High coercivity rare earth–cobalt films

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Rare earth–cobalt (RCo, R=Sm, Pr) films with thicknesses from 30 to 700 nm have been prepared with and without a Cr underlayer by dc magnetron sputtering from a R_2Co_7 composite target. The as-deposited SmCo films with a Cr underlayer (SmCo‖Cr) have magnetic coercivities of about 500–2800 Oe and the PrCo‖Cr films have coercivities of about 100–300 Oe, but after annealing at 500 °C coercivities as high as 31 kOe for SmCo‖Cr films and 10 kOe for PrCo‖Cr films were observed. The as-deposited PrCo films are composed mostly of an amorphous phase with about 30 vol % of crystallites but after annealing at 500 °C the film is transformed completely to crystallites of about 10 nm diameter as revealed by high-resolution transmission electron microscopy (HRTEM). Nanodiffraction and HRTEM studies show that the crystallites have a closed-packed hexagonal structure. HRTEM study also shows that the annealed SmCo films with a Cr underlayer have grain sizes of about 20 nm and the SmCo films without the Cr underlayer have grain sizes of about 10 nm. The large increase in coercivity for the annealed films is due to the growth of the crystallites. [S0021-8979(96)33808-1]

INTRODUCTION

Thin films of hard magnetic materials such as rare earth–transition metal alloys are of interest for device applications and magnetic recording media. Among rare earth semi-hard magnetic films, SmCo films with a Cr underlayer prepared at room temperature with high magnetic coercivity (H_c) of 3–4 kOe, small grain size and high uniaxial anisotropy have shown good potential for high density recording media.[1–3] Velu *et al.*[4] have shown that $SmCo_4$ films on a Cr underlayer have a coercivity value of 3 kOe at room temperature. Recently, Okumura *et al.*[5] reported H_c of about 3.5 kOe for $Sm_{15}Co_{85}$‖Cr films. Liu *et al.*[6–8] reported systematic studies of the microstructure of SmCo‖Cr films including the Cr underlayer, SmCo layer, and the nanocrystallites in the SmCo layer. The dependence of H_c on the SmCo composition[1–3] is unclear but it has been shown that the H_c strongly depends on the sputtering condition such as substrate temperature and Ar pressure during deposition of Cr and SmCo. This dependence may be related to the microstructure of the films. The Cr underlayer helps to increase the coercivity by controlling the grain size and morphology of the SmCo layer and also improves the in-plane magnetization. Hence if crystallinity and grain growth is promoted in the SmCo layer a much higher value of coercivity can be obtained. This can be achieved by either depositing the film at high substrate temperature or by post-annealing the as-deposited films. A coercivity of 30 kOe was obtained for 4000-Å-thick $Co_{3.65}Cu_{1.35}Sm$ films prepared at substrate temperature of 600 °C by Theurer *et al.*[9] Cadieu *et al.*[10] have shown that $SmCo_5$ films directly crystallized on to a heated substrate have H_c of about 23 kOe. The reason for this high coercivity was associated with the high magnetic anisotropy and the fine grain structure.

In the rare earth–cobalt system the low Co phase adjacent to $SmCo_5$ is in general of the Sm_2Co_7 type which has reasonably high anisotropy field $H_A > 200$ kOe.[11] The PrCo compounds also feature excellent intrinsic magnetic properties comparable to the SmCo compounds. The Pr_2Co_7 phase has $H_A > 100$ kOe[11] and the Pr_5Co_{19} phase has $H_A > 38$ kOe.[12] In this work we report the effect of post-annealing for Pr_2Co_7 and Sm_2Co_7 films with and without the Cr underlayer.

EXPERIMENTAL PROCEDURE

R_2Co_7 (R=Sm, Pr) films with thickness from 30 to 700 nm were prepared with and without a Cr underlayer by dc magnetron sputtering from a composite target. All the films have a Cr overlayer of 10 nm to protect the RCo layer. The Sm_2Co_7 target was made by pressing the Sm_2Co_7 powder and then sintering in vacuum at 1100 °C for 30 min and the Pr_2Co_7 target was made by pressing the Pr_2Co_7 powder and then sintering in vacuum for 30 min at 1050 °C. The Cr target was obtained commercially and had a 99.9% purity. The base pressure of the sputtering system was 5×10^{-8} Torr and the Ar pressure during sputtering was 20 mTorr. The sputtering rate for Pr_2Co_7 and Sm_2Co_7 was 1.1 Å/s and for Cr was 5 Å/s.

The magnetic properties of the films were measured with an alternating gradient force magnetometer (AGFM) and SQUID magnetometer. The composition of the films was analyzed by energy dispersive x-ray analysis (EDAX) and was found to be close to the target composition. The structure was studied by x-ray diffraction and high resolution electron microscopy (HRTEM).

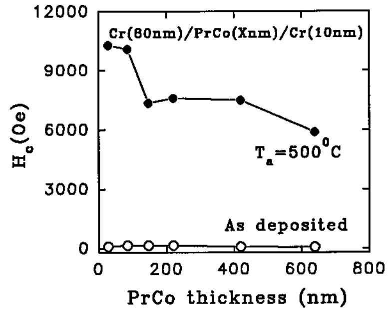

FIG. 1. Coercivity vs PrCo layer thickness for the as-deposited and annealed at 500 °C PrCo‖Cr films with a Cr underlayer of 80 nm.

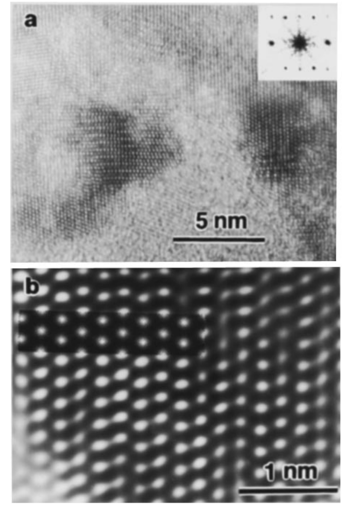

FIG. 2. (a) HRTEM image of Cr(80 nm)/PrCo(28 nm)/Cr(10 nm) film annealed at 500 °C. (b) HRTEM image of a crystallite in (a).

RESULTS AND DISCUSSION

We first discuss the magnetic and structural properties for the as-deposited and annealed PrCo films. Figure 1 shows the dependence of the coercivity on the PrCo layer thickness for the PrCo‖Cr films with a Cr underlayer of 80 nm. The as-deposited films show a coercivity of only about 100–300 Oe but after annealing at 500 °C in vacuum for 20 min there is a large enhancement of coercivity. The H_c of the films annealed at 500 °C decreases from about 10 to 5.9 kOe as the film thickness increases from 28 to 640 nm. It was also observed for the 28-nm-thick PrCo‖Cr film that upon annealing up to 350 °C, H_c was nearly unchanged but at 400 °C H_c increased drastically to about 7.7 kOe[13] and at 500 °C the H_c reached about 10 kOe. A bright-field TEM micrograph of the 28-nm-thick PrCo‖Cr film annealed at 500 °C is shown in Fig. 2. The as-deposited films are composed of a mostly amorphous PrCo layer with about 30% volume fraction of crystallites and have small coercivity values because of the mostly amorphous PrCo layer. The film annealed at 500 °C shown in Fig. 2(a) contains nearly 100% crystallites with a grain size of 10 nm resulting in the large increase in the coercivity. The x-ray diffraction pattern of the as-deposited 420-nm-thick PrCo film only shows the (110) diffraction peak of bcc Cr and no PrCo peaks are observed for the films with and without the Cr underlayer. This is due to the large amount of amorphous phase and small crystallites in the PrCo films. After annealing at 500 °C the PrCo layer is crystallized and we observe a few sets of peaks from the x-ray diffraction pattern. The two most intense reflections are observed for 2θ=35.5° and 2θ=42°. It is difficult to identify the crystal structure unambiguously from the x-ray diffraction pattern because of the limited number of peaks and the several possible phases around the Pr/Co atomic ratio of 3.5, these include the $PrCo_3$, Pr_2Co_7 and Pr_5Co_{19} phases. The detailed crystal structure of the annealed 28-nm-thick PrCo‖Cr film was then investigated by nanodiffraction and HRTEM. It was found that the crystallites as shown in Fig. 2(b) have a hexagonal closed packed structure with frequent stacking faults. The nanodiffraction pattern can be well matched to the hexagonal closed packed structure.

In order to investigate whether the Cr underlayer was crucial for the enhancement of coercivity after annealing we compared the magnetic properties of a 420-nm-thick PrCo film with and without a Cr underlayer. It was observed that for the 420-nm-thick PrCo film with no Cr underlayer but with a Cr overlayer of 10 nm the H_c was about 9 kOe and $M_S \approx 400$ emu/cc after annealing at 500 °C whereas for the 420-nm-thick PrCo film with a Cr underlayer of 80 nm and a Cr overlayer of 10 nm the H_c was about 7.5 kOe and $M_s \approx 300$ emu/cc after annealing at 500 °C. Both the samples have squareness $S(M_r/M_s)=0.8$, but the coercivity squareness S^* for the film with the Cr underlayer was 0.7 and for the film without the Cr underlayer the S^* was about 0.35. Hence we show that if crystallinity and grain growth are promoted a large increase in coercivity can be obtained for the PrCo films with and without the Cr underlayer, except that the films with a Cr underlayer have a better hysteresis loop squareness.

Next we report the magnetic properties of the as-deposited and annealed SmCo films with and without the Cr underlayer. Figure 3 shows the dependence of the coercivity on the SmCo layer thickness for the SmCo‖Cr films with and without the Cr underlayer. The as-deposited films show H_c of about 500–2800 Oe but after annealing at 500 °C for 20 min in vacuum there is a large increase in coercivity. The coercivity of the films with the Cr underlayer of 80 nm and a Cr overlayer of 10 nm annealed at 500 °C varies from 21 to 29 kOe with the maximum coercivity value obtained for 100-nm-thick SmCo film. The H_c of the SmCo film without the

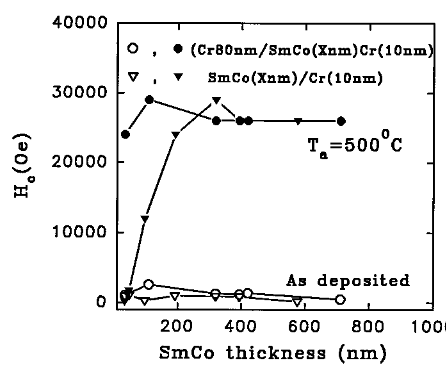

FIG. 3. Coercivity vs SmCo layer thickness for the as-deposited and annealed at 500 °C SmCo films with and without a Cr underlayer.

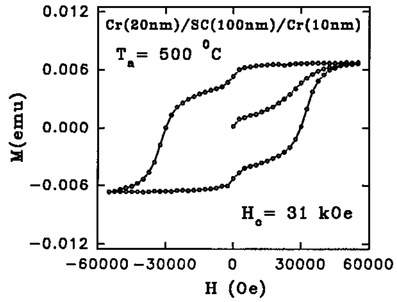

FIG. 4. Hysteresis loop for the 100-nm-thick SmCo film with a Cr underlayer of 20 nm annealed at 500 °C.

Cr underlayer but with a Cr overlayer of 10 nm after annealing at 500 °C shows a large increase in coercivity only for SmCo films with thickness of at least 100 nm and above. A maximum H_c value of 29 kOe is obtained for 300-nm-thick SmCo film. For films without the Cr underlayer and SmCo layer thickness less than 100 nm the reason for no remarkable increase in coercivity after annealing is not clear at this point. This behavior is also observed for the PrCo film with thicknesses less than 100 nm and no Cr underlayer. The M_s of the as-deposited SmCo films is about 400 emu/cc and after annealing at 500 °C the M_s value for the films with the Cr underlayer of 80 nm is about 200 emu/cc and for the films without the Cr underlayer the M_s is about 300 emu/cc. For the SmCo films with a Cr underlayer thickness less than 80 nm there is not a significant change in the coercivity but the M_s value of the films is slightly higher compared to the films with a Cr underlayer of 80 nm. For the 100-nm-thick SmCo film with a Cr underlayer of only 20 nm the M_s was about 250 emu/cc and the H_c was about 31 kOe after annealing at 500 °C. The hysteresis loop for the annealed 100-nm-thick SmCo film with a Cr underlayer of 20 nm measured with a maximum applied field of 55 kOe parallel to the film surface is shown in Fig. 4. The film shows a coercivity of 31 kOe.

Liu *et al.*[6] have observed that for the as-deposited films the Cr underlayer has grain size of about 24 nm and the SmCo layer consist of nanocrystallites about 5 nm diameter embedded in an amorphous matrix. Figure 5 compares the dark field images taken from the SmCo films with and without a Cr underlayer. The film with the Cr underlayer has grain sizes of about 20 nm while the film without the Cr underlayer has grains sizes of about 10 nm. Nanodiffraction and HRTEM study to determine the crystal structure of the annealed films is in progress. The reason for the large enhancement in coercivity after annealing is very likely due to the crystallization of the SmCo grains.

CONCLUSION

In this work we have shown that 28-nm-thick PrCo films with a Cr underlayer of 80 nm after annealing at 500 °C have in-plane coercivity as high as 10 kOe, $S=0.9$ and $S^*=0.75$. The PrCo‖Cr films have magnetic properties and microstructure which show potential as high density recording media. Nanodiffraction and HRTEM studies show that the crystallites in the annealed film have a hexagonal closed packed structure with frequent stacking faults. The enhancement of H_c after annealing is likely due to the crystallization of the PrCo grain.

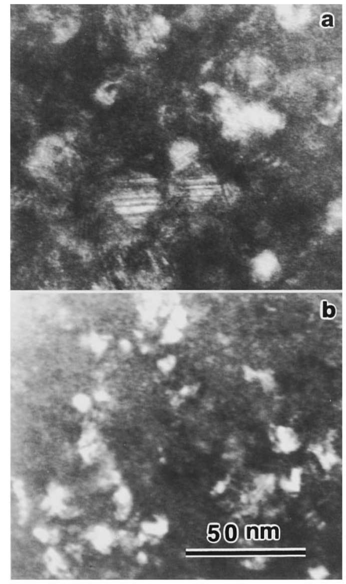

FIG. 5. Comparison of dark field images taken from a SmCo films (a) with the Cr underlayer and (b) without the Cr underlayer.

After annealing at 500 °C H_c as high as 31 kOe was obtained for 100-nm-thick SmCo film with a Cr underlayer of 20 nm and H_c of about 29 kOe for 300-nm-thick SmCo film without the Cr underlayer. By post-annealing the as-deposited films with and without the Cr underlayer, crystallization, and grain growth is promoted for the SmCo films resulting in a large increase in coercivity.

ACKNOWLEDGMENTS

We are grateful for financial support from the National Storage Industry Consortium (NSIC) and the Advanced Research Projects Agency (ARPA) under Grant No. MDA972-93-1-0009 and from the National Science Foundation under Grants No. DMR-9222976 and No. OSR-9255225.

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