Magnetic Properties of Co-P and Co-P-Cr Thin Films for Longitudinal Magnetic Recording

Pyung Woo Jang

Dept. of Physics, Chongju University

36 Naeduk-dong, Chongju 360-764, Korea

Hong Kyun Sohn

Dept. of Metall. Eng., Seoul National University

56-1 Sillim-dong, Kwanak-ku Seoul 151-742, Korea

Taek Dong Lee

Dept. of Advanced Mater. Eng., Seoul Campus, Korea Adv. Inst. of Sci. & Tech

207-43 Cheongryangri-dong, Seoul 130-012, Korea

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In order to develop new magnetic media with higher coercivity, we have investigated the magnetic properties of Co-P /Cr and Co-P-Cr /Cr films. The coercivity of Co-P binary films deposited at RT was around 835 Oe in the range of 9-12 at.% P. In the Co-P binary system coercivity decreased with increasing substrate temperature for P contents of 9-12 at.%, which may be due to the decomposition of Co-P single phase to Co and Co_2P phase. However, the coercivity of the films containing more than 12 at. % P is very low due to the formation of amorphous phase. The coercivity of Co-P-Cr ternary films increased with increasing Cr contents and reached the maximum value of 1020 Oe in the water cooled $Co_{84}P_{10}Cr_6$ film.

I. Introduction

High coercivity and high S /N ratio are essential for the high density longitudinal magnetic recording. For these purposes many processing methods and materials have been developed and used. One general method is to increase the substrate temperature during sputtering. In this case, probability of crystallization of Ni-P amorphous layer, and probability of curling or protrusion of aluminium substrate are disadvantages. Another method is to apply bias voltage during sputtering. This method has the same disadvantages as the first because high substrate temperature is also required for effective bias sputtering[1]. Another approach is to develop alloy system such as Co-Pt-X and Co-Rare Earth. However Co-Pt-X and Co-Rare Earth alloy systems use expensive Pt element and have poor chemical stability, respectively. As an alternative to these materials we tried to develop new alloy systems which have high coercivity and high S /N ratio when sputtered at low substrate temperature.

New system must be Co alloy systems because of its uniaxial magnetic anisotropy. Very cheap element of P is chosen as an additive because Co-P electroless or electrodeposited thin films have been reported to have P rich non-magnetic channels between grains and inferred to have high S /N ratio. This anticipation was verified by Natarajan who annonounced excellent noise characteristics of Co-P /Cr sputtered media[2]. However, he used thick Cr underlayer of 500 nm and did not report magnetic properties with varying P contents and sputtering condition. Thick Cr underlayer is not recommanded for commercialization. Moreover third element must be added to enhance the chemical stability of Co-P alloy system. Cr was chosen as a third element because Cr has been known as an unique element for chemical stability and magnetic properties.

Therefore, we first tried to optimize P and Cr contents by investigating the magnetic properties of Co-P and Co-P-Cr alloy system and also tried to elucidate the reason for the magnetic behavior of Co-P-Cr magnetic thin films.

Ⅱ. EXPERIMENTAL PROCEDURE

A DC magnetron sputtering method was used for deposition of the films. Film compositions were varied by changing the number of high purity Cr and Co_4P_3 chips which were placed on 6 inch pure cobalt target. The film thickness were 45-50 nm for magnetic layer and 100 nm for Cr underlayer. Other sputter conditions are listed in Table 1. The magnetic properties, crystalline structure, magnetic structure and film compositions were analysed by VSM, XRD, TEM, x-band FMR spectroscopy and EDS, respectively.

Table. Ⅰ. Sputtering conditions for Co-P / Cr and Co-P-Cr / Cr thin films.

Target	Cr (99.9%) Co-P-Cr composite target
Substrate	Textured Ni-P / Al-Mg Corning 2948 glass
Background Pressure	less than 5×10^{-7} torr
Sputter Pressure	10 mTorr (99.999 % Ar)
Ar flow rate	15 SCCM
Sputter Power	Cr Underlayer : 460 W Magnetic layer : 300 W
Substrate Temperature	RT, 150, 260 ℃

Ⅲ. RESULTS AND DISCUSSIONS

3-1. Co-P binary alloy system

Fig. 1 shows variations of saturation magnetization (Ms) of Co-P thin films deposited at room tempertue (RT) with varying P contents. With increasing P contents up to 12 at.%, Ms decreases linearly with the slope of 34 emu / cc per 1 at.% P when fitted by least square method. By the extrapolation of Fig. 1, it can be deducted that Co-P thin films looses ferro-magnetism at 41.3 at.% P. According to Hüller who has electrodeposited Co-P thin films up to 25 at.% P, Ms decreases linearly up to experimental point and becomes zero at 39.5 at.% P by extrapolation of the experimental data [3]. Thus it can be concluded that Ms behavior of the sputtered Co-P thin films is congruous with that of the electrodeposited Co-P films. From this Ms behavior of Co-P sputtered films, P contents of our sputtered films were estimated by those Ms values. One of interesting points is some increase or ambiguity in Ms near 12 at.% P. This was also reported in the electroless or electrodeposited Co-P thin films by Hüller and others as shown in Fig. 1 [3, 4, 5]. From the TEM microstructural analysis Chen supposed that this was related to the existence of element P or phosphide between grains[4]. However, the abrupt increase was found to be related to the amorphorization of the Co-P films[3, 5]. Co-P films with more than 12 at.% P is amorphous and the formation of amorphous is an origin of very low coercivity as reproted by others

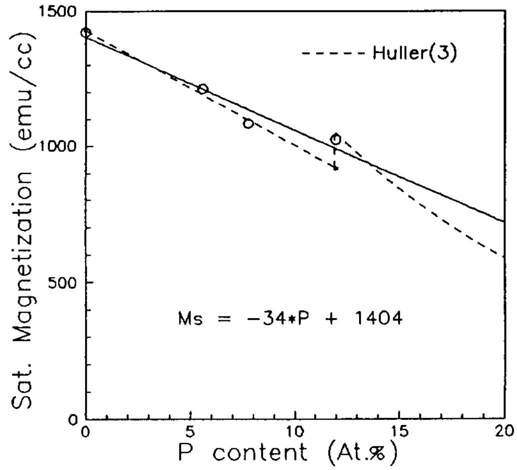

Fig. 1. Variation of saturation magnetization of Co-P thin films deposited at room temperature with varying P contents.

[3, 5, 6] Therefore it is recommended that P contents must be less than 12 at. % in the Co-P or Co-P-Cr films to yield good magnetic properties.

Fig. 2 shows variations of coercivity of Co-P thin

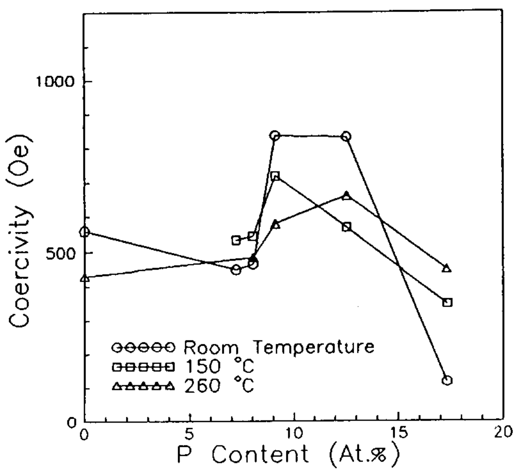

Fig. 2. Variations of coercivity of Co-P thin films with P contents.

films with P contents. Without any phosphorus, pure cobalt shows coercivity of 550 and 420 Oe at room temperature and 260 ℃, respectively. With increasing P content coercivity rapidly increases in the region of around 8 at.%, and then reaches relatively high coercivity of 850 Oe in the Co-P binary alloy films without substrate heating. When P addition exceeded 12.5 at.% P, coercivity decreases rapidly. One of remarkable feature in Fig. 2 is that the coercivities of films deposited at the elevated temperature is lower than those deposited at RT. This may be attributed to the decomposition of Co-P single phase into pure Co and phosphide. With XRD analysis, however, we cannot detect any trace of phosphorus compound such as Co_2P which is expected to exist in equiliburium phase diagram. In the region of 12.5 at.% P and over, rapid decrease of coercivity is attributed to the formation of Co-P amorphous phase as mentioned above. Coercivity of $Co_{82.7}P_{17.3}$ films deposited at RT is lower than those deposited at elevated temperature because the formation of an amorphous phase is suppressed at higher temperature.

Fig. 3 shows variations of coercivity squareness

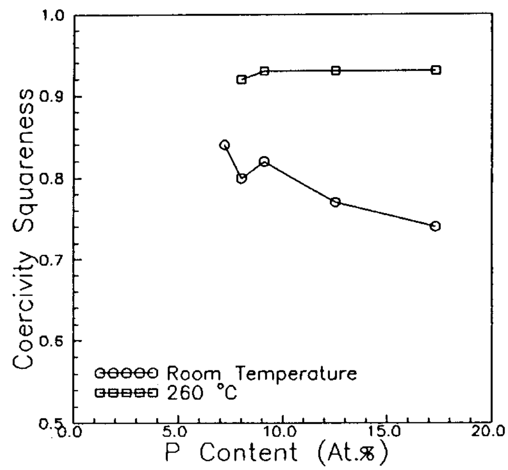

Fig. 3. Variations of coercivity of Co-P thin films with varying P contents.

of Co-P thin films with varying P contents. Coercivity squareness of films deposited at RT gradually decreases from 0.85 to 0.74. On the contrary films deposited at 260 ℃ keep nearly constant value of 0.93. In Fig. 3 coercivity squareness increases with increasing deposition temperature, which is just opposite to the trend of commercialized Co-Cr-Ta and Co-Ni-Cr films. The reason is thought to be no solubility of phosphorus in Co. If Co-P single phase decomposes into magnetically soft Co phase, it enhances magnetic interaction between isolated grains and thus increase coercivity squareness. Microstructural analysis is needed for confirmation. $Co_{87.5}P_{12.5}$ film deposited at RT has low value of 0.77, and is expected to have excellent noise characteristics[7].

Fig. 4 shows variations of squareness of Co-P films with P contents. Squareness decreases with P contents regardless of deposition temperature and high deposition temperature gives high squareness for a given P contents. The low squareness of Co-P films deposited at RT is expected not to be harmful to the magnitude of reproduced voltage because of its high Ms of more than 1000 emu /cc.

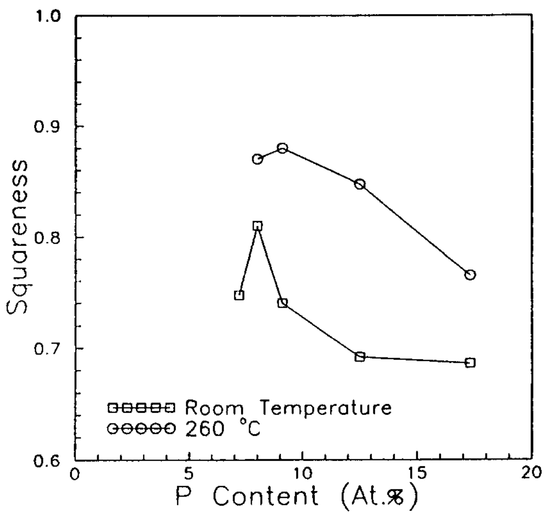

Fig. 4. Variations of squareness of Co-P films with P contents.

To understand characteristic behavior of Co-P films, XRD analysis has been done as shown in Fig 5. To avoid strong diffraction line from Al (111) plane which have nearly same inter-planar spacing as Co(0002), Cr(110) and Cr(200) plane, we used glass substrate. As shown in Fig. 5(a) we can find diffraction lines of hexagonal Co-P alloy only and cannot find any trace of Co phosphide. Co-P /Cr thin film texture relationship follows the generally known CoX /Cr relationship, which is Co(10$\bar{1}$0) /Cr(110) or /and Co(10$\bar{1}$0) /Cr(110) at RT and Co(10$\bar{2}$0) /Cr(200) at elevated deposition temperature. In Fig. 5(b) we can find typical amorphous pattern of $Co_{82.7}P_{17.3}$ films deposited at RT and diffraction lines from crystalline Co-P films deposited at elevated temperature. Higher coercivity of these films depostied at higher deposition temperature in Fig. 2 is attributed to the crystalline Co-P phase. But any trace of Co phosphide was not detected also in these films with high P contents. This was also confirmed in the TEM analysis of $Co_{94.4}P_{5.6}$ films although it contains small amount of P. Detailed microstructural analysis is needed for full understanding.

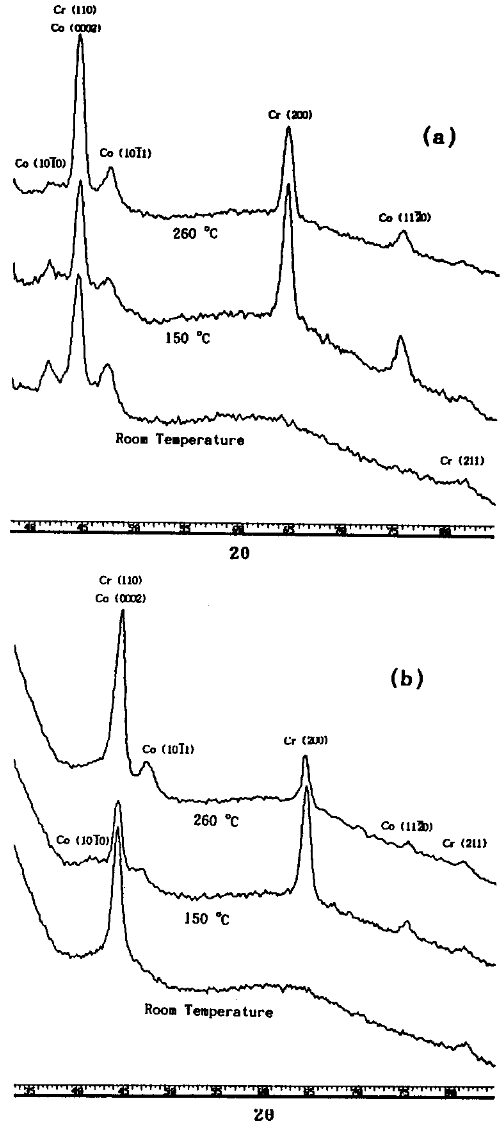

Fig. 5. X-ray diffractometry of $Co_{90.9}P_{9.1}$ /Cr (a) and $Co_{82.7}P_{17.3}$ /Cr (b) thin film.

3-2. Co-P-Cr ternary alloy system

As mentioned before third element of Cr was added to improve the magnetic properties and chemical stability. Ni-P substrate was heated up to 150 °C to avoid crystallization. The Cr contents in ternary films were determined by those Ms value instead of direct chemical analysis. In Co-Cr binary system containing less than 15 at.% Cr, Ms decreases by 51.5 emu /cc per 1 at.% Cr[8, 9].

Fig. 6 shows the variations of coercivity of $Co_{96-x}P_4Cr_x$ films with Cr contents deposited from Co-P composite target. Without Cr addition $Co_{96}P_4$ films shows low coercivities of around 430 Oe. With increasing Cr contents coercivity increases. Coercivities of films deposited at lower substrate

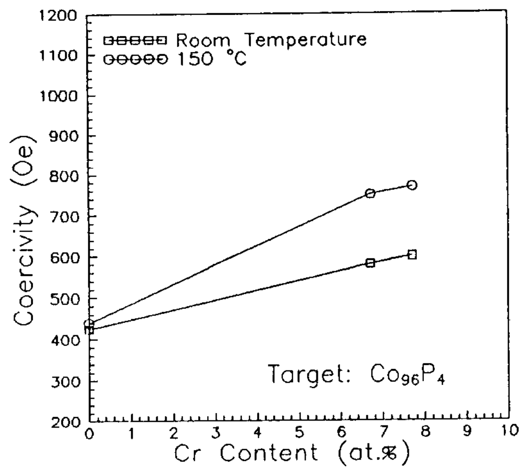

Fig. 6. Variations of coercivity of $Co_{90-x}P_4Cr_x$ films with Cr contents.

temperature is lower than those deposited at higher temperature. In Co-Cr-X binary or ternary system, it is well known that coercivity increases with increasing substrate temperature and Cr content because of Cr segregation enhancement. Therfore, the coercivity mechanism of Co-P-Cr films with 4 at.% P is considered to be similar to that of Co-Cr binary system and small amount of P is less effective for aquiring high coericvity of Co-P-Cr films at low substrate temperature.

Fig. 7 shows the variations of coercivity of $Co_{90-x}P_{10}Cr_x$ films with Cr contents deposited from Co-P composite target. Without Cr addition coercivities of Co-P binary films deposited at RT and 150 ℃ are 810 Oe and 770 Oe, respectively. Coercivity, however, increases with increasing Cr contents and reaches maximum value of 1020 Oe at 6 at.% Cr. High coercivity of around 1000 Oe can be obtained without substrate heating in Co-P-Cr alloy system. In Fig. 7 coercivity increases with

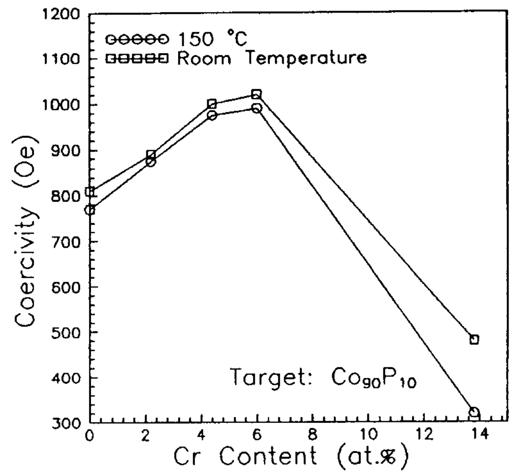

Fig. 7. Variations of coercivity of $Co_{90-x}P_{10}Cr_x$ films with Cr contents.

increasing Cr content up to 6 at.% Cr because of Cr segregation enhancement. However, it decreases with increasing Cr contents more than 6 at.% because of small magnetic energy in films. In contrast to $Co_{96-x}P_4Cr_x$ films the coercivity behavior of $Co_{90-x}P_{10}Cr_x$ films contanining large amount of phosphorus with changing substrate temperature can be understood from Fig. 2. of Co-P binary system.

Fig. 8 and 9 show the variations of squareness

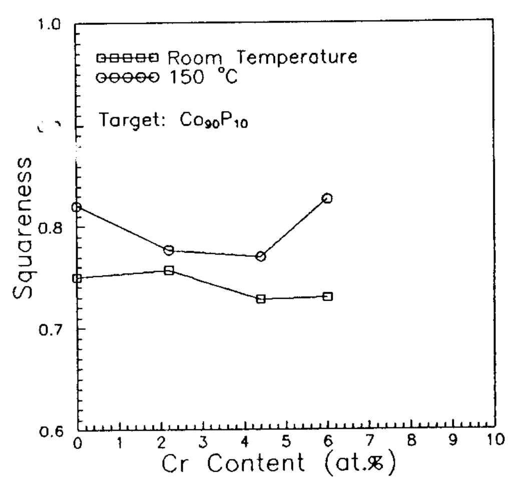

Fig. 8. Variations of coercivity of $Co_{90-x}P_{10}Cr_x$ films with Cr contents.

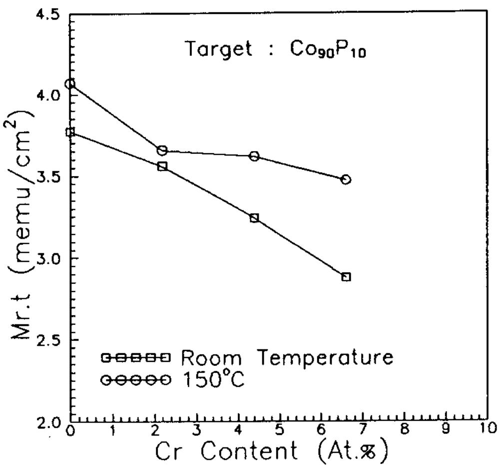

Fig. 9. Variations of Mr·t of $Co_{90-x}P_{10}Cr_x$ films with Cr contents.

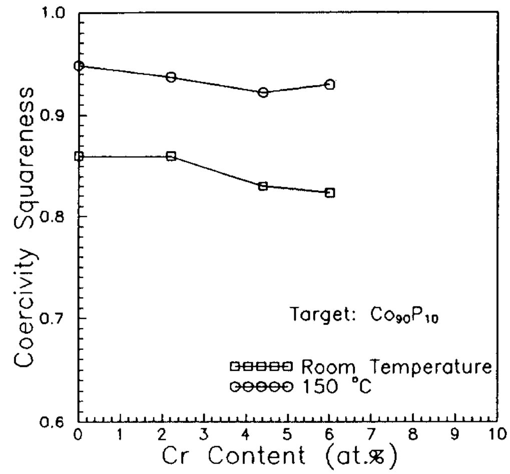

Fig. 10. Variations of coercivity squareness of $Co_{90-x}P_{10}Cr_x$ films with Cr contents.

and Mr·t of $Co_{90-x}P_{10}Cr_x$ films with Cr contents, respectively. As shown in Fig. 8 squareness of the films deposited on water cooled substrate is smaller than those of the films deposited on 150 ℃ heated substrate and decreases gradually with increasing Cr contents. The squaresss of water cooled and 150 ℃ heated cases are 0.73 and 0.83 at 6 at.% Cr, respectively. It is due to the same reason as in Fig. 4. Mr·t decreases monotonously with Cr contents and the films of higher substrate temperature gives higher value at an given Cr contents because of large squareness.

Fig. 10 shows the variations of coercivity squareness of $Co_{90-x}P_{10}Cr_x$ films with Cr contents. Coercivity squareness is known that it is related to the noise properties and the smaller the coercivity squareness is, the higher the S/N ratio is[7]. Compared with the typical value of 0.85 – 0.96 of commercialized media, the value of 0.82 in Fig. 10 is promising for better noise characteristics.

One of interesting feature of Co-P-Cr media is that orientation ratio (OR) of the 150 ℃ heated films varies with Cr contents as shown in Fig. 11. The water cooled films, however, gives OR values of 0.97 – 1 and is almost isotropic. In 150 ℃ heated films the maximum anisotropy of $Co_{90-x}P_{10}Cr_x$ films appears at the Cr content of 6.0 at.% and

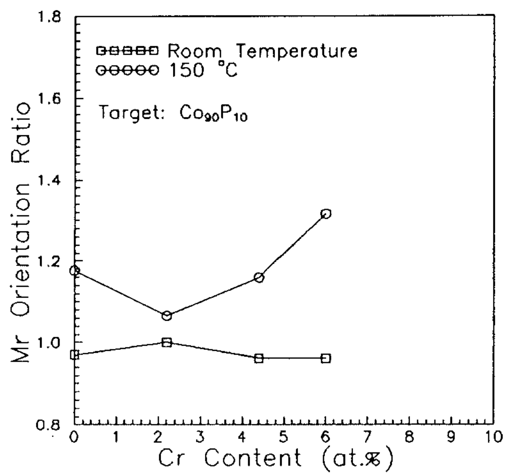

Fig. 11. Variations of Mr orientation ratio of $Co_{90-x}P_{10}Cr_x$ films with Cr contents.

its anisotropy energy measured by torque magnetometer is 5×10^5 erg/cc. It is well known that mechanical texturing induces anisotropy due to the c-axis alignment in the circumferencal direction of the commercialized media[10]. Media deposited on non-textured Ni-P substrate was isotropic in this experiment. However, the charateristics of thin film growth in the textured groove has not been well known yet. In order to understand the effect of Cr content on the anisotropy behavior of the Co-P-Cr films, further study is needed.

In order to increase the coercivity further we made the films with the P content of 12 at.% and over. The coercivities of these films, however, were as low as 250 Oe and its measured value of Ms is larger than expected. Therefore, the formation of amorphous phase is obvious in these films with high content of more than 12 at.% P.

Ⅳ. CONCLUSION

In order to develope new magnetic media with higher coercivity, we have investigated the magnetic properties of Co-P /Cr and Co-P-Cr /Cr films, and the following results were obtained.

(1) Saturation magnetization of the Co-P films deposited at room temperature decreases linearly by 34 emu /cc per 1 at.% P with increasing P contents up to 12 at.%.

(2) The coercivity of Co-P binary films deposited at RT was around 835 Oe in the range of 9 – 12 at.% P. In the Co-P binary system coercivity decreased with increasing substrate temperature for a given P contents, which may be due to the decomposition of Co-P single phase to Co and Co_2P phase. However, the coercivity of the films containing more than 12 at.% P is very low due to the formation of amorphous phase.

(3) The coercivity of Co-P-Cr ternary films increased with increasing Cr contents and reached the maximum value of 1020 Oe in the water cooled $Co_{84}P_{10}Cr_6$ film. $Co_{90-x}P_{10}Cr_x$ films showed higher coercivity at lower substrate temperature. In contrast, $Co_{96-x}P_4Cr_x$ films showed higher coercivity at higher substrate temperature.

REFERENCES

[1] C. R. Paik, I. Suzuki, N. Tani, M. Ishikawa, Y. Ota and K. Nakamura, IEEE Trans. Magn., 28, 3084(1992)

[2] B. R. Natarajan and E. S. Murdock, IEEE Trans. Magn. 24, 2724(1988)

[3] K. H ller, G. Dietz, R. Hausmann and K. Kolpin, J. Magn. Magn. Mater., 53, 103(1985)

[4] Tu Chen, D. A. Rogowski and R. M. White, J. Appl. Phys., 49, 1816(1978)

[5] Luciano Lanotte and Flavio Porreca, Proc. of the sysposium on magnetic properties of amorphous metals, pp. 129-131, Benalmadena Spain, 1987

[6] F. Stein and G. Dietz, J. Magn. Magn. Mater., 117, 45(1992)

[7] G. J. Tarnolpolsky, H. N. Bertram and L. T. Trans, J. Appl. Phys., 69, 4730(1991)

[8] P. W. Jang, Ph. D. Thesis, Seoul National University (1991)

[9] M. Sagoi, R. Nishikawa and T. Suzuki, IEEE Trans. Magn., 22, 1335(1986)

[10] J. A. Brain, B. M. Clemens, S. M. Brennan and H. Kataoka, IEEE Trans. Magn., 29, 300 (1993)

수평자기기록용 Co-P, Co-P-Cr 박막의 자기적특성

장평우
청주대학교 물리학과
충북 청주시 내덕동 *36, 360-764*

손홍균
서울대학교 금속공학과
서울시 관악구 신림동 산*56-1, 151-742*

이택동
한국과학기술원 서울분원
서울시 동대문구 청량리동 *207-43, 130-012*

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고보자력의 새로운 수평자기기록용 매체를 개발하기위해서 Co-P /Cr과 Co-P-Cr /Cr박막의 자기적 특성을 연구하였다. 상온에서 성막된 Co-P 이원합금의 경우 P의 함량이 9 -12 at.%에서 835 Oe의 보자력을 나타내었다. Co-P 이원합금의 경우 P의 함량이 9 -12 at.%에서 기판온도가 높을수록 보자력은 오히려 감소하였으며, 이것은 Co-P단일상이 Co와 Co_2P상으로의 분해에 기인하는 것으로 판단된다. 그러나 P을 12 at.%이상으로 첨가하면 비정질상의 형성으로 보자력은 급격히 감소하였다. Co-P-Cr 삼원합금박막의 보자력은 Cr 함량이 증가함에 따라 증가하여 상온에서 성장한 $Co_{84}P_{10}Cr_6$의 박막에서 1020 Oe의 높은 보자력을 얻을 수 있었다.