

# Improvement of the magnetic properties of CoNiCr thin films by annealing

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The changes in the magnetic properties of CoNiCr/Cr thin films with annealing are found to depend not only on the annealing conditions but also on the Cr underlayer thickness  $d_{Cr}$ . After vacuum anneal, the in-plane coercivity  $H_c$  increased initially with total annealing time  $\tau_a$  and then leveled off. The  $H_c$  increase was greater at higher annealing temperatures  $T_a$  and in samples with thicker Cr underlayers.  $H_c$  values as high as 1800 Oe were obtained. The squareness  $S^*$  decreased with  $\tau_a$ , and the saturation magnetization  $M_s$  decreased slightly with  $\tau_a$ . No significant change was found in the grain size and the crystal texture of the films after annealing, regardless of the Cr underlayer thickness. However, for the sample with a large  $H_c$  increase following anneal, it was found that the corresponding Lorentz micrograph image changed dramatically. TEM x-ray energy dispersive data indicated that the Cr concentration in the CoNiCr layer increased after anneal. The changes in  $H_c$ ,  $S^*$ , and  $M_s$  following air anneal were similar to those found following vacuum anneal. However, at the same  $T_a$ , the increase in  $H_c$  was less; also  $M_s$  was found to decrease noticeably. We believe that the changes in magnetic properties following anneal are associated with increased Cr content in the grain boundaries.

## I. INTRODUCTION

Large values of in-plane coercivity  $H_c$  and saturation magnetization  $M_s$  are desired in longitudinal magnetic recording media.<sup>1</sup> Sputtered CoNiCr thin films have been considered as good candidates for longitudinal media.<sup>2</sup> In a previous paper<sup>3</sup> we reported an increase in  $H_c$  by the deposition of a Cr underlayer ( $H_c$  values as large as 700 Oe were observed), but still higher coercivity values are expected to be needed for future applications.<sup>4</sup> In CoCr/glass media, post processing by annealing has been found to improve the magnetic properties.<sup>5</sup> In this article we present the results of our investigation on the effects of annealing on the magnetic properties of CoNiCr/Cr thin films.

## II. EXPERIMENTAL METHODS

Bilayer CoNiCr/Cr thin films were deposited on glass substrates by rf sputtering in a LH Z400 system. After evacuation to  $5 \times 10^{-7}$  Torr, the Ar pressure was set at 10 mT in the deposition chamber during sputtering. Cr underlayers were deposited at 5 nm/min. The Cr underlayer thicknesses  $d_{Cr}$  ranged between 5 and 350 nm. The CoNiCr layers were deposited at 5.5 nm/min; the CoNiCr layer thickness was fixed at 100 nm. Annealing was carried out in a  $1 \times 10^{-5}$  Torr vacuum as well as in air. Annealing temperatures,  $T_a$ , ranged from 360 to 550 °C; total annealing time  $\tau_a$  ranged from 0.5 to 12 h. The in-plane coercivity  $H_c$ , coercivity squareness,  $S^*$ , and saturation magnetization  $M_s$  were measured by vibrating-sample magnetometer (VSM). Composition depth profiles were obtained by Auger analysis. The microstructure of the thin films was observed by transmission electron microscopy (TEM). Magnetic domain struc-

tures were studied by Lorentz microscopy (LEM) with the objective lens current turned off.

## III. RESULTS AND DISCUSSION

### A. Vacuum anneal

Samples with five different underlayer thicknesses between 5 and 350 nm were annealed at 360 and 400 °C. For the 360 °C anneal, the samples were annealed for a time sequence totaling 12 h. The magnetic properties of the samples were measured after each time increment. For the 400 °C anneal, the samples were annealed in one step for 2.5 h. The changes in magnetic properties were found to be sensitive to  $T_a$ ,  $d_{Cr}$ , and  $\tau_a$ .  $H_c$ ,  $S^*$ , and  $M_s$  are plotted in Figs. 1(a) and 1(b) as a function of  $\tau_a$ .

For  $d_{Cr} > 45$  nm,  $H_c$  initially increased with  $\tau_a$  and then leveled off. Samples with larger  $d_{Cr}$  required longer  $\tau_a$  times to reach  $H_c$  saturation. The increase in  $H_c$  was greater for the larger  $d_{Cr}$  samples. We can see in Fig. 1(a) that, after 12 h of anneal, the  $d_{Cr} = 45$  nm sample has reached  $H_c$  saturation; however, the  $H_c$  of the  $d_{Cr} = 250$  and 350 nm samples still had not leveled off.  $S^*$  decreased with  $\tau_a$  for all samples; the  $d_{Cr} = 45$  nm sample had the greatest decrease in  $S^*$  after 12 h of anneal.  $M_s$  decreased slightly with annealing.

At  $T_a = 400$  °C [Fig. 1(b)], the  $H_c$  of the  $d_{Cr} = 5$  nm sample did not change much with annealing. For the larger  $d_{Cr}$  samples the  $H_c$  increased progressively with  $d_{Cr}$ . Compared with  $T_a = 360$  °C,  $H_c$  increased with  $\tau_a$  much more rapidly and the magnitude of the  $H_c$  increase was much greater.  $H_c$  reached 1800 Oe for the  $d_{Cr} = 350$  nm sample after anneal.  $S^*$  decreased with annealing, more so than at  $T_a = 360$  °C.  $M_s$  only decreased slightly.

Figures 2(a) and 2(b) are the bright field TEM images and the corresponding selected area diffraction (SAD) patterns of as-sputtered and annealed (at 360 °C) 100-nm-thick CoNiCr thin films deposited on a 350-nm Cr underlayer.

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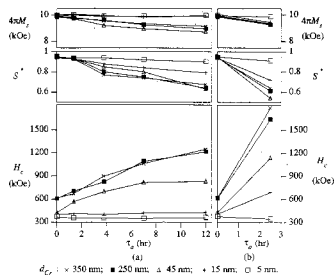


FIG. 1. Variation of  $H_c$ ,  $S^*$ , and  $M_c$  of CoNiCr/Cr films after vacuum anneal at (a)  $T_a = 360^\circ\text{C}$  and (b)  $T_a = 400^\circ\text{C}$ .

The average grain sizes before and after anneal are all about 30 nm. The SAD patterns are also similar. Although no major microstructural differences due to annealing were found, the  $H_c$  of (100-nm) CoNiCr/(350-nm) Cr increased remarkably after the anneal. Therefore, the coercivity increase must be associated with a mechanism other than microstructural changes.

In order to see if some chemical composition change occurred during the anneal, annealed and as-sputtered (100-nm) CoNiCr on (350-nm) Cr film specimens were exam-

ined by x-ray energy dispersive spectroscopy (EDS) in a transmission electron microscope. After annealing for 12 h at  $360^\circ\text{C}$ , the Cr concentration was found to have increased from 7.5% to 9.8% in the CoNiCr layer. This increase in Cr content suggests that Cr diffused from the Cr underlayer to the CoNiCr layer during anneal. Since the grain-boundary diffusion constant generally is larger than the bulk diffusion constant, the mass transport by diffusion must be governed by grain-boundary diffusion. If the grain boundaries act as diffusion channels, one would expect a higher Cr concentration in the grain boundaries than within the grains of the CoNiCr layer. Cr segregation is another mechanism by which the Cr concentration at the grain boundaries could be increased. A high Cr concentration at the grain boundaries could reduce the magnetic coupling between grains; hence, the coercivity would increase and the squareness would decrease.<sup>6</sup> Although we are unable to measure the Cr concentration at the grain boundaries directly, the trends in the magnetic data with annealing are consistent with this hypothesis. The high  $S^*$  value ( $S^* > 0.9$ ) in our as-sputtered samples is probably due to strong coupling between grains, whereas after anneal the  $S^*$  values are closer to the isolated particle situation.<sup>6</sup>

The Lorentz microscopy study also suggested that the coupling between grains is reduced after annealing. The Lorentz micrographs of the as-sputtered and annealed (at  $360^\circ\text{C}$  for 12 h) samples with  $d_{Cr} = 350$  nm are shown in Figs. 3(a) and 3(b). For the as-sputtered sample, a "feather-like" ripple structure was observed. The length of the ripple branches<sup>7</sup> is about 250 nm. This number roughly represents

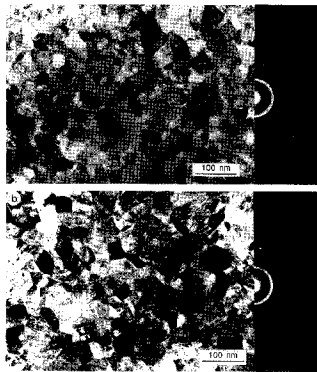


FIG. 2. Bright field TEM images and corresponding SAD patterns taken from the top of the CoNiCr layer of (a) as-sputtered and (b) vacuum-annealed, 12-h at  $360^\circ\text{C}$ , (100 nm) CoNiCr/(350 nm) Cr samples.

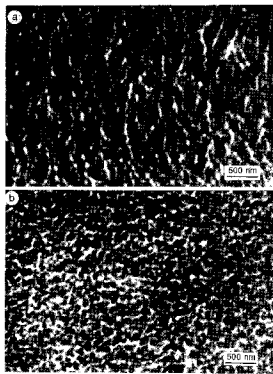


FIG. 3. Lorentz micrographs of (a) as-sputtered and (b) vacuum-annealed, 12-h at  $360^\circ\text{C}$ , (100 nm) CoNiCr/(350 nm) Cr samples.

the size of the clusters in which grains are magnetically coupled together. Since the grain size is about 30 nm, each such cluster would contain about 20 strongly coupled grains (see Ref. 7). The Lorentz micrograph of the annealed sample is dramatically different. The ripple branches have disappeared. Also, the length and width of the feathers have become so small that we no longer see a "featherlike" structure. The magnetic regions are randomly oriented. We know that (a) the contrast in Lorentz images is related to local changes in the direction of magnetization and (b) the  $c$  axes of the hcp grains in our film are randomly oriented in the film plane. If the magnetic coupling between grains is weak, the direction of magnetization of each grain will be influenced more by its own magnetocrystalline easy axis than by the magnetization of neighboring grains. The change of the direction of magnetization over a small length in such a film would produce a Lorentz image such as the one in Fig. 3(b). Therefore, we conclude from the changes of the Lorentz images from Fig. 3(a) to 3(b) that the magnetic coupling between grains is significantly reduced after annealing.

### B. Annealing in air

We also annealed samples in air at 360 and 400 °C sequentially for various time intervals. The values of  $H_c$ ,  $S^*$ , and  $M_s$  as measured after each anneal are plotted in Figs. 4(a) and 4(b) as a function of  $\tau_a$ .

At  $T_a = 360$  °C,  $H_c$  increased only slightly with  $\tau_a$ .  $S^*$  did not change much.  $M_s$  decreased with  $\tau_a$  [Fig. 4(a)]. At  $T_a = 400$  °C, for the  $d_{Cr} \leq 15$  nm samples,  $H_c$  did not change much with annealing. For the  $d_{Cr} \geq 45$  nm samples,  $H_c$  increased with  $\tau_a$ . It seems that  $H_c$  tended to saturate with increased  $\tau_a$  values.  $S^*$  decreased with  $\tau_a$ . The decrease in the values of  $S^*$  is greater for samples with  $d_{Cr} \geq 45$  nm.  $M_s$  decreased with  $\tau_a$ . Again, the initial decrease of  $M_s$  with  $\tau_a$  is large and the subsequent decrease of  $M_s$  with  $\tau_a$  is smaller.

We also obtained the depth profile by Auger analysis for the 350-nm-thick sample after an air anneal at  $\tau_a = 400$  °C. A high oxygen concentration was found near the surface of the annealed sample. The Co content in this oxide layer is large close to the surface-air interface; the Cr content is small. As the depth increases, the Co content decreases and the Cr content increases; Co and Cr return to their bulk values in the nonoxidized region. This suggests that after annealing in air, Co oxides are formed at the very top surface. At larger depths Cr oxides are formed. Co oxide formation can decrease the  $M_s$  of the film. This may explain the larger decrease in  $M_s$  following air anneal as compared to vacuum anneal; for the latter we found by Auger analysis that only a thin layer of Cr oxide was formed after the anneal.

TEM studies in these samples also indicated no change in the grain size and texture of the films following annealing. It is likely that in air annealing, the change in magnetic properties is associated with the same mechanism that we believe obtains in vacuum annealing, namely, the diffusion to and segregation of Cr in the grain boundaries of the films. The oxidation effect following air annealing seems to reduce the increase in  $H_c$  that would otherwise have been expected.

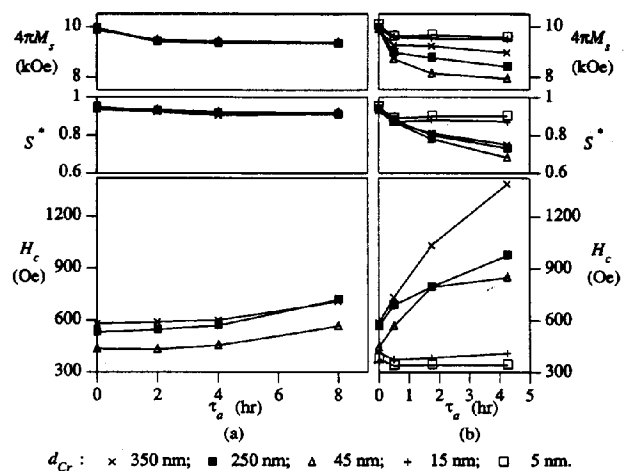


FIG. 4. Variation of  $H_c$ ,  $S^*$ , and  $M_s$  of CoNiCr/Cr films after air anneal at (a)  $T_a = 360$  °C and (b)  $T_a = 400$  °C.

### IV. CONCLUSIONS

The magnetic properties of the samples with  $d_{Cr} \leq 15$  nm did not change very much with annealing. For vacuum annealing, the  $H_c$  increase with  $\tau_a$  was greater for larger  $d_{Cr}$  samples.  $S^*$  decreased with annealing.  $M_s$  decreased slightly after annealing. The grain size and crystal texture did not change significantly after annealing. EDS data indicated that the Cr concentration in the CoNiCr layer increased after annealing. It is likely that during anneal Cr diffused from the Cr underlayer to the CoNiCr layer through the grain boundaries. A high Cr concentration at the grain boundaries could reduce the magnetic coupling between grains and hence increase  $H_c$  and decrease  $S^*$ . The disappearance of the ripple branches in the Lorentz images also suggested that magnetic coupling between grains was reduced by annealing. The increase in  $H_c$  following air anneal was smaller than for vacuum anneal;  $M_s$  decreased more after air anneal. After the vacuum anneal, only a thin surface layer of Cr oxide was formed, whereas after air anneal, a thicker surface layer both of Co oxide and Cr oxide was formed. On the basis of this study, vacuum annealing would be preferred for CoNiCr/Cr/glass media intended for recording applications.

### ACKNOWLEDGMENTS

This research has been supported in part by the Magnetic Materials Research Group at Carnegie Mellon University under NSF Grant No. DMR-8613386. We wish to thank D. N. Lambeth for valuable discussions.

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