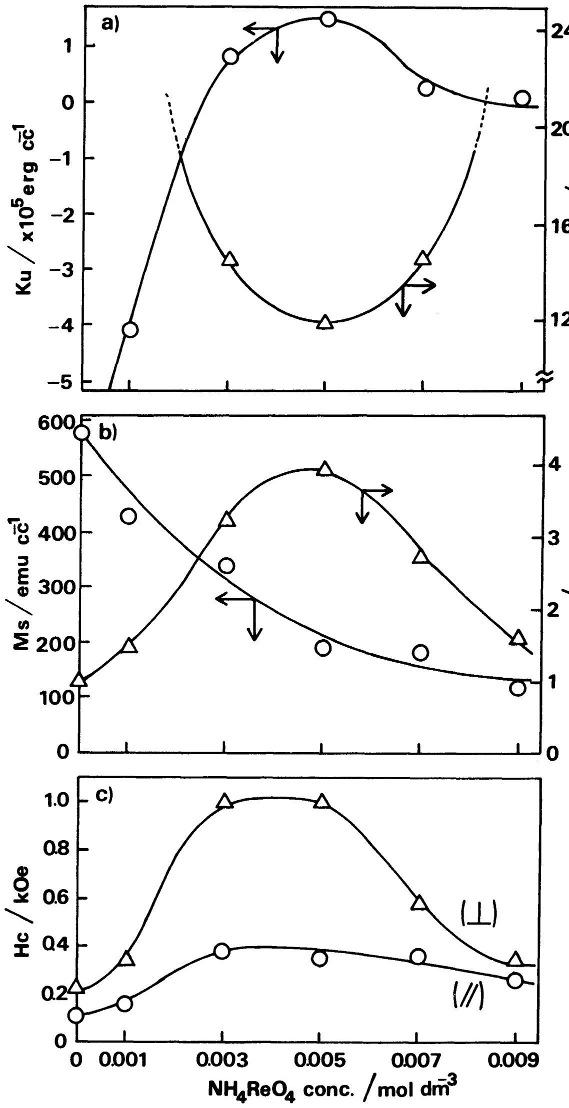

Fig. 1. Effects of NH_4ReO_4 concentration on magnetic properties and $\Delta\theta_{50}$ of (002) plane for plated films using 0.5 μm thickness.

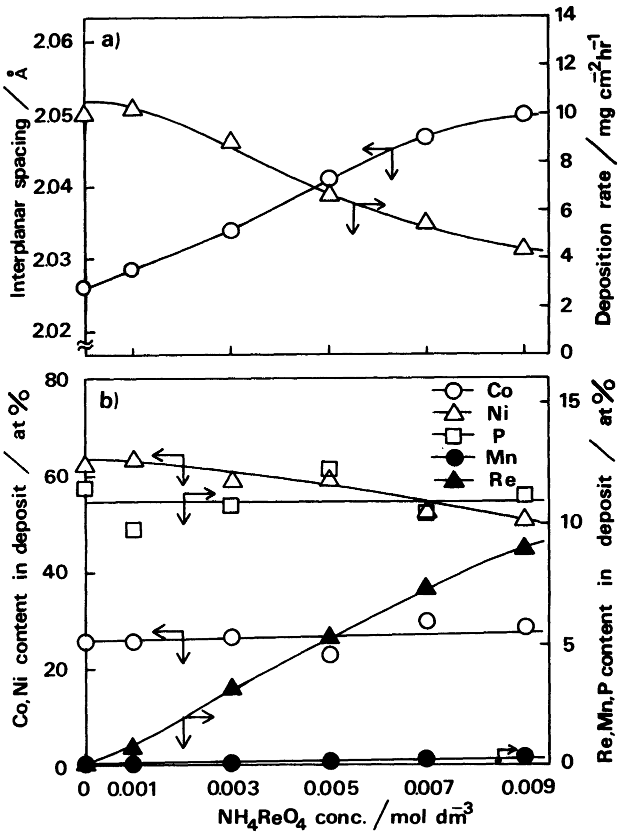

Fig. 2. Effect of NH_4ReO_4 concentration on film composition, interplanar spacing and deposition rate for plated films using 0.5 μm thickness.

0.006 mol dm^{-3} NH_4ReO_4. The $\Delta\theta_{50}$ value also reached its minimum in the same concentration region and reached the minimum value of 12 degrees at 0.005 mol dm^{-3} NH_4ReO_4.

The compositional analysis for the variation in the NH_4ReO_4 concentration is demonstrated in Fig. 2(b). The film composition for Co and P was independent of the NH_4ReO_4 concentration, while the increase in the NH_4ReO_4 concentration made the rhenium content increase linearly, accompanied by the decrease in the Ni content. The very small manganese codeposition (Mn=0.05—0.40 at%) slightly increased with the increase in the NH_4ReO_4 concentration. In Fig. 2(a), the interplanar spacing value, d, from the hcp structure, calculated from the X-ray diffraction patterns, increased with an increase in the NH_4ReO_4 concentration, *i.e.*, the increase in the Re content. This is unlike the case of the $NiSO_4$ variation, in which the d value was independent of the $NiSO_4$ concentration. It can be concluded by the above results that the replacement of Re atoms with Co atoms produces a widening of the d value in the hcp lattice, because the atomic radius of Re is larger than that of Co. For reference, the deposition rate of the films is also shown in Fig. 2(a). The deposition rate decreased with an increase in the NH_4ReO_4 concentration. It became 6—7 mg cm^{-2} h^{-1} in the optimum condition region.

Figure 3 shows the effect of the $MnSO_4$ concentration on the magnetic properties and the $\Delta\theta_{50}$ value. As has already been stated, the $MnSO_4$ addition to the bath causes a perpendicular orientation of the hcp structure, in spite of the very small manganese codeposition into the film. The Ku and the $\Delta\theta_{50}$ values greatly increased and decreased, respectively, up to 0.04 mol dm^{-3} $MnSO_4$. The Ku value decreased with the increase in the $MnSO_4$ concentration from the above concentration. The X-ray diffraction peaks were not obtained in a $MnSO_4$ concentration region more than 0.05 mol dm^{-3}. The optimum conditions for magnetic properties lie in the region between 0.03 and 0.05 mol dm^{-3} $MnSO_4$. In Fig. 4(b), the dependence of the $MnSO_4$ concentration on the film composition indicates that each content is almost independent of the $MnSO_4$ concentration up to 0.03 mol dm^{-3}. Further, the phosphorus content increases

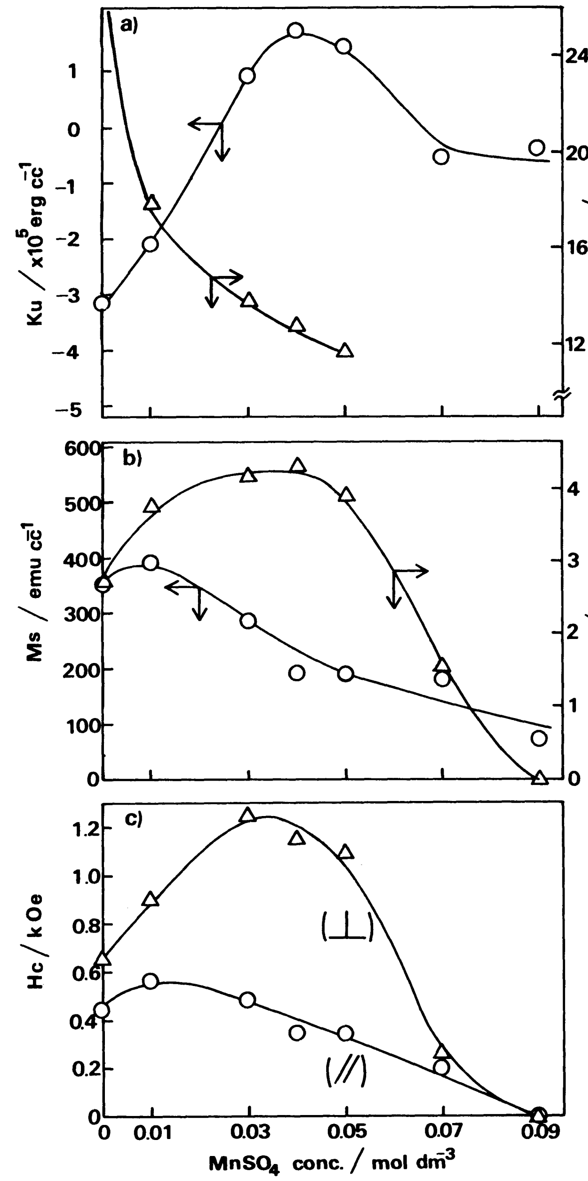

Fig. 3. Effect of $MnSO_4$ concentration on magnetic properties and $\Delta\theta_{50}$ of (002) plane for plated films using 0.5 μm thickness.

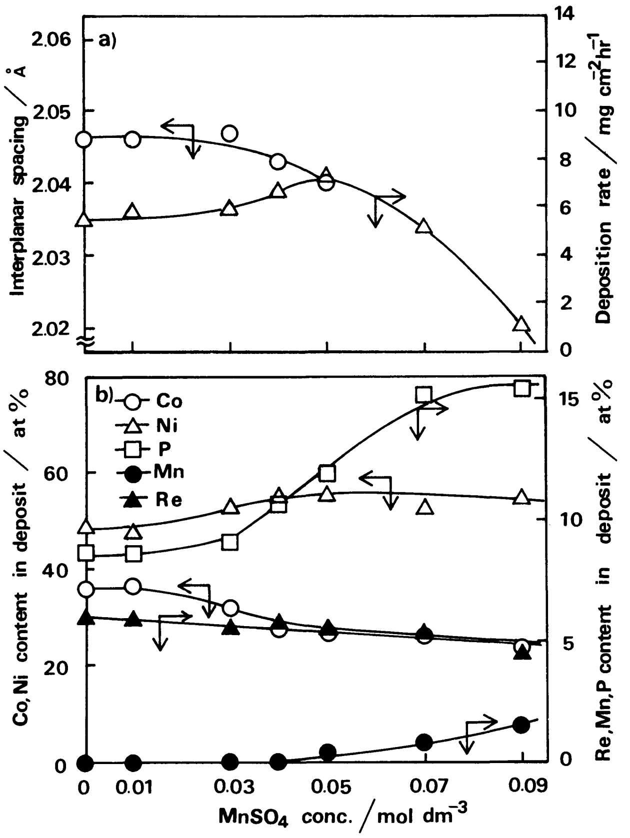

Fig. 4. Effect of $MnSO_4$ concentration on film composition, interplanar spacing and deposition rate for plated films using 0.5 μm thickness.

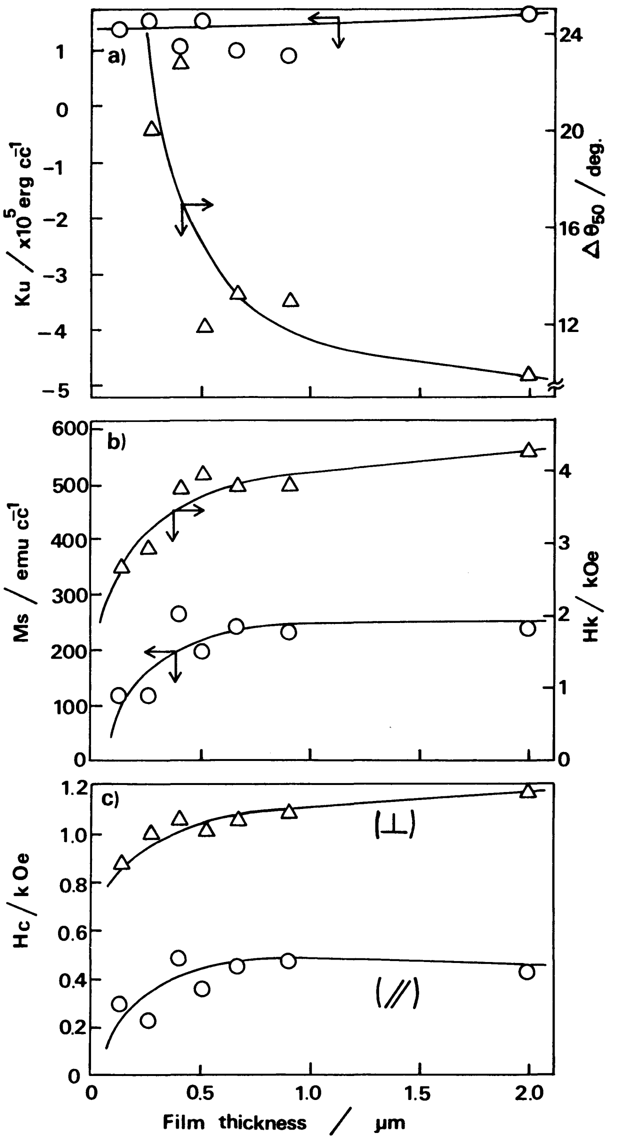

Fig. 5. Effect of film thickness on magnetic properties and $\Delta\theta_{50}$ of (002) plane for plated films.

when the manganese starts to codeposit into the film. A small decrease in the *d* value also appeared from the initial point of Mn codeposition, as may be seen in Fig. 4(b). Thus, the variation in the *d* value and the increase in the P content simultaneously occurs upon the small amount of Mn codeposition. The effect of the manganese codeposition on the structure and its deposition mechanism are considered to be quite different from the rhenium codeposition, considering the reverse results regarding the *d* value variation in the Re and Mn codeposition. The amorphous states for non X-ray diffraction peaks in the concentration region of more than 0.05 mol dm^{-3} $MnSO_4$ is probably caused by the increase in the phosphorus content. The perpendicular orientation phenomenon produced by the addition of $MnSO_4$ can't be explained clearly in the present state. However, it might be assumed from the results of the small amount of manganese codeposition, in spite of the addition of a large amount of $MnSO_4$ to the bath, that the specifically adsorbed manganese intermediate at the interface causes the selective deposition at the initial deposition stage, and that, furthermore, thus the perpendicular orientation of the c-axis epitaxially grows on the initially selective deposited particles.

In Fig. 5, the most typical film thickness effect on the magnetic properties was obtained at one of the optimum conditions listed in Table 1, with the fixed concentrations of 0.12 mol dm^{-3} $NiSO_4$, 0.005 mol dm^{-3} NH_4ReO_4, and 0.05 mol dm^{-3} $MnSO_4$. The *Ku* value was interestingly independent of the film thickness. However, the other magnetic factors, *i.e.*, *Hk*, *Hc*(⊥), *Hc*(//), and *Ms*, depended on the film thickness in the initial thin region, up to 0.5 μm, and then reached constant values at a thickness of more than 0.5 μm. The structural factor, $\Delta\theta_{50}$, showed the largest dependence in the initial thin film region. It greatly improved with the increase in the film thickness, as may be seen in Fig. 5(a).

SEM Observation of Cross Section of Co Alloy Films. Figure 6 shows a typical cross section of Co alloy films plated to 0.5 μm under the same conditions as those in Fig. 5. Figures 6(a) and 6(b), which show the same cross section portion with different magnifications of 20000 and 50000 respectively, indicate the columnar growth structure of the hcp structure, although no clear columnar structure such as that shown

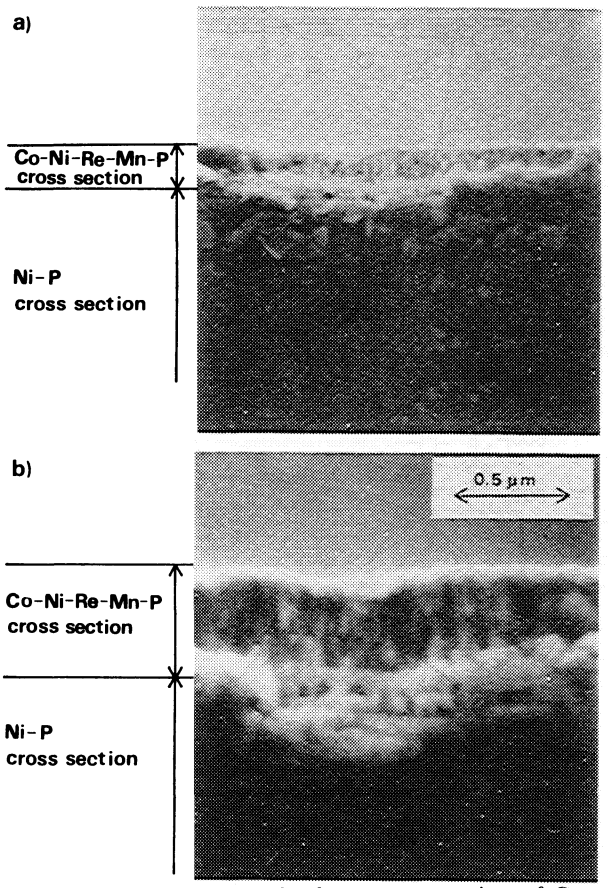

Fig. 6. SEM photographs for a cross section of Co alloy film plated 0.5 μm thick on Ni-P substrate. a) ×20000, b) ×50000.

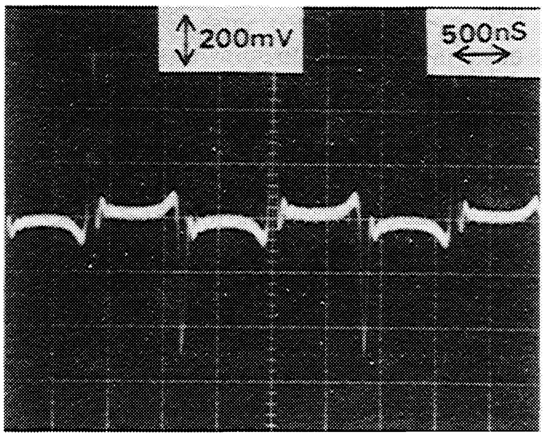

Fig. 7. Reproduced waveform at low recording density of 2540 FRPI for disk A using 0.20 μm spacing.

in previous results[12] is observed. Since the shape of the columnar structure at the cross section is reported to become unclear for the uniformly finer oriented film,[19] the film might be a finer oriented one, then the previously reported one.[12] By the SEM observation, the plated film is also concluded to be suitable for a perpendicular recording medium.

Read/Write Characteristics for Eight Inch Disks with a Combination of the Ring Head. Eight inch disks were prepared by using the optimum plating bath conditions listed in Table 1 at the fixed concentrations

TABLE 2. DISK AND HEAD CHARACTERISTICS

Items \ Disks	Disk A	Disk B	Disk C
Medium material	Co–Ni–Re–Mn–P		
Medium thickness/μm	0.50	0.25	0.20
Overcoat thickness/μm	0.05	0.05	0.02
Substrate material	Polished Ni–P on Al alloy		
Core material	Mn-Zn ferrite		
Gap length/μm	0.33		
Track width/μm	155		
Flying height/μm	0.10, 0.15 at 7.9 m/s at 12 m/s	0.10, 0.15 at 7.9 m/s at 12 m/s	0.10 at 7.9 m/s

of 0.12 mol dm^{-3} $NiSO_4$, 0.005 mol dm^{-3} NH_4ReO_4, and 0.05 mol dm^{-3} $MnSO_4$. The results for disks prepared at 0.10 mol dm^{-3} $NiSO_4$, under the same conditions as for the other factors, have already been reported in a previous paper.[16,17] The disk and head characteristics, as well as the read/write conditions, are shown in Table 2. The three medium thicknesses, *i.e.*, 0.20, 0.25, and 0.50 μm, and three head-medium spacings, 0.12, 0.20, and 0.25 μm, were used in these experiments. Here, the disks with magnetic film 0.50, 0.25, and 0.20 μm thick are designated as Disk A, Disk B, and Disk C respectively.

Figure 7 shows a typical reproduced waveform at a low bit density of 2540 FRPI for Disk A, with 0.20 μm head-medium spacing. The output voltage waveform at a low bit density in perpendicular magnetic recording in combination with the ring head is confirmed to display a dipulse shape.[20] As may be seen in Fig. 7, the dipulse shape at the low bit density recording is clearly observed. This finding supports the concept that the perpendicular recording mode is performed in a system using the plated disk combined with a ring head.

Figure 8 shows the recording density characteristics for Disks A, B, and C with the read/write conditions listed in Table 2. The recording density value at a half output voltage for a long wavelength, D_{50}, always became over 50 kFRPI under these conditions. The D_{50} values of the disks prepared at 0.12 mol dm^{-3} $NiSO_4$ were somewhat higher than the values for those prepared at 0.10 mol dm^{-3} $NiSO_4$, which were shown in the previous paper,[16,17] when the same read/write conditions are compared. This is due to the more advanced magnetic properties at the point of the 0.12 mol dm^{-3} $NiSO_4$ concentration. When considering the 0.33 μm head gap length, such recording density D_{50} values are fairly high. The recording density D_{50} values are scarcely restricted at all by the film properties, but are mainly restricted by the read/write conditions for such a magnetic anisotropy film, when using these read/write conditions. Figures 8(a) and 8(b) show the spacing effects on the recording characteristics for Disks A and B. The spacing decrease from 0.20 to 0.15 μm makes the D_{50} value higher. Furthermore, the medium thickness decrease also somewhat improves the D_{50}

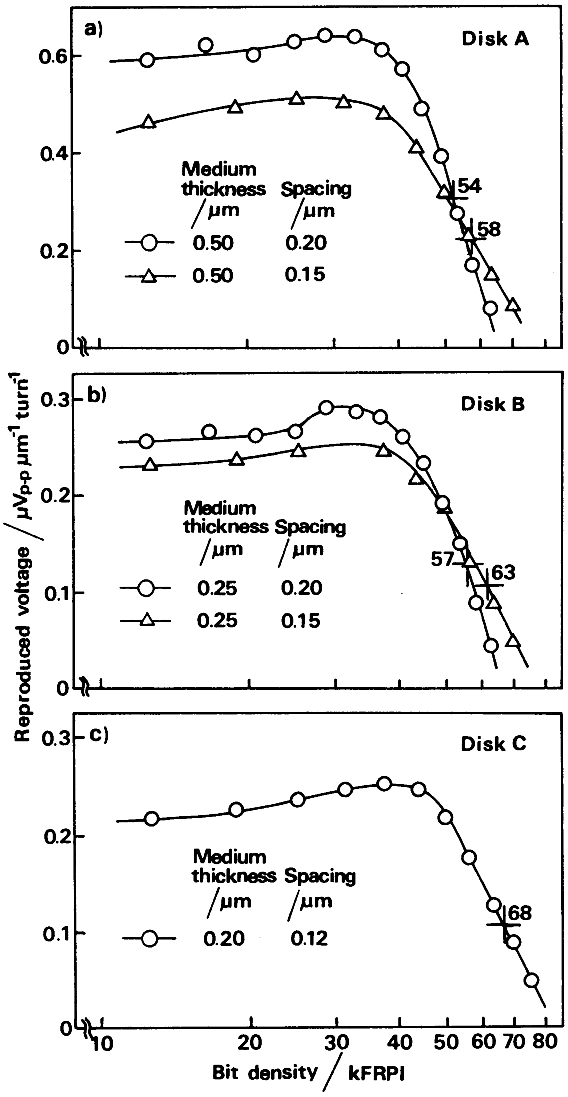

Fig. 8. Reproduced voltage dependence on recording density for Disks A, B, and C.

value. The spacing decrease from 0.25 to 0.20 μm more greatly developed the recording density D_{50} from 40 to 54 kFRPI, as was shown in previous papers.[17,18] Since a favorable *SNR* value and a flattened envelope were also obtained for these disks, with practically usable 0.20 μm spacing conditions, as in the previous data,[17] the electroless plated disks have been found to have a high potential for practical use. When the medium thickness and spacing values were reduced to 0.20 and 0.12 μm respectively, in obtaining a higher recording density, a high recording density, D_{50}= 68 kFRPI, was attained by using the 0.33 μm gap length head. The spacing used here means the total value of the 0.02 μm overcoat thickness and the 0.10 μm flying height. A very high potential for these plated disks as a perpendicular recording medium is also supported by such a high recording density with the more advanced read/write conditions.

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