Influence of Sputtering Conditions for Co/Pd Multilayer on its Magnetic Properties and Crystalline Microstructure

Junichi Sayama*, Jun Kawaji*, Mutsumi Tanaka*, Toru Asahi**, Satoshi Matsunuma***, and Tetsuya Osaka*,**

*School of Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

**Advanced Research Institute for Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

***Development and Technology Division, Hitachi Maxell, Ltd., 6-20-1 Kinunodai, Yawaramura, Ibaraki 300-2496, Japan

The effects of substrate temperatures during deposition and N₂ gas addition to Ar sputtering gas on the magnetic properties and crystalline microstructure of Co/Pd multilayered films were investigated. The Co/Pd multilayered film deposited at a substrate temperature of 230 °C with Ar containing N₂ of 0.06 mTorr exhibited weaker intergranular exchange coupling than that deposited at room temperature without N₂ addition. Plan-view TEM observation revealed that the crystal grains in the Co/Pd multilayered film, which was subjected to the heating process with N₂ additive gas, were physically isolated by vacant grain boundaries, resulting in the decrease in intergranular exchange coupling.

Key words: Co/Pd multilayered film, perpendicular magnetic recording media, intergranular exchange coupling, substrate temperature, N₂ gas addition

1. Introduction

Co/Pd multilayered films are promising candidates for perpendicular magnetic recording media with high thermal stability because of their high perpendicular magnetic anisotropy^{1), 2)}. However, the high medium noise of Co/Pd multilayered media is a critical issue. The high medium noise results from large magnetic clusters brought about by strong intergranular exchange coupling along the film plane. Decreasing the intergranular exchange coupling is essential for the reduction of medium noise. Many studies have been carried out in order to decrease the intergranular exchange coupling. Appropriate sputtering conditions, *e.g.*, deposition under high Ar gas pressure³⁾, sputtering using Kr gas instead of Ar gas⁴⁾, and O₂ gas addition to Ar sputtering gas for deposition of Co-B/Pd-B multilayered films⁵⁾, promoted isolation of the Co/Pd crystal grains and thereby reduced the intergranular exchange coupling. In most studies, Co/Pd multilayered films are deposited by sputtering at room temperature. Interestingly, Co/Pt multilayered films fabricated by electron beam evaporation have been reported to show weak intergranular exchange coupling when deposited onto a heated substrate⁶⁾. The addition of N₂ to Ar sputtering gas has also been known to result in fine crystal grain structure⁷⁾.

In this study, heating of the substrate during deposition and addition of N₂ to Ar gas were applied to sputter-deposited Co/Pd multilayered films. Their effects on magnetic properties, crystalline microstructure, and

read-write (*R/W*) characteristics of the Co/Pd multilayered perpendicular magnetic recording media were investigated in detail.

2. Experiment

The samples composed of [Co (0.2 nm)/Pd (0.8 nm)]₂₀/Pd (5 nm)/substrate were prepared by dc magnetron sputtering. The crystallized glass disks with 2.5 inch in diameter were used as substrates. The sputtering conditions are listed in Table 1. The substrate temperature during deposition was set to 20 or 230 °C. The partial pressure of N₂ gas was 0.3 % of Ar gas pressure, *i.e.*, 0.06 mTorr. The layer structure of the samples for the *R/W* experiments was C (5 nm)/[Co (0.2 nm)/Pd (0.8 nm)]₂₀/Pd (5 nm)/C (5 nm)/CoZrNb (300 nm)/substrate. The values of saturation magnetic flux density and coercivity for the CoZrNb soft magnetic underlayer (SUL) were 14 kG and 10 Oe, respectively.

Magnetic properties were measured by using a vibrating sample magnetometer (VSM, maximum applied field H_{max} = 15 kOe), a torque magnetometer (H_{max} = 20 kOe), and a polar Kerr effect magnetometer (H_{max} = 20 kOe). Magnetic anisotropy field (H_k) was calculated by using the following equation involving magnetic anisotropy constant (K_u) and saturation magnetization (M_s):

$$H_k = 2K_u / M_s. \quad (1)$$

The value of K_u was obtained by adding a demagnetization field energy, $2\pi M_s^2$, to the experimental value of the magnetic anisotropy constant, K_{eff} . Surface roughness and magnetic domain structure of the samples were observed by an atomic force microscope (AFM) and a magnetic force microscope (MFM), respectively. The crystalline microstructure was analyzed with an X-ray diffractometer

Table 1 Sputtering conditions.

Background pressure [Torr]		< 3.0 × 10 ⁻⁷
Ar pressure [mTorr]	Co/Pd	20 (+ N ₂ 0.06)
	Pd	100
	C	50
	CoZrNb	5
Substrate temperature [°C]	Co/Pd	20 or 230
	Pd	20 or 230
	C	20
	CoZrNb	20

Table 2 Magnetic properties of Co/Pd multilayered films.

Film	Sub. temp. [°C]	N ₂ pressure [mTorr]	M_s [emu/cm ³]	H_c [kOe]	α [-]	$D_{cluster}$ [nm]	H_k [kOe]
A	20	0	320	5.3	3.6	169 ± 30	23.4
B	230	0	340	4.7	3.6	167 ± 37	20.0
C	20	0.06	240	4.2	2.6	143 ± 25	21.2
D	230	0.06	310	5.2	2.0	135 ± 26	17.7

(XRD) using Cu-K α radiation at an acceleration voltage of 50 kV and an emission current of 200 mA, and with a transmission electron microscope (TEM) with an acceleration voltage of 200 kV. The compositions of the grains and grain boundaries were determined by energy dispersive X-ray spectroscopy (EDS). The R/W characteristics were evaluated with a merged MR head for recording (gap length $G_r = 0.28 \mu\text{m}$, track width $T_w = 1.45 \mu\text{m}$) and reading (shield-to-shield gap length $G_{s-s} = 0.2 \mu\text{m}$, $T_w = 0.9 \mu\text{m}$). The linear velocity was 6.35 m/s. The reproduced voltage was measured as the peak-to-peak amplitude of the fundamental component of the signal by using a spectrum analyzer. The medium noise was calculated by subtracting the system noise power from the total noise power and integrating up to 50 MHz.

3. Results and Discussion

3.1 Magnetic properties

Table 2 shows magnetic properties for the Co/Pd multilayered films used in this study. These films were deposited under four sputtering conditions (A-D); varying the substrate temperature and the N₂ partial pressure (Table 2). The values of M_s , coercivity in the direction perpendicular to the film surface (H_c), and the M - H loop slope parameter (α) defined as $4\pi(dM/dH)_{H=H_c}$ were measured by using a VSM. The value of α is regarded as a parameter reflecting the magnitude of intergranular exchange coupling⁸⁾ and have been reported to be closely related to magnetic cluster diameter ($D_{cluster}$)⁹⁾. The squareness ratio ($SQR = M_r / M_s$, where M_r is remanent magnetization) was equal to unity within the experimental error and a nucleation field (H_n) exhibited a large negative value (< -2.3 kOe) for all samples used. The values of H_c

for films B and C are small as compared with films A and D. The α value of film C is smaller than that of film A, which is thought to come from the decrease in not only the intergranular exchange coupling but also the exchange coupling within the grains, because the value of M_s for film C was markedly reduced. Film D has values of M_s and H_c similar to film A, although it has a smaller α value than film A. These results reveal that intergranular exchange coupling in Co/Pd multilayered films can be suppressed without a decrease in H_c by depositing the films on heated substrates in an Ar + N₂ atmosphere.

Table 2 also shows the values of $D_{cluster}$ for films A-D. Here, they are calculated as an average and a standard deviation of diameter of circles whose areas are equal to those of magnetic domains observed in the MFM images at the ac demagnetized state. The values of $D_{cluster}$ correlate with the α values. Namely, the smaller magnetic clusters are obtained for films exhibiting the lower α values. For film D, the decrease in intergranular exchange coupling leads to the formation of fine magnetic clusters.

3.2 Crystalline microstructure

Figures 1 (a) and (b) show plan-view TEM bright field images of Co/Pd multilayer for films A and D, respectively. The average and the standard deviation of the Co/Pd crystal grain diameter (D_{grain}) for these two films are 13.9 ± 2.5 and 19.8 ± 3.5 nm, respectively. The crystal grains for film D are larger than that for film A, while the grain boundaries for film D are more well-defined than those for film A. The grain boundaries turned out to be voids from EDS measurement results, consistent with the decrease in intergranular exchange coupling for film D. Nitrogen was detected in both the grains and the grain boundaries for film D with EDS, but the two-dimensional distribution of nitrogen composition could not be determined. The formation of nitrides was not confirmed in the electron diffraction patterns.

Figure 2 (a) shows the XRD patterns of films A-D together with that of the glass substrate. Figure 2 (b) represents XRD patterns where the glass substrate contribution is subtracted and only the reflection peak from fcc-Co/Pd(111) is observed. The 2θ values for the fcc-Co/Pd(111) of all the films varies within ± 0.1 deg., but in this study these differences are considered to be due to a systematic error in determining the origin of the 2θ angle. Film C deposited with N₂ additive gas shows a smaller peak than film A without it. In the case of films deposited onto a heated substrate, the peak intensity of film D deposited with N₂ additive gas is similarly lower

Fig. 1 Plan-view TEM bright field images of Co/Pd multilayer for films A (a) and D (b) listed in Table 2.

Fig. 2 (a) XRD patterns in the range of $2\theta = 37\text{--}45$ deg. of films A, B, C, and D together with that of glass substrate. (b) XRD patterns in the range of $2\theta = 39\text{--}43$ deg., where the counts of glass substrate are subtracted. The sign ▼ indicates the peak for fcc-Co/Pd (111) reflection.

than that of film B without it. The decrease in the peak intensity is thought to be attributed to the suppression of the growth of Co/Pd crystal grains by adding N_2 . The peak intensities of films B and D deposited on the heated substrate are greater than those of films A and C deposited at room temperature, respectively. This result indicates that the deposition on the heated substrates enlarges the Co/Pd crystal grains and/or enhances the fcc-Co/Pd(111) preferred orientation. By comparing the peak intensities of fcc-Co/Pd(111) in XRD measurements and the values of D_{grain} obtained from TEM observation between films A and D, we infer that the increase in the peak intensity reflects the enlargement of the Co/Pd crystal grains. The heating of the substrate during deposition enhances the Co/Pd grains growth in the lateral direction, which was observed as in the case of the Co/Pt films deposited with electron beam evaporation⁶⁾. Film B deposited on the

heated substrate is considered to consist of larger grains than film A, although the values of D_{cluster} for both films are similar. This suggests that the isolation of Co/Pd grains is promoted and the clustering of magnetic domains is suppressed by raising the substrate temperature during deposition as reported in the previous paper⁶⁾. Especially in this study, the effect of deposition on high substrate temperatures is found to be pronounced in the case of film D deposited with N_2 additive gas.

3.3 Evaluation of surface magnetic anisotropy

Film D exhibits weaker intergranular exchange coupling than film A, but at the same time it has a slightly lower perpendicular magnetic anisotropy, as shown in Table 2. The origin of perpendicular magnetic anisotropy in Co/Pd multilayered films have been said to be surface magnetic anisotropy at the interfaces of Co and Pd layers¹⁾. We evaluated the surface magnetic anisotropy of films A and D from the relationship between $K_{\text{eff}}\lambda$ and t_{Co} , as shown in Fig. 3, by using the following phenomenological equation¹⁰⁾.

$$K_{\text{eff}}\lambda = 2K_s + K_v t_{\text{Co}}, \quad (2)$$

where λ is the Co/Pd bi-layer period, K_s is surface magnetic anisotropy energy, K_v is volume magnetic anisotropy energy, and t_{Co} is the thickness of a constituent Co layer. Table 3 lists the values of K_s and K_v for films A and D, which are determined as the intercept with the ordinate and as the slope of the straight line obtained by the least-square fitting in Fig. 3, respectively. There is little difference between the K_v values of these two films,

Fig. 3 Relationship between $K_{\text{eff}}\lambda$ and t_{Co} .

Table 3 Values of K_s and K_v for films A and D.

Film	K_s [erg/cm ²]	K_v [10 ⁶ erg/cm ³]
A	0.325	− 9.52
D	0.252	− 9.89

Fig. 4 XRD patterns in the range of $2\theta = 6-10$ deg. of films A and D together with that of glass substrate. The sign ▼ indicates the peak corresponding to the bi-layer periodicity of Co and Pd layers.

but the value of K_s for film D is smaller than that for film A. The degradation of perpendicular magnetic anisotropy in film D is caused by the decrease in surface magnetic anisotropy energy.

An XRD measurement in the low angle region of 2θ enables us to evaluate the regularity of periodic bi-layer structure of Co and Pd layers. Figure 4 shows XRD patterns in the range of 6 to 10 deg. of films A and D together with the result of the glass substrate. The peak intensity in the low angle region corresponding to the regularity of bi-layer structure for film D is lower than that for film A, whereas film D has larger Co/Pd crystal grains and exhibits a greater peak intensity for fcc-Co/Pd(111) than film A as shown in Figs. 1 and 2, respectively. These results indicate the deterioration of the regularity of the bi-layer structure in film D. This could be due to inter-diffusion between Co and Pd sublayers, which was promoted by heating the substrate during deposition. From AFM observations, deposition on the heated substrate and with N_2 additive gas increased surface roughness of the films, which may also lead to the bi-layer structure deterioration. The irregularity in the bi-layer structure decreased the surface magnetic anisotropy energy, causing a low perpendicular magnetic anisotropy.

3.4 Application to double-layered media

It was confirmed that the sputtering process proposed in this study was useful for the fabrication of Co/Pd

multilayered films with weak intergranular exchange coupling ($\alpha \sim 2$). The above deposition process was applied to the recording layer of double-layered media with a SUL. Magnetic properties and R/W characteristics for the media using films A and D as the recording layer, which were designated as media A' and D', respectively, are listed in Table 4. Magnetic properties for the media were measured by using a Kerr effect magnetometer. For estimation of α values, values of M_s for single-layered films measured with the VSM were used. The tendencies of the magnetic properties are not affected by the addition of an SUL.

The reproduced voltage for medium D' was similar to that for medium A'. On the other hand, medium D' exhibited much lower medium noise than medium A', especially at high linear recording density over 200 kFRPI. As a result, S/N ratio for medium D' is higher by 7-8 dB than that for medium A' at over 200 kFRPI, as shown in Table 4. It is considered that the decreases in intergranular exchange coupling and magnetic cluster diameter lead to the improvement of R/W characteristics in medium D'. The perpendicular magnetic anisotropy for film D is slightly less than that for film A, as shown in Table 2 and Fig. 3. However, the reproduced voltage at the low linear recording density of 2 kFRPI for medium D' remained up to 1800 seconds analogous to medium A', owing to the SQR of unity and a large value of $-H_n$.

4. Conclusion

The effects of substrate temperature and N_2 gas addition to Ar sputtering gas on magnetic properties, especially intergranular exchange coupling, and crystalline microstructure of Co/Pd multilayered films were investigated. By depositing Co/Pd multilayered films at 230 °C with N_2 partial pressure of 0.06 mTorr, the intergranular exchange coupling was suppressed without a decrease in H_c , which came from the enhancement in the physical isolation of Co/Pd crystal grains. This film possessed smaller magnetic clusters and exhibited higher S/N ratio than the film deposited at room temperature without N_2 gas addition. These results indicate that the sputtering process proposed in this study was effective for fabricating low noise Co/Pd multilayered double-layered media.

Acknowledgement

This work was carried out at the "Center for Practical Nano-Chemistry" for the 21C-COE Programme of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and was also financially

Table 4 Magnetic properties and R/W characteristics for double-layered media.

Medium	Sub. temp. [°C]	N_2 pressure [mTorr]	H_c [kOe]	α [-]	S_{p-p}/N_{rms} ratio (at 200 kFRPI)
A'	20	0	6.1	5.3	0.7
D'	230	0.06	5.7	1.9	8.2

supported by Center of Excellence Research on “Establishment of Molecular Nano-Engineering by Utilizing Nanostructure Arrays and its Development into Micro-System” from MEXT. The authors express their gratitude to Dr. K. Tagami and Mr. N. Ohshima, NEC Corporation, for their cooperation in the torque measurement.

References

- 1) P. F. Carcia, A. D. Meinhaldt, A. Suna: *Appl. Phys. Lett.*, **47**, 178 (1985).
- 2) B. M. Lairson, J. Perez, C. Baldwin: *Appl. Phys. Lett.*, **64**, 2891 (1994).
- 3) L. Wu, S. Yanase, N. Honda, K. Ouchi: *IEEE Trans. Magn.*, **33**, 3094 (1997).
- 4) W. Peng, O. Keitel, R. H. Victora, E. Koparal, J. H. Judy: *IEEE Trans. Magn.*, **36**, 2390 (2000).
- 5) H. Ohmori, A. Maesaka: *J. Magn. Magn. Mater.*, **235**, 45 (2001).
- 6) D. Weller, L. Folks, M. Best, E. E. Fullerton, B. D. Terris, G. J. Kusinski, K. M. Krishnan, G. Thomas: *J. Appl. Phys.*, **89**, 7525 (2001).
- 7) Y. Sano, H. Muraoka, I. Watanabe, Y. Nakamura: *J. Magn. Magn. Mater.*, **155**, 212 (1996).
- 8) I. Tagawa, A. Takeo, Y. Nakamura: *J. Magn. Magn. Mater.*, **155**, 341 (1996).
- 9) O. Kitakami, Y. Shimada: *Jpn. J. Appl. Phys.*, **40**, 4019 (2001).
- 10) H. J. G. Draaisma, W. J. M. de Jonge, F. J. A. den Broeder: *J. Magn. Magn. Mater.*, **66**, 351 (1987).

Received October 9, 2002; Accepted January 17, 2003.