

EFFECT OF SPUTTERING CONDITIONS, ANNEALING AND THE MICROSTRUCTURE OF Cr UNDERLAYER
ON THE MAGNETIC PROPERTIES OF CoNiCr/Cr THIN FILMS

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Abstract

The effects of rf power P , substrate heating and substrate bias V_b on the structure and magnetic properties of CoNiCr thin films were studied. The films were deposited on glass and Cr/glass substrates by rf diode sputtering. For films deposited at higher rf power P and at elevated substrate temperature T_s , the grain size increased. The $\langle 001 \rangle$ texture in the Cr underlayer was increased at higher T_s ; this was accompanied by an increase in the $\langle 2\bar{1}10 \rangle$ texture in the CoNiCr film. In-plane coercivity H_c also increased with P and T_s ; this is probably related to the increase in grain size as well as to the increase in $\langle 2\bar{1}10 \rangle$ CoNiCr texture. In the samples deposited with an applied substrate bias voltage V_b , the grains were considerably larger than when prepared without bias. The H_c value and the magnetic domain morphology also changed with V_b ; this is probably related to the increase in grain size. The H_c of CoNiCr thin films also increased following annealing in vacuum.

I. Introduction

Sputtered CoNiCr thin films have been proposed as recording media for their high in-plane coercivity H_c , high saturation magnetization M_s and high squareness S values¹. The magnetic properties and the structures of as-sputtered CoNiCr thin films have been studied extensively^{1,2}. Although it is well known that sputtered thin film properties are sensitive to the sputtering conditions (such as rf power, substrate temperature and substrate bias) and subsequent annealing, relatively little has been reported on the effects of sputtering conditions and annealing on the properties of CoNiCr thin films. In this paper we present our results on the dependence of the structure and the magnetic properties of CoNiCr/Cr thin films on the rf power P , on substrate heating and on the value of the substrate bias voltage V_b . The magnetic properties are correlated with the film structure. We also discuss the effect of vacuum annealing.

II. Experimental Details

Thin CoNiCr films were deposited on glass and on Cr/glass substrates by rf diode sputtering in a LH Z400 system employing a Co-30%Ni-7.5%Cr (at.%) alloy target and a Cr target. The area of the targets was 45.6 cm². For microstructure study purposes, carbon-coated Cu grids were also used as substrates. The vacuum in the deposition chamber was about 5×10^{-7} Torr. The argon pressure was set at 10 mTorr and the rf forward power and the substrate bias voltage were varied. During some depositions the substrates were heated. The maximum temperature reached by each substrate was inferred from *Tempilabel* temperature monitors; in this manner we could measure temperatures between 40 °C and 260 °C. Substrate temperatures beyond this range were estimated by extrapolation. Some CoNiCr/Cr samples were also annealed in vacuum (10^{-5} Torr) at 360 °C for up to 12 hours. The magnetic properties were measured by vibrating sample magnetometry (VSM). The microstructure was examined by transmission electron microscopy (TEM).

III. Results and Discussion

A. RF Power and Substrate Heating Effects

The rf power P and substrate temperature T_s are important deposition parameters. In one particular sequence, we deposited four CoNiCr/Cr films. The CoNiCr layers were all deposited at the same P and argon pressure and for the same deposition time; but the Cr underlayers were deposited at P values of 30 and 200 W respectively. At each P value two samples were deposited, with substrates unheated and heated, respectively. Since the deposition rate changes with P , we adjusted the

deposition time to keep the thickness of the Cr underlayer constant. In this sequence the CoNiCr film thickness is 15 nm and the Cr underlayer thickness is 40 nm. The magnetic properties of these four samples are shown in Table I along with the substrate temperatures T_s . From Table I we see that, for samples deposited at the same P , H_c increases significantly with T_s as well as with P . The saturation magnetization M_s and squareness S did not change significantly with P and T_s .

Table I.
CoNiCr/Cr Magnetic Properties. Cr deposition at various P and T_s values.

	Substrate Unheated		Substrate Heated	
	P=30 W	P=200 W	P=30 W	P=200 W
H_c (Oe)	518	1047	768	1400
T_s (°C)	65	220	≈ 400	≈ 500

TEM plane views of these CoNiCr/Cr films are shown in Fig. 1. At $P=30$ W, the CoNiCr film grain sizes in unheated (Fig. 1a1) and heated (Fig. 1b1) films are 20 nm and 40 nm respectively. The crystallographic texture of the CoNiCr film in the unheated sample is more or less random; however the CoNiCr film in the heated sample is composed mostly of $\langle 2\bar{1}10 \rangle$ zone axes in which the c -axes of the various crystallites are in-plane. We have examined the orientation of the Cr underlayer in order to determine the crystallographic relation between the CoNiCr films and the Cr underlayers. For the unheated sample the SAD pattern of the Cr underlayer has all rings present whereas for the heated sample the $\{112\}$ ring is missing. Also, microdiffraction shows that many $\langle 100 \rangle$ grains are present in the heated sample whereas the unheated sample is composed of various orientations. Thus the texture of the Cr underlayer in the unheated sample is random; the Cr underlayer in the heated sample is $\langle 100 \rangle$ textured. Fig. 2a is the microdiffraction pattern of a grain with $[001]$ zone axes in the Cr underlayer. We show the microdiffraction pattern of a CoNiCr grain with a $[2\bar{1}10]$ zone axis in Fig. 2b. Fig. 2c is the microdiffraction pattern of two

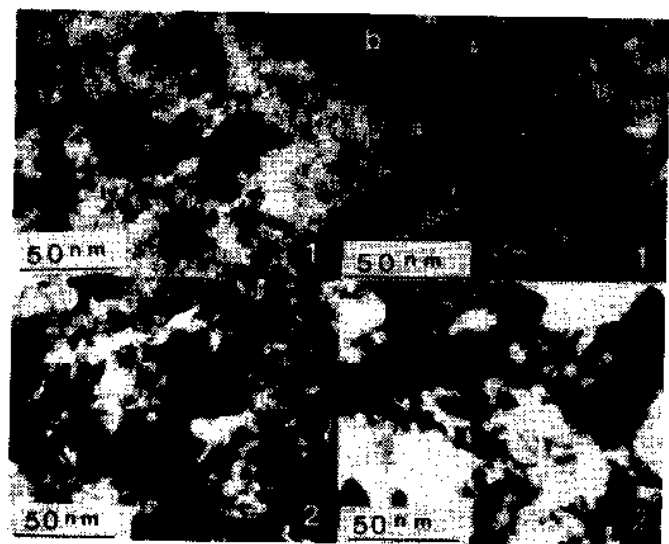


Fig. 1. TEM plane views of CoNiCr/Cr. Cr deposited with
1) substrate unheated, 2) substrate heated;
rf power at a) 30 W and b) 200 W.

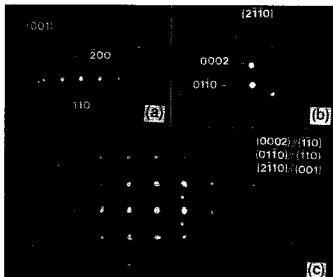


Fig. 2. Microdiffraction patterns of a) a Cr grain with $z=[001]$, b) a CoNiCr grain with $z=[2110]$, c) two CoNiCr grains with $z=[2110]$ above a Cr grain with $z=[001]$.

$[2110]$ zone axis CoNiCr grains on top of a $[001]$ zone axis Cr grain. This figure clearly demonstrates the epitaxial relation between the $[2110]$ CoNiCr planes and the $[001]$ Cr planes; this epitaxial relation is reasonable since the $[2110]$ CoNiCr planes have a small mismatch with the $[001]$ Cr planes.

At $P=200$ W we also observed a grain size difference between the unheated (Fig.1a2) and the heated (Fig.1b2) films, i.e. 30 nm and 60 nm respectively. Furthermore, the $\langle 001 \rangle$ texture in the Cr underlayer was increased by substrate heating during deposition. Due to the epitaxial relation between the CoNiCr film and the Cr underlayer, the $\langle 2110 \rangle$ texture in the CoNiCr film was also dramatically increased by substrate heating. Similar increases in grain size and texture were observed for films deposited at $P=30$ W.

By comparing the magnetic results in Table I with the above structural results, we conclude that the increase in H_c with P and T_s in the CoNiCr films probably is related to the increase in the grain size as well as to the increase in the $\langle 2110 \rangle$ texture.

B. Substrate Bias Effects

Properties of sputtered films can also be changed significantly by applying a bias voltage V_b to the substrate during deposition³. We studied sequences of single layer CoNiCr/glass samples in which the CoNiCr film was deposited at various V_b settings. We also studied sequences of bilayer CoNiCr/Cr/glass samples in which the CoNiCr film was deposited with the substrate grounded and the Cr underlayer was deposited at various V_b settings. Since the deposition rate also changes with V_b , the deposition time was varied appropriately to keep film thickness constant. The saturation magnetization M_s did not change significantly with V_b , the in-plane coercivity H_c of both the single layer and the bilayer films increased significantly with V_b . In Fig. 3 we plot the coercivity H_c and squareness S of both CoNiCr/glass and CoNiCr/Cr/glass films as functions of V_b . It should be noted that for the single CoNiCr films, the in-plane coercivity H_c value was tripled at an applied substrate bias of -200 V!

Application of bias voltage to the substrate during sputtering enhances the ion bombardment of the substrate; this could affect the composition of the thin film⁴. Consequently the CoNiCr/glass single layer films deposited with applied V_b were analyzed by energy dispersive X-ray spectroscopy (EDS); the data indicated that the film composition did not change with V_b and corresponded to the target composition. This is reasonable because Co, Ni and Cr have nearly the same sputtering yields⁵; evidently the re-sputtering caused by ion bombardment on the substrate did not change the composition of the films.

TEM plane views of CoNiCr/Cr films, in which Cr underlayers were deposited at $V_b=0$ and at $V_b=-400$ V, are shown in Figs. 4a1 and 4b1, respectively. At $V_b=0$ V, the grain size is about 20 nm; at $V_b=-400$ V, the

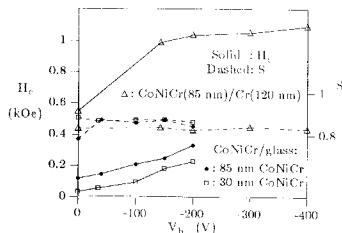


Fig. 3. H_c and S of CoNiCr and CoNiCr/Cr films vs. V_b .

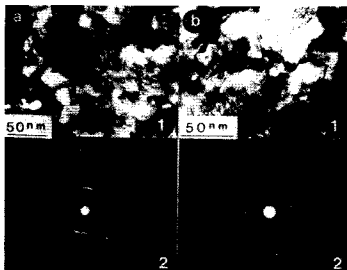


Fig. 4. 1) TEM plane views of CoNiCr/Cr deposited on carbon-coated Cu grids, 2) representative SAD patterns of the CoNiCr layers; Cr deposited with V_b at a) 0 V and b) -400 V.

grain size is about 70 nm. We have reported that CoNiCr films deposited on Cr underlayers grow epitaxially on the Cr and that the grain size of the CoNiCr film mimics that of Cr underlayer⁶. However, an oxide on the Cr underlayer may promote copious nucleation of CoNiCr grains, thereby producing a film that has a smaller grain size than the Cr underlayer. Oxygen in the Cr underlayer can be reduced by ion bombardment⁷ or by the electrostatic repulsion effect⁸. By applying a substrate bias, which enhances both ion bombardment and the electrostatic repulsion, the grain size of the thin film would be expected to increase.

The micrographs in Figs. 4a1 and 4b1 reveal that many grains contain striations, suggesting that the films are not $\langle 0001 \rangle$ textured. Texture can be identified by selected area diffraction (SAD) and by microdiffraction. Typical SAD patterns for the CoNiCr films deposited on Cr underlayers with the Cr deposited at V_b values of 0 and -400 V are shown in Figs. 4a2 and 4b2, respectively. For the zero bias film, strong (0002) and $(01\bar{1}2)$ diffraction rings were observed; but the $(1\bar{1}0\bar{1})$ ring was not observed. This indicates that the film is textured with the c -axes of the grains parallel to the film plane. For the biased film, nearly all diffraction rings were observed. This indicates that in the biased film there are CoNiCr grains in the film with c -axes out of the film plane. Microdiffraction results indicated that both films contained many grains with $\langle 2110 \rangle$ zone axes; the $V_b = -400$ V film had $\langle 0110 \rangle$ and $\langle 0111 \rangle$ grains as well. Microdiffraction results also indicated that the Cr underlayer was composed predominantly of $\langle 001 \rangle$ zone axes. The $\langle 2110 \rangle$ CoNiCr film texture is likely the consequence of epitaxial growth on the Cr underlayer, as in the films deposited at higher P and T_s (Fig. 2).

The H_c values of both the zero bias film and the biased film are relatively high. This is probably due to the combined effects of the $\langle 2110 \rangle$ texture as well as their respective grain size. It is known that the application of V_b results in compressive stress due to the increase in Ar bombardment on the substrate⁹. It is possible that an increase in compressive stress also contributed to the increase in H_c in these films.

We have investigated the change in magnetic domain morphology as a function of V_b . The magnetic domain contrast of the film deposited at $V_b=0$ is shown in Fig. 5a. The magnetic domain configuration of the film in the demagnetized state with the Cr underlayer deposited at $V_b=-400$ V is shown in Fig. 5b. When compared to Fig. 5a we find that the branches of most of the ripples disappear and that the domain size becomes much smaller. The difference between Figs. 5a and 5b is evident, but the explanation is not yet known. This difference in domain morphology may be related to the grain size difference and/or to a change in the in-plane stress component caused by substrate bias.

For CoNiCr/glass films deposited with applied V_b , it was also found that the grain size increased with V_b ; domain morphology changed little as V_b increased.

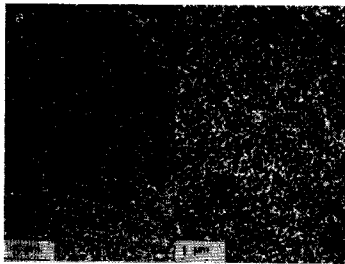


Fig. 5. Lorentz images of CoNiCr/Cr deposited on carbon-coated Cu grids: a) $V_b=0$ and b) $V_b=-400$ V.

C. Annealing Effects

The effect of annealing in vacuum on properties of sputtered CoNiCr thin films was studied. The change in magnetic properties of annealed CoNiCr/Cr films was found to be sensitive to annealing time t_a and to the Cr underlayer thickness t_{Cr} . In Fig. 6 we plot H_c as a function of t_a for a sequence of CoNiCr/Cr films. The CoNiCr film thickness was 100 nm. The Cr underlayer thickness ranged from 5 to 350 nm. We can see that H_c initially increases with t_a but then approaches a saturation value. Thicker Cr underlayer films require a longer time to reach H_c saturation. The increase in H_c with t_a is also larger for the thicker Cr films. Saturation magnetization M_s and squareness S did not change significantly with annealing.

IV. Conclusions

The magnetic properties and structures of CoNiCr and CoNiCr/Cr films change with sputtering conditions and annealing. The grain size increased in the films deposited at higher rf power P and at elevated substrate temperature T_s . The $\langle 001 \rangle$ texture in the Cr underlayer increased with substrate heating; because of the epitaxial relation between the CoNiCr film and the Cr underlayer, the $\langle 2110 \rangle$ texture in the CoNiCr film also increased. The in-plane coercivity H_c increased with P and T_s ; this is presumably related to the increase in grain size and to the increase in the $\langle 2110 \rangle$ texture in such CoNiCr films. When the Cr underlayer in CoNiCr/Cr/glass film was deposited with an applied substrate bias voltage V_b , the grain size also increased. This was probably due to the reduction of oxygen in the Cr underlayer by enhanced ion bombardment and to

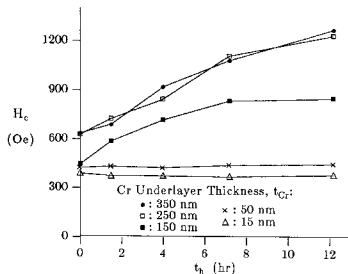


Fig. 6. H_c vs. t_a for CoNiCr/Cr films prepared at various t_{Cr} values. CoNiCr thickness at 100 nm.

electrostatic repulsion during deposition. The increase in H_c and the sensitivity of magnetic domain morphology to V_b are probably associated with the increase in grain size and/or a change in the in-plane stress component that can be caused by substrate bias.

The change in magnetic properties of annealed CoNiCr/Cr films is sensitive to annealing time t_a and to the Cr underlayer thickness t_{Cr} . The coercivity H_c increased with annealing for larger t_{Cr} films but changed little with annealing for films with $t_{Cr} < 15$ nm.

V. Acknowledgments

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VI. References

1. T. Yamada, N. Tari, M. Ishikawa, Y. Ota, K. Nakamura and A. Itoh, IEEE Trans. Magn. **MAG-21**, 1429 (1985).
2. Ga-Lane Chen, IEEE Trans. Magn. **MAG-22**, 334 (1986).
3. A. J. Griest and B. L. Flur, J. Appl. Phys. **38**, 1431 (1967).
4. L. Maissel, "Handbook of Thin Film Technology", edited by L. Maissel and R. Glang, McGraw-Hill, New York (1970), Chap. 4.
5. N. Laefreid and G. K. Wehner, J. Appl. Phys. **32**, 365 (1961).
6. S. L. Duan, K. R. Mountfield, J. O. Artman, J.-W. Lee, B. Wong and D. E. Laughlin, ICM-88, Paris (to be published in the J. de Physique).
7. W. N. Hamner and K. Y. Ahn, J. Vac. Sci. Tech. **17**, 804 (1980).
8. E. Krikorian and R. J. Sneed, J. Appl. Phys. **37**, 3674 (1966).
9. R. D. Bland, G. J. Kominiak and O. M. Mattox, J. Vac. Sci. Tech. **11**, 671 (1974).