Structural Control of Electroless-Plated Magnetic Recording Media by Underlayers

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ABSTRACT

The structural control of electroless-plated CoP film was investigated using underlayers of electroless-plated CoNiMnP and CoNiP films. The CoNiMnP film showed a high degree of orientation of the hcp Co c-axis normal to the film plane, whereas the CoNiP film hardly showed any preferred orientation. The CoP film plated onto the CoNiMnP underlayer showed a high degree of preferred orientation, while the CoP film plated onto the CoNiP underlayer showed a low degree of preferred orientation. Thus, the microstructure of the CoP film is clearly influenced by the underlayer structure. In the case of the CoP film onto the CoNiMnP underlayer. an epitaxial-like growth was observed up to a thickness of 0.25 μm, and this reduced to the intrinsic microstructure at a thickness of 0.5 μm. Recording characteristics were measured on the 5 in. flexible disks, fabricated by plating the high-oriented CoP film or the low-oriented CoP film with a ring-type head of a commercial VHS video head. Perpendicular recording was performed on the high-oriented CoP film to demonstrate the best characteristics. The use of an oriented underlayer is thus confirmed to be a useful method of controlling the structure of the magnetic film in addition to controlling the bath plating parameters.

The perpendicular recording system is especially suitable for high-density magnetic recording (1). The most popular medium for the system is a CoCr alloy film produced by a vacuum process such as sputtering or evaporation.

The authors have developed perpendicular recording media using the electroless-plating method (2-5). An electroless CoNiReP alloy film has the highest potential for this use (6). The film has a high orientation of hcp-Co c-axis normal to the film plane. Moreover, the perpendicular coercivity for films up to 0.5 μm thick is controllable by varying one of the plating bath parameters (7). A change in the depth profile of perpendicular coercivity is due to a change in the microstructure toward depth direction. The degree of orientation of the Co hcp crystals (8) in particular. The crystal orientation can be controlled by plating bath parameters (7).

The structure of perpendicular recording media are reported to be influenced by their underlayers (6, 9-11). This implies that the microstructure can be controlled by the selection of the underlayer. In the present paper we investigate the possibility of controlling the microstructure of electroless-plated fundamental CoP films (12, 13) by using electroless-plated underlayers, CoNiMnP (3) and CoNiP (14). In addition, the effect of crystal orientation on recording characteristics is studied.

Experimental Procedure

Figure 1 is a schematic diagram of the structures of various CoP films used in the study. An electroless NiP substrate is used except for the recording test with flexible disks. A CoP film directly plated onto a substrate is designated as the CoP single-layer film. The CoP film plated onto the CoNiMnP underlayer is designated as CoP on CoNiMnP film and plated onto the CoNiP underlayer as CoP on CoNiP film, respectively. The CoP, CoNiP, and CoNiMnP films were electroless-plated from baths detailed in Table I. Magnetic properties were measured using a vibrating sample magnetometer (VSM). The crystal orientation of the film surface was determined by reflection high-energy electron diffraction (RHEED). Five-inch flexible disks were fabricated for the CoP single layer and CoP on CoNiMnP films. After coating with a liquid lubricant, the recording characteristics were measured under the conditions detailed in Table II. The ring-type head used was a commercial VHS video head.

Results and Discussion

Crystal orientation and magnetic properties.—The RHEED patterns for the various films are shown in Fig. 2. A low degree of crystal orientation is indicated for the CoP single-layer film (Fig. 2a), since each reflection forms a continuous ring pattern. However, arc patterns are produced by the CoNiMnP film (Fig. 2b). The arc patterns only consist of reflections from the hcp Co crystals, and the Miller indexes are indicated in Fig. 2b. All the arcs in Fig. 2b indicate that the c-axis is oriented normal to the film plane. The CoNiP film (Fig. 2d) shows little preferred orientation, *i.e.*, it is similar to the CoP film. The two films, CoNiMnP and CoNiP, were used as underlayers typical of well-oriented and randomly oriented films, respectively.

The RHEED patterns of electroless-plated CoP films, 0.25 μm thick, plated onto these underlayers are given in Fig. 2c and 2e. Arc patterns indicating preferred orientation of c-axis normal to the film appear for the CoP film plated onto the well-oriented CoNiMnP film (Fig. 2c), whereas ring-like patterns indicating little or no preferred orientation appear for the CoP film plated onto the randomly oriented CoNiP film (Fig. 2e). These results suggest that the growth of CoP film is strongly influenced by the microstructure of the underlayer and that the microstructure of a CoP film is formed by epitaxial-like crystal growth.

Hysteresis loops for the films shown in Fig. 2 are given in Fig. 3 and are arranged in the same order as in Fig. 2. The CoP film shows a high squareness ratio of the loop measured in the in-plane direction (Fig. 3a). Figure 3b indicates that high coercivities are present in the CoNiMnP film, and that the perpendicular coercivity is larger than the in-plane one. The properties for the CoNiP film (Fig. 3d) are

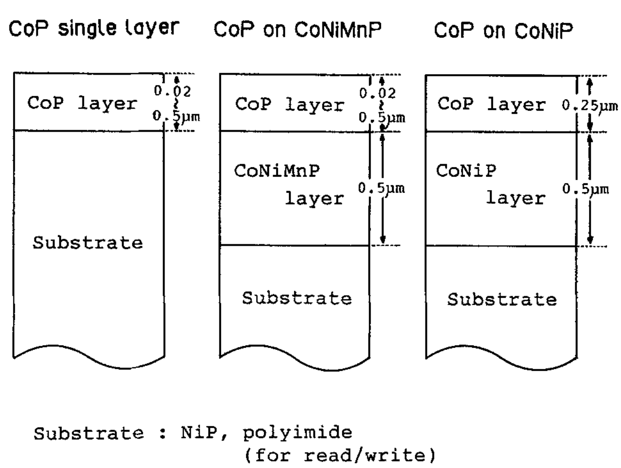

Fig. 1. Schematic cross section of films

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Table I. Basic bath compositions and operating conditions

Chemical	CoP	CoNiP	CoNiMnP
	Concentration/mol dm^{-3}		
$NaH_2PO_2\ H_2O$	0.20	0.20	0.20
$(NH_4)_2SO_4$	0.50	0.10	0.50
$CH_2(COONa)_2\ H_2O$	—	0.30	0.50
$C_2H_3OH(COONa)_2$	—	0.40	0.05
$C_2H_4(COONa)_2\ 6H_2O$	—	0.50	—
$C_2H_2(OH)_2(COONa)_2\ 2H_2O$	0.50	—	—
$CoSO_4\ 7H_2O$	0.05	0.06	0.035
$NiSO_4\ 6H_2O$	—	0.04	0.01
$MnSO_4\ 5H_2O$	—	—	0.04
Bath temperature	80°C	80°C	80°C
pH	9.2 adjusted by NH_4OH	9.1 adjusted by NH_4OH	9.6 adjusted by NH_4OH

Table II. Head properties and read/write conditions

Core material	MnZn ferrite
Gap length	0.35 ± 0.05 μm
Track width	60 μm
Coil turns	22
Relative velocity	1 m s^{-1}

between the other two, and both perpendicular and in-plane coercivities are almost the same.

The cases for CoP on CoNiMnP film and of CoP on CoNiP film are shown in Fig. 3c and 3e, respectively. These show more than the characteristics of the CoP films since they are measured with the underlayer. The features noted for their underlayers are still present in both the CoP films, namely, for the CoP on CoNiMnP film (Fig. 3c), the perpendicular coercivity is still larger than in-plane one, and for the CoP on CoNiP film (Fig. 3e), both coercivities are almost the same.

The next stage is to investigate two films, the CoP single-layer film and the CoP on CoNiMnP film, in more detail.

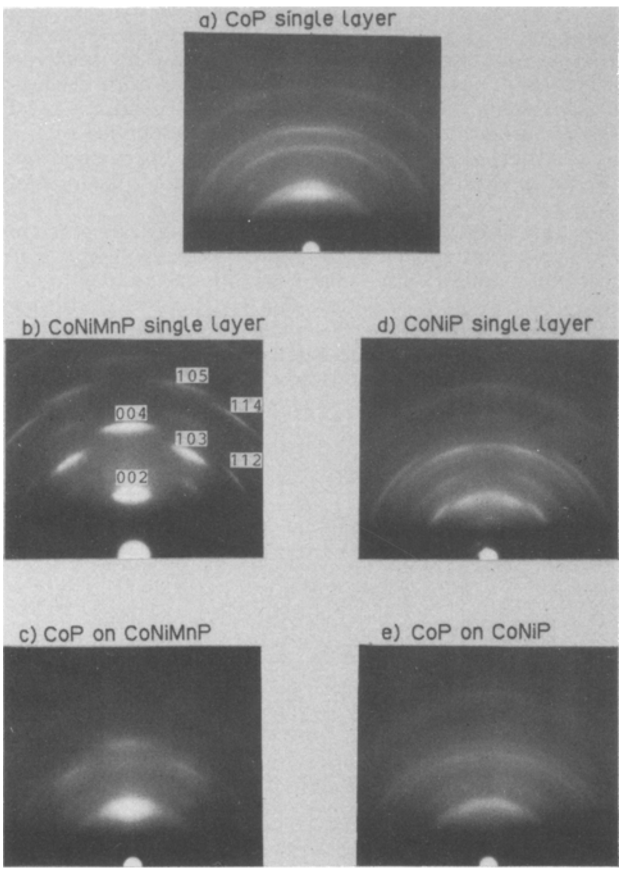

Fig. 2. RHEED patterns of: (a) CoP film (0.25 μm), (b) CoNiMnP film (0.5 μm), (c) CoP film (0.25 μm) on CoNiMnP film (0.5 μm), (d) CoNiP film (0.5 μm), and (e) CoP film (0.25 μm) on CoNiP film (0.5 μm).

Figure 4 shows the RHEED patterns for the two films as the thickness of the CoP layer is varied from 0.02 up to 0.5 μm. Ring patterns appear for the CoP single-layer films for all thicknesses indicating little preferred orientation (Fig. 4a-e). In the CoP on CoNiMnP films, the arc patterns are produced indicating a high degree of orientation, reflecting the high orientation of the CoNiMnP underlayer (Fig. 4f-i). Such behavior is seen up to a film thickness of 0.25 μm. For thicker films, the orientation decreases, and at 0.5 μm, both films show the same patterns (Fig. 4e and 4j).

It is concluded that the microstructure of a CoP film can be controlled up to the thickness of 0.25 μm by control of the underlayer structure. However, the intrinsic (*i.e.*, random) structure, which is not influenced by the underlayer, appears for film thickness of 0.5 μm.

The magnetic properties for the combination of CoP with the CoNiMnP underlayer are given in Fig. 5. Figure 5a is the hysteresis loops for CoP single-layer film, and Fig. 5e is the differential curve of differentiated magnetization by magnetic field for the in-plane loop. Magnetization reversal is indicated as a peak in the differential curve. A dispersion of coercivity is clearly shown in a differential curve.

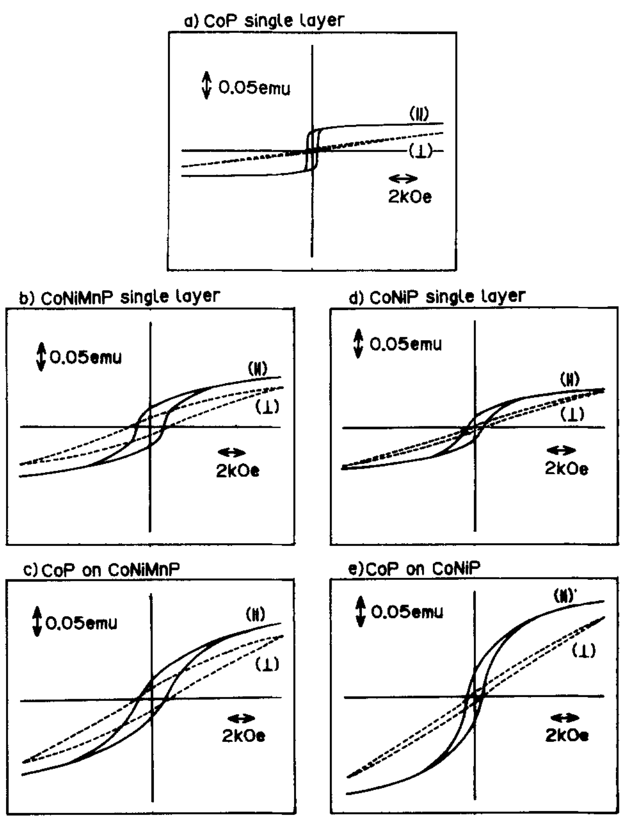

Fig. 3. Hysteresis loops of: (a) CoP film (0.25 μm), (b) CoNiMnP film (0.5 μm), (c) CoP film (0.25 μm) on CoNiMnP film (0.5 μm), (d) CoNiP film (0.5 μm), and (e) CoP film (0.25 μm) on CoNiP film (0.5 μm).

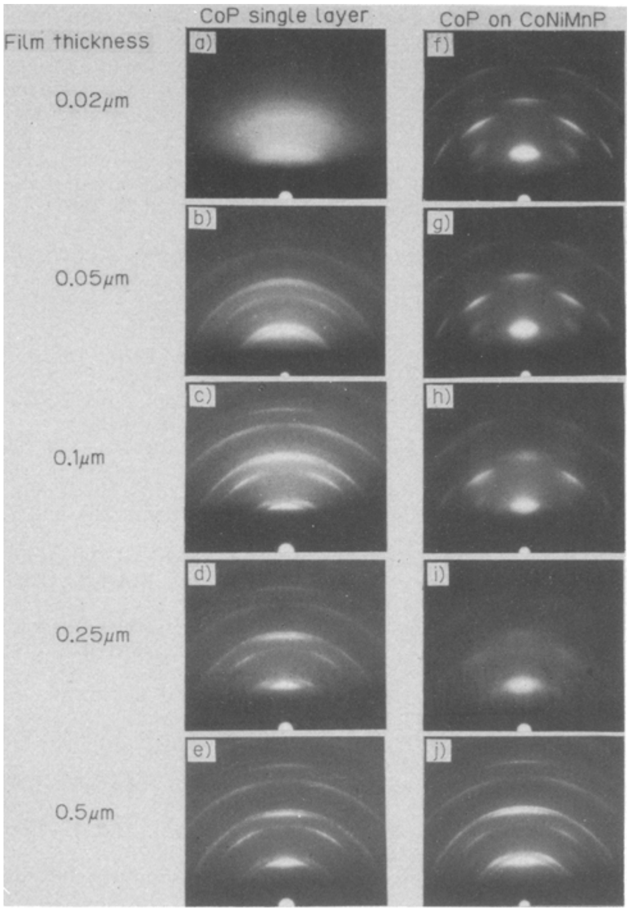

Fig. 4. RHEED patterns of: (a-e) CoP film, and (f-j) CoP film on CoNiMnP film.

As indicated in Fig. 5e, the CoP film consists of elements of low coercive force showing a narrow dispersion. The CoNiMnP film consists of those of higher coercive force than the CoP film, and it shows a wider dispersion, Fig. 5f. Figure 5c shows the loops measured for the two samples at one time, for CoP single-layer film settled closely upon the CoNiMnP film. Although the shape of the loop is different from the sum of the two loops for the CoP and CoNiMnP films because of magnetic interactions, the constriction appears in the in-plane loop, which suggests the elements of two kinds of coercive forces. This is more clearly demonstrated in the differential curve shown in Fig. 5g. In this curve, two peaks—the peak of low coercive force for the CoP film and the shoulder of high coercive force for the CoNiMnP film—are clearly shown. However, for the case of the CoP on CoNiMnP film (Fig. 5h), the peak and the shoulder are reduced to one broad peak. In particular, the sharp peak of the low coercive force for the CoP film disappears. Smaller amounts of low coercive elements are shown in the CoP film plated onto the CoNiMnP film.

From the above results, we see that the CoP film plated onto the CoNiMnP film is magnetically different from the CoP single-layer film. The CoP film plated onto the CoNiMnP film is both crystallographically and thus, magnetically influenced by the underlayer.

Recording characteristics.—The recording performance of the typical two films, single CoP and CoP on CoNiMnP, are shown in Fig. 6 and 7. In Fig. 6, the recording current dependence on the output voltage shows maximum for the CoP single-layer film; namely, the output voltage increases to a peak and then significantly decreases. On the other hand, the output voltage for the CoP on CoNiMnP film tends to saturate at a constant value. The former behavior corresponds well to the characteristics of in-plane recording, while the latter behavior of a saturating output voltage suggests the perpendicular recording. These results suggest that the increase in c-axis orientation causes

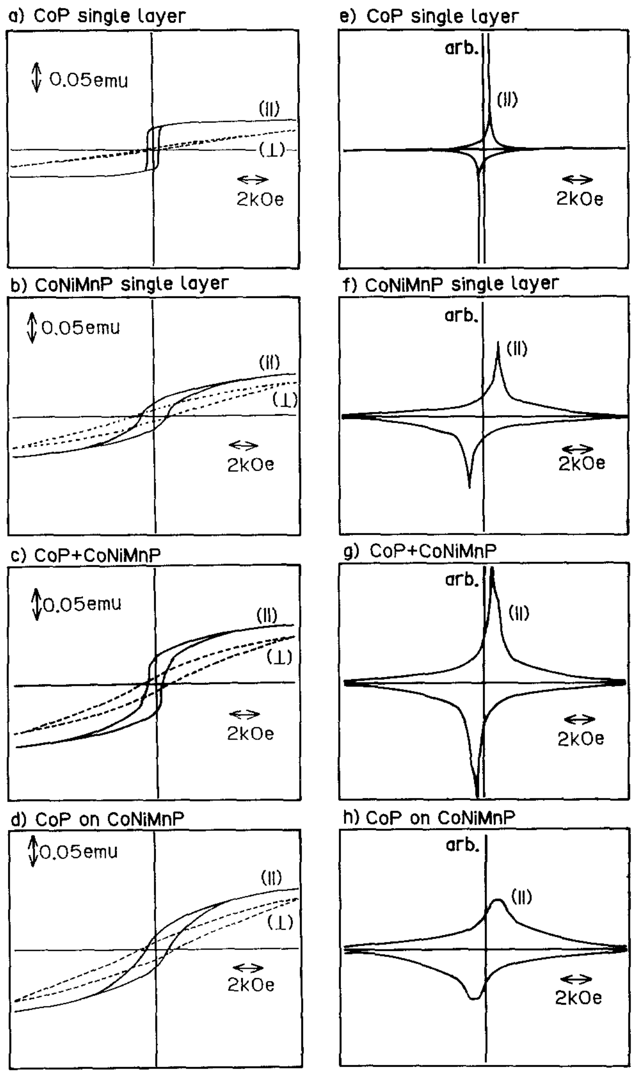

Fig. 5. Hysteresis loops of: (a) CoP film (0.25 μm), (b) CoNiMnP film (0.5 μm), (c) CoP film (0.25 μm) + CoNiP film (0.5 μm), and (d) CoP film (0.25 μm) on CoNiP film (0.5 μm). The differentials of (a-d) in-plane loops for (e) CoP film (0.25 μm), (f) CoNiMnP film (0.5 μm), (g) CoP film (0.25 μm) + CoNiP film (0.5 μm), and (h) CoP film (0.25 μm) on CoNiP film (0.5 μm).

the essential changes in recording mode. That is to say, a perpendicular recording is achieved for the CoP film that has the c-axis of hcp Co oriented normal to the film plane.

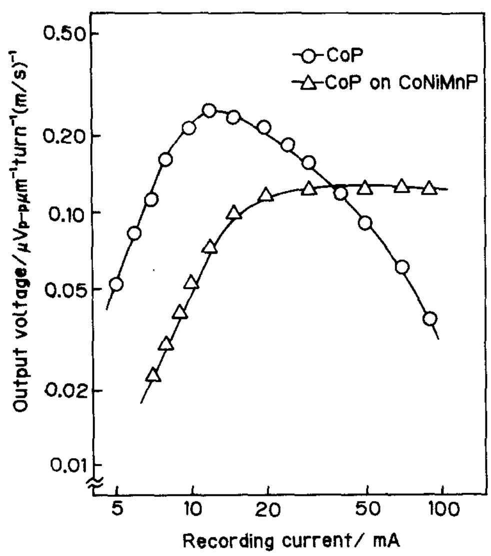

Fig. 6. Dependence of recording current on reproduced voltage for various films at 24 kFRPI.

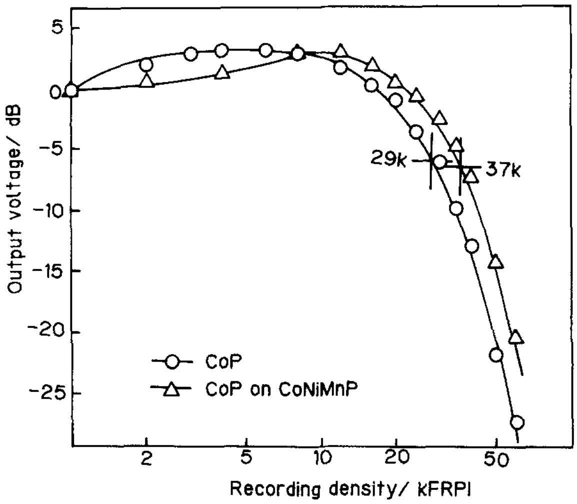

Fig. 7. Dependence of recording density on reproduced voltage for various films.

This is reflected in the recording density characteristics as given in Fig. 7.

The CoP on CoNiMnP film shows an increased D_{50} value compared to that for the CoP single-layer film. Thus, the increase in perpendicular orientation of c-axis of hcp cobalt for the CoP film is effective in proceeding a higher density recording.

Conclusions

The main findings of this study are as follows:

1. The crystal orientation of electroless-plated CoP film is influenced by the structure of the underlayer.
2. This influence extends for films up to 0.25 μm in thickness.
3. The coercivity is also influenced by the underlayer.
4. The CoP film, the c-axis of which is perpendicularly oriented, demonstrates better recording characteristics than a less oriented one. This is due to the recording perpendicularity.
5. Structural control of electroless-plated Co alloy magnetic recording films is possible by control of underlayer structure as well as by control of plating bath parameters.

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Fundamental Study of Acid Copper Through-Hole Electroplating Process

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ABSTRACT

Through-hole plating experiments were carried out with a gap cell and with Plexiglas boards. The gap cell provided good simulation of the plated through-hole system and allowed accurate and nondestructive profile analysis of copper deposits. As the current density and the aspect ratio were increased, the copper distribution inside the hole (gap) became more nonuniform. Plugging of holes was observed at high current levels due to current crowding into the hole entrance where the mass transport rate was high. The experimental findings were confirmed by mathematical models which were developed on the basis of electrochemical engineering principles and were applied to the geometric domain that included both the surface of the board and the through-hole wall. The limits of present through-hole plating technology are pointed out and possible means for process improvement are discussed.

In the economic evaluation of printed circuit board fabrication, three process characteristics for copper electroplating of through-holes are considered important. They are: (*i*) deposit thickness distribution in through-holes, as it relates to the thickness on the board surface; (*ii*) metallurgical structure of the copper deposits; and (*iii*) speed of the plating process.

The development of additives that are compatible with the high throwing-power acid copper sulfate baths has greatly improved the metallurgical properties of the copper deposits, especially the ability to resist corner and barrel cracking in the plated through-holes during the solder float test. The plating bath used in this study contained commercially available additives and the metallurgical properties of the copper deposits were assumed to meet the industrial standards, hence our efforts were focused on the current and plating thickness distribution rather than on the metallurgy.

In general it is desired that the plated-through holes should have a uniform copper thickness inside the holes, and that the surface-to-hole copper thickness ratio be as close to one as possible. Nonuniform thickness distribution inside the holes is commonly referred to as "dogboning." Dogboning has detrimental effects, such as lowering

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