A Study of Redistribution Phenomenon of Solute Atoms in CoCrTa and CoCr Perpendicular Recording Films by Annealing

Chung Ho HWANG¹, Taek Dong LEE², Kyung Ho SHIN³, and Yong Soo PARK¹

1)Dept. of Metal. Eng. Yonsei Univ., Seodaemun-ku, Seoul 120-749, Korea

2) Dept. of Advanced Materials Eng., KAIST, Dongdaemun-ku, Seoul, 130-650, Korea

3) Division of Metals, KIST, Seongbuk-ku, Seoul 136-791, Korea

Abstract ---- In the previous work¹, we have reported Ta addition is effective in increasing perpendicular coercivity of the films with Cr content lower than 17 at% Cr region and not effective in those with higher than 19 at% Cr region. Also the higher coercivity of the CoCrTa films is interpreted as the enhanced Cr segregation than Ta segregation itself. In the present work, we studied the redistributing behaviour of solutes of the as-deposited films by analysing changes of structures and magnetic properties before and after vacuum annealing. It was found that the redistributing atomic species during the annealing is Cr rather than Ta, which is in good agreement with our previous claims that Ta enhances Cr segregation in CoCrTa system.

I. INTRODUCTION

Higher coercivity at thinner film thickness is an essential requirement for a high density recording medium in perpendicular recording as well as in longitudinal recording. So far CoCr and CoCrTa films have been widely studied as strong candidates for the media. CoCrTa perpendicular recording films have superior magnetic properties to CoCr films. Small addition of Ta is more effective in raising the perpendicular coercivity than further addition of Cr to CoCr films containing 19 at% or less¹.

We have reported the higher coercivity behaviour of CoCrTa films is not associated with the segregation of Ta itself but associated with promotion of enhanced segregation of Cr due to the existence of Ta¹. This conclusion was drawn based on grain size examination, X-ray analysis and comparison of magnetic properties. An sputtering result has been reported by other researchers² suggesting Ta may not preferentially segregated but uniformly dispersed within grains in longitudinal sputtered films.

The purpose of this work is to study redistribution behaviour in sputter deposited films of Co_{81.4}Cr_{16.6}Ta₂ by analysing the changes of magnetic properties and structures by annealing. Co₈₁Cr₁₉ films were selected and studied as a reference. By comparing the magnetic properties of CoCrTa films with those of CoCr films before and after annealing, we tried to analyse the redistributing atomic species.

II. EXPERIMENTAL PROCEDURE

The films of different compositions were prepared by an rf sputtering method on polyimide substrates. For

compositional variation Ta chips and Cr chips of 99.99% purity were placed on Co₈₃Cr₁₇ and Co₈₁Cr₁₉ alloy targets. The compositions of the films were analysed with EPMA. For annealing experiments, 2.5 μ m thick free standing films were prepared by dissolving the substrates and were heat-treated isothermally at various temperatures in a vacuum of better than 1×10^{-5} torr. Magnetic properties were measured by a VSM and a torque magnetometer at room temperature. The structures of the films were studied by TEM and XRD.

III. RESULTS AND DISCUSSION

Fig.1 shows the variation of Ms in Co₈₁Cr₁₉ and Co_{81.4}Cr_{16.6}Ta₂ films deposited on 100°C substrates with varying annealing temperatures. The change of the

Fig.1 Variation of Ms of Co₈₁Cr₁₉ and Co_{81.4}Cr_{16.6}Ta₂ films with annealing temperature

As-sputtered

As-sputtered

550°C

550°C

650°C

(a)

650°C

(b)

Fig 2. TEM micrographs of $\text{Co}_{81}\text{Cr}_{19}$ films (a) and $\text{Co}_{81.4}\text{Cr}_{16.6}\text{Ta}_2$ films (b) before and after 550°C and 650°C anneal (2.5 μm , $T_{\text{sub}}=100^\circ\text{C}$)

perpendicular coercivity ($H_{\perp}$) of the two different composition films with annealing was very similar to the change of M_s . In the specimens of both compositions, when annealing temperature exceeds 500°C, M_s and $H_{\perp}$ decrease very rapidly. The ternary films deposited on water cooled substrate, however, did not show any change of M_s during the same heat treatments. The drops of M_s and $H_{\perp}$ are interpreted as being associated with redistribution of the solute atoms segregated during depositing process at a high substrate temperature. The CoCr film showed the increase of M_s after 1 hr annealing at 150°C but the coercivity did not change. In the previous works³⁻⁵, this type of M_s increase was not reported. The cause of this increase is not clearly understood.

Extensive structural analyses were done for both composition specimens before and after annealing by TEM and XRD. There were no appreciable grain growth and no second phase formation up to 550°C and 650°C annealing as shown in Fig. 2.

The in-plane micrographs were taken from mid-section of 2.5µm thick films. Average grain sizes of the all specimens were about 700Å while those of the as-sputtered films of 0.2µm thickness were in the range of 200~300Å. The grain size difference is originating from conical growth characteristics of the films. The larger grain size in the 2.5µm thickness films seems also to be associated with the lower coercivity.

X-ray diffraction showed about 1 degree increase in a half width of the rocking curve of the c plane diffraction peak in both binary and ternary films after the anneal at 550°C. $\Delta\Theta_{50}$ of (0002) plane diffraction increased linearly with increasing annealing temperature up to 550°C in both composition specimens. After annealing the as-sputtered films at 550°C, $\Delta\Theta_{50}$ increased from 5° to 6° in CoCr films and from 4° to 5° in CoCrTa films.

The fact that there is no grain growth and no appreciable c-axis alignments change during the anneal indicates the coercivity change by annealing should be associated with the solute atom redistribution.

In the earlier work¹, we have reported higher coercivity behaviour in CoCrTa system is not associated with segregation of Ta itself but associated with promotion of enhanced segregation of Cr due to the existence of Ta in the Co matrix. This prediction was later confirmed in a CoCrTa longitudinal medium by EDX studies in FE-TEM where Ta content was uniform within grains and Cr content was higher in grain boundary region⁶. To study the redistribution behaviour of the segregated solutes, we have measured the change of magnetic properties of CoCr and CoCrTa films at room temperature by varying annealing time at 550°C. Fig. 3, 4 and 5 show respectively the change of M_s , the perpendicular coercivity and the perpendicular anisotropy (K_{prep}) of the CoCr and CoCrTa films

deposited on 100°C substrates.

Fig 3. Variation of normalized M_s of $\text{Co}_{81}\text{Cr}_{19}$ and $\text{Co}_{81.7}\text{Cr}_{16.7}\text{Ta}_{1.6}$ films with annealing time

Fig 4. Variation of perpendicular coercive of $\text{Co}_{81}\text{Cr}_{19}$ and $\text{Co}_{81.7}\text{Cr}_{16.7}\text{Ta}_{1.6}$ films with annealing time

Fig 5. Variation of perpendicular anisotropy of $\text{Co}_{81}\text{Cr}_{19}$ and $\text{Co}_{81.7}\text{Cr}_{16.7}\text{Ta}_{1.6}$ films with annealing time

It is very interesting to observe that the hard magnetic properties drop more rapidly for the early stage of annealing and this trend is stronger in the ternary system. This may indicate either higher concentration of segregated solute atoms are existing in the CoCrTa system than the CoCr binary system in the as-sputtered films or the diffusivity of the solute atoms in CoCrTa films is higher than that in CoCr films due to the addition of larger Ta atoms.

Both the higher concentration gradient and the higher diffusivity will bring about more rapid drop of the coercivity and K_{perp} during the anneal. Considering the amount of defects existing in as-sputtered films and the above-mentioned higher coercivity of the as-sputtered CoCrTa films, it is concluded that the concentration of the solute atoms in the segregation region is higher in the ternary films than in the binary films. After the 12 hrs anneal, M_s , the perpendicular coercivity and K_{prep} in both films become the same value. This suggests the same kind of solute atoms is redistributing during the anneal and less than 2 at% Ta existing in grains as solid solution is not effective in decreasing either the perpendicular coercivity or K_{prep} .

To analyse which atomic species are redistributing during the anneal, the change of lattice spacing in both films after annealing at various temperatures for 1 hr was measured as shown in Fig 6.

Fig 6. Variation of d spacing in $\text{Co}_{81}\text{Cr}_{19}$ and $\text{Co}_{81.7}\text{Cr}_{16.7}\text{Ta}_{1.6}$ films with annealing time

The slopes of the decrease in the lattice spacing were the same, which strongly suggests the redistributing atomic species in both films is Cr. If Ta segregated preferentially near the grain boundary should exist and be redistributed, the slope should be different in the ternary system. The decrease of d spacing in both specimens may be due to either reduction of residual stress or Cr redistribution. However, it was found that increase of Cr in CoCr system does not change the d spacing as shown in Fig 7. This result suggests that the

reduction in the d spacing in Fig 6 is due to reduction of residual stress during the annealing. From the above results, we conclude it is Cr which is redistributing during the anneal.

Fig 7. Variation of d spacing in $\text{Co}_{81}\text{Cr}_{19}$ and $\text{Co}_{81.7}\text{Cr}_{16.7}\text{Ta}_{1.6}$ films with Ta, Cr content

IV. CONCLUSION

By analysing the results of the annealing experiments of CoCrTa films, we found that the redistributing atomic species is Cr rather than Ta. Accordingly these results are supporting our earlier claim that higher coercivity in CoCrTa films than that in CoCr films is associated with the enhanced Cr segregation due to the existence of Ta in the matrix.

REFERENCES

1. C.H.Hwang, Y.S. Park, P.W.Jang and T.D.Lee: IEEE Trans. on Magnetics. 29, No 6, 3733 (1993)
2. Y. Deng, D.N.Lambeth, D.E.Laughlin: IEEE Trans. on Magnetics. 29, No 6, 3676 (1993)
3. P.W.Jang, Y.H.Kim, T.D.Lee and T.Kang: IEEE Trans. on Magnetics. 25, No 5, 4168 (1989)
4. M.Ishizuka, T.Komoda, S.Tsuchiimoto, M.Yoshikawa, S.Ishio and M.Takahashi: J. Magn.Magn. Mater. 35, 286 (1983)
5. J.E.Snyder, K.R.Mountfield and M.H.Kryder: J.Appl.Phys. 61, 3146 (1987)
6. J.Nakai, E.Kusumoto, T.Miyamoto, K.Yoshikawa and K.Itayama: DB-11, 6th Joint MMM-Intermag Conference