Soft Magnetic Properties of Obliquely Deposited Co-Zr-O Films

Yuqin Sun
C. R. Sullivan
Weidong Li
D. P. Kopp
F. Johnson
S. T. Taylor

From *IEEE Transactions on Magnetics,* vol. 43, no. 12, pp. 4060–4063.

Soft Magnetic Properties of Obliquely Deposited Co–Zr–O Films

Yuqin Sun[1], Charles R. Sullivan[1], Weidong Li[1], David Kopp[2], Francis Johnson[3], and Seth T. Taylor[3]

[1]Thayer School of Engineering at Dartmouth, Hanover, NH 03755 USA
[2]Department of Electrical Engineering, University of Notre Dame, Notre Dame, IN 46556 USA
[3]GE Global Research, Niskayuna, NY 12309 USA

We have studied obliquely sputtered Co–Zr–O films. We found that oblique deposition gives rise to the formation of columnar morphology and thus higher perpendicular magnetic anisotropy in the films, which finally results in the occurrence of stripe domains and degradation of soft magnetic properties. Applying substrate bias during Co–Zr–O film deposition gave some improvement in magnetic softness with small slope angles, but did not provide any improvement for large angles. Using a multilayer structure Co–Zr–O/ZrO$_2$ effectively eliminates the columnar structure and helps the films regain favorable soft magnetic properties.

***Index Terms*—Co–Zr–O, granular metal-nonmetal films, multilayer, nano-composite films, oblique deposition, shadowing effect, soft magnetic properties, stripe domains.**

I. INTRODUCTION

SOFT magnetic Co–Al–O, Co–Zr–O, and Co–Pd–Al–O granular films have been developed previously on planar substrates for their promise in high-frequency micro-inductor applications [1]–[5]. Such soft magnetic Co-based granular films can possess properties such as high saturation magnetization M_s, high in-plane anisotropy field H_k, and high resistivity ρ. It has been found that good soft magnetic properties of the sputtered films are only found in limited composition ranges [1], [2], [4] and require low sputter pressure [4]. Otherwise stripe domains appear as a result of perpendicular magnetic anisotropy, causing poor soft properties. The columnar structure and slight hcp (002) texture of Co grains account for the perpendicular anisotropy [4].

However, the characteristics of such granular films on tilted substrates have seldom been explored, even though sloping surfaces are sometimes inevitable in practical core shapes of inductors, transformers, and other magnetic devices [6], [7]. This work is the first report of the magnetic properties of obliquely deposited granular Co–Zr–O films. Stripe domains and associated degradation of soft magnetic properties were observed, although the films were sputtered with deposition conditions similar to those used for the deposition of good soft magnetic Co–Zr–O films on planar substrates in [4]. The stripe domains imply the existence of a significant perpendicular magnetic anisotropy (PMA) in the films [8]–[10]. Microstructure of the films was analyzed and used to explain the increase of PMA. Methods such as applying substrate bias and multilayer film structure were utilized to improve the microstructure and suppress PMA. The effectiveness of the methods is examined and explained in Section III.

II. EXPERIMENTS

Single-layer Co–Zr–O films were deposited on sloping water-cooled silicon or glass substrates by DC magnetron sputtering of a Co$_{85}$Zr$_{15}$ (at. %) alloy target in an Ar+O$_2$ atmosphere. The substrates were placed on aluminum wedges with angles 30°, 45°, and 55°. A magnetic field of about 400 Oe was applied in the substrate plane in the direction shown in Fig. 1, in order to induce in-plane anisotropy with the easy axis in the same direction. This direction is chosen in order to have the hard axis up and down the slope of the tilted substrate, which would be the flux direction in a practial device. The sputter pressure was kept at about 1.5 mTorr.

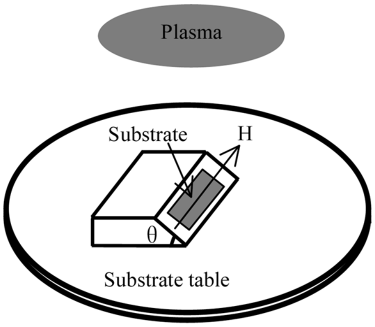


Fig. 1. Schematic setup for the sputter deposition on sloping substrate.

In our previous planar film deposition work, the Co–Zr–O films were also sputtered from Co$_{85}$Zr$_{15}$ alloy targets, with other deposition conditions the same. Those films deposited on planar substrates and with good soft magnetic properties have resistivity around 300 ± 50 $\mu\Omega\cdot$cm, and a narrow composition which is around Co$_{66.5}$Zr$_{6.8}$O$_{27.7}$ (at. %) [4]. For the obliquely deposited films, oxygen gas flow rate was carefully controlled in order to match the resistivity and composition. Film thickness was kept around 600–700 nm.

For multilayer Co–Zr–O/ZrO$_2$ films, the Co–Zr–O and ZrO$_2$ layers were alternately deposited by sputtering Co+Zr targets and a Zr target, both in an Ar+O$_2$ atmosphere. Other parameters were the same as those used in single-layer Co–Zr–O film deposition.

With a vibrating sample magnetometer (VSM) and a B–H loop tracer, in-plane hysteresis loops of the films were measured along the directions parallel to the external magnetic field applied in deposition process and along the in-plane orthogonal direction. The magnetic domain patterns of the films were recorded by magnetic force microscopy (MFM) with

Digital Object Identifier 10.1109/TMAG.2007.907503

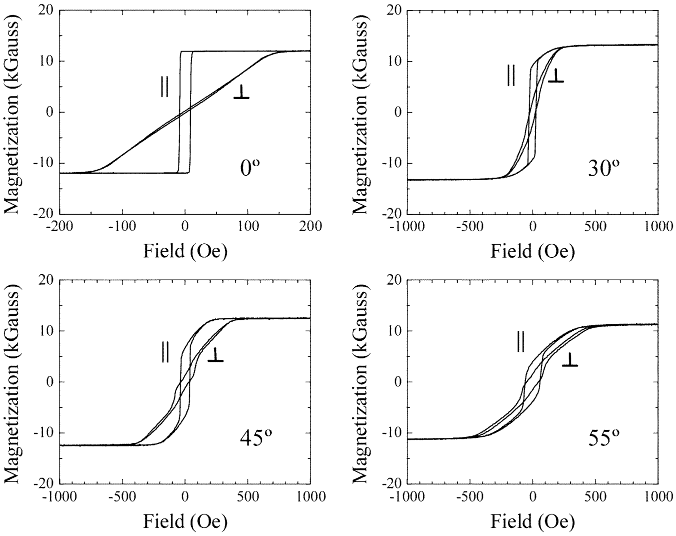
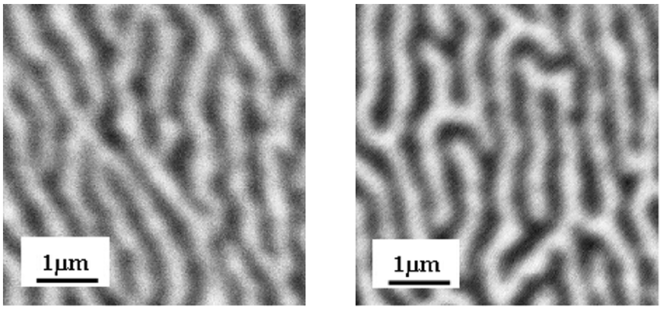
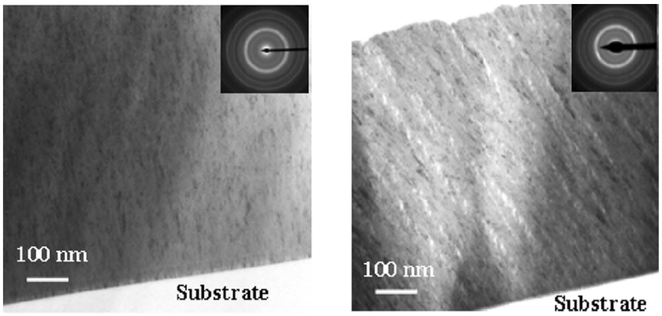


Fig. 2. In-plane hysteresis loops of Co–Zr–O films deposited on 0°, 30°, 45°, and 55° tilted substrates. Note that the 0° plot has different horizontal scale. || represents the direction parallel to the applied external magnetic field during film deposition; and ⊥ represents the orthogonal direction in the film plane. If in-plane anisotropy is induced by the external magnetic field, || also corresponds to the easy axis; and ⊥ corresponds to the hard axis.



a) b)

Fig. 3. MFM images of the Co–Zr–O films sputtered on (a) 30° and (b) 55° tilted substrates.



a) b)

Fig. 4. Cross-section TEM images of the Co–Zr–O films on (a) 0° and (b) 55° titled substrates.

zero applied field. The electrical resistivity was measured with the four-point method. Cross-sectional transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the film microstructure and measure crystal size. All the cross sections of the TEM samples were made perpendicular to the static magnetic field applied during film deposition and perpendicular to the substrate surface.

III. RESULTS AND DISCUSSION

As can be seen in Fig. 2, the single-layer Co–Zr–O film on a 0° substrate has good soft magnetic properties with narrow easy- and hard-axis hysteresis loops. Large in-plane anisotropy is also obtained [4]. It has been successfully applied to a V-groove power micro-inductor [7]. However, for the films deposited on tilted substrates, the coercivity H_c is increased and permeability μ is decreased, i.e., the soft magnetic properties are deteriorated. All the films have saturation magnetization $4\pi M_s$ around 12 kG. The shapes of B–H loops of films on titled substrates are characteristic for stripe domains; the presence of stripe domains is confirmed by the MFM images in Fig. 3. No stripe domains are observed in the single-layer films deposited with the conditions described in Section II. The occurrence of stripe domains and degradation of soft magnetic properties are due to an increase in perpendicular magnetic anisotropy (PMA) [8]–[10], and the increase in PMA can be ascribed to the shadowing effect which is intrinsic in oblique film deposition [11]–[13]. The shadowing effect can lead to the growth of significant inclined columnar structures and consequently large perpendicular shape anisotropy. Fig. 4 compares the microstructures of Co–Zr–O films sputtered on 0° and 55° slopes. The film on a 0° substrate exhibits a uniform structure with very few columnar features, if any. A severe columnar structure with the columns 26° from the substrate normal is evident in the film on 55° slope. Furthermore, the shadowing effect is expected to be more severe, resulting in larger PMA for higher angle deposition. According to Fig. 2, larger in-plane saturation fields H_s are observed with higher angle films, and in stripe-domain films, a higher H_s corresponds to a larger PMA [8].

A. Effect of Substrate Bias

Applying substrate bias during film deposition has become established as an effective method to eliminate or compensate for the influence of oblique deposition in Permalloy films [12] and Fe-based soft magnetic films like FeTaN [13], [14]. In Permalloy, the substrate bias was believed to realign and densify the NiFe columns, and thus overcome the shadowing effect [12]. Substrate bias has been reported to play a different role in FeTaN films. Changing film stress and the orientation of Fe grains contributed to suppression of the perpendicular anisotropy existing in FeTaN films on sloping surfaces [13], [14].

For Co–Zr–O films deposited on 30° tilted substrates, small substrate bias did improve the soft magnetic properties. As shown in Fig. 5, with the RF substrate bias power increasing from 0 to 15 W, the coercivity along hard axis decreased from 22 to 0.7 Oe, and the saturation field decreased from 187 to 102 Oe, whereas further increases of substrate bias power worsened the soft magnetic properties. For slopes of 45° and 55°, substrate bias did not provide any improvement.

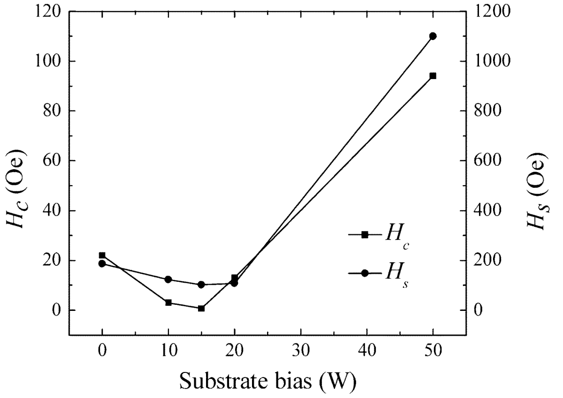


Fig. 5. Dependence of coercivity (H_c) and saturation field (H_s) in the hard axis direction on substrate bias power for Co–Zr–O films deposited on 30° tilted substrates. (The hard axis direction is in the film plane and orthogonal to the direction of applied external magnetic field during film deposition).

The effect of low substrate bias on Co–Zr–O films sputtered on small-angle substrates can be understood on the basis that low substrate bias effectively helps overcome a slight shadowing effect. The worsening of soft magnetic properties with high-power substrate bias in Co–Zr–O films is not usually seen in other soft magnetic films [12]–[14]. We found that high substrate bias leads to larger size and stronger hcp (002) texture of cobalt particles, and even more severe columnar structure. Fig. 6 is an XRD comparison of Co–Zr–O films sputtered on 30° tilted substrates without and with 50 W RF substrate bias. Calculated cobalt grain size of the film without bias is about 6 nm, while cobalt particles in the film with 50 W bias are as large as about 25 nm. The XRD result also displays a very strong cobalt hcp (002) texture for the film with 50 W bias. Fig. 7 shows a severe columnar structure for this film. The effect of high substrate bias on film microstructure can be ascribed to the fact that (002) is the closest-packed plane of hcp cobalt. Enhanced Ar ion bombardment on film surface during deposition caused by substrate bias may impel the preferred growth of the closed-packed plane (002) of hcp Co. Therefore, stronger (002) cobalt crystal texture will be promoted with higher bias. The ion bombardment may also help remove the loosely bonded cobalt–oxide interface and drive the continuous growth of cobalt and oxide columns. Due to this special microstructure, PMA is increased with high substrate bias. The PMA is composed of perpendicular magnetocrystalline anisotropy from preferred hcp (200) orientation of cobalt crystals and perpendicular shape anisotropy from the columnar structure. We know that since <001> is the easy direction of hcp cobalt, a (002) texture means that the easy axes of cobalt crystals are inclined to be aligned along the film normal. Eventually the increased PMA lead to stripe domains and deterioration of soft magnetic properties.

As implied by the larger saturation fields as can be seen in Fig. 2, Co–Zr–O films sputtered on larger angle substrates underwent a larger shadowing effect. Low substrate bias would not be strong enough to overcome large shadowing effect, while high bias would give rise to a worse effect as has been discussed in the 30° case. Consequently, substrate bias did not help get soft magnetic properties in Co–Zr–O films deposited on substrates with substrate angle larger than 45°.

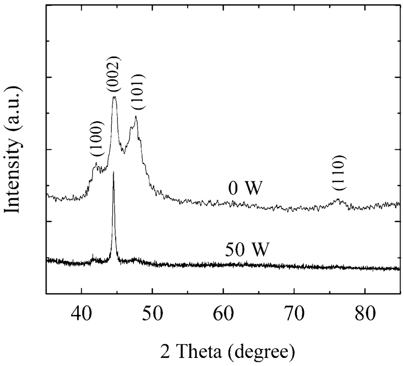


Fig. 6. XRD of Co–Zr–O films deposited on a 30° sloping surface without and with 50 W RF substrate bias.

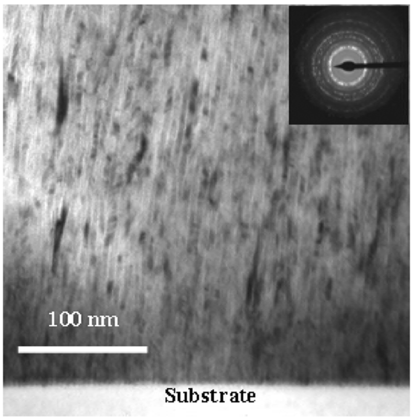
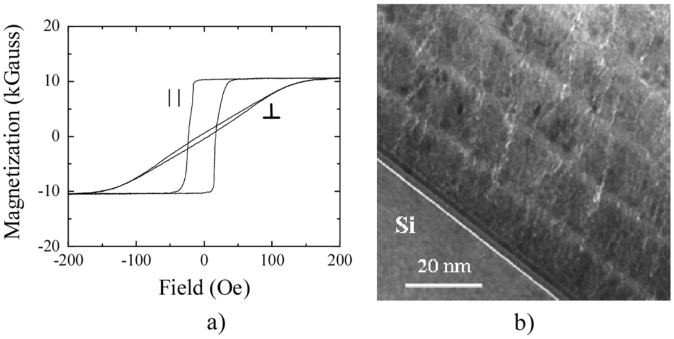


Fig. 7. Cross-section TEM image of Co–Zr–O film deposited on a 30° sloping surface with 50 W RF substrate bias.



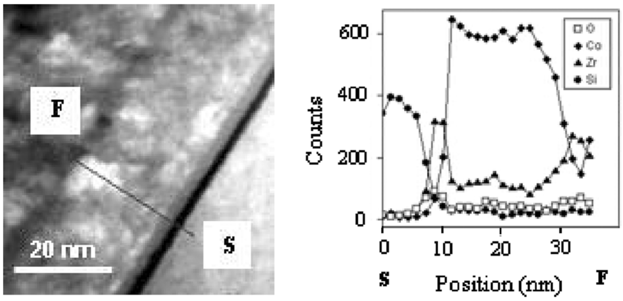
a) b)

Fig. 8. (a) In-plane hysteresis loops and (b) cross-section TEM image of a multilayer $[\text{Co–Zr–O}_{19\ \text{nm}}/(\text{ZrO}_2)_{4\ \text{nm}}]_{15}$ film deposited on 55° tilted substrates.

B. Multilayer Structure

Better than applying substrate bias, adopting a multilayer structure Co–Zr–O/ZrO$_2$ did effectively help regain the soft magnetic properties for large substrate tilting angles. Fig. 8(a) shows in-plane B–H loops of a multilayer $[\text{Co–Zr–O}_{19\text{nm}}/(\text{ZrO}_2)_{4\ \text{nm}}]_{15}$ film with a 55° substrate angle. Good soft magnetic properties were observed.

Fig. 8(b) is a bright field cross-section TEM image of the multilayer film. A fine and uniform granular structure can be observed in each Co–Zr–O layer, similar to the structure in granular films deposited on planar substrates [1], [2], [4]. An



a) b)

Fig. 9. Multilayer film $[\text{Co–Zr–O}_{19\ \mathrm{nm}}/(\mathrm{ZrO}_2)_{4\ \mathrm{nm}}]_{15}$: (a) dark-field high-resolution image of the first several layers, (b) qualitative elemental concentration across the first two layers. S: substrate, F: film.

enlargement of the first two Co–Zr–O and $\mathrm{ZrO_2}$ layers near the substrate is shown in Fig. 9(a). Fig. 9(b) illustrates the qualitative elemental concentration across the first Co–Zr–O and $\mathrm{ZrO_2}$ layers. The $\mathrm{ZrO_2}$ layers can be considered as substrates for each thin Co–Zr–O layer above whose growth thus can be treated almost individually. According to the theory of oblique film deposition, columnar morphology and shadowing effect do not develop severely until the film is thick enough [11]. Therefore, it is not surprising that the columnar structure in the multilayer film was prevented, and the perpendicular magnetic anisotropy (PMA) due to the micro-shape anisotropy was avoided. On the other hand, the nonmagnetic oxide layers can also compensate for the PMA, if any. With the suppression of perpendicular magnetic anisotropy, good soft magnetic properties were finally restored. Multilayer films were also tested with 0° substrates angle, and found to exhibit similar good soft magnetic properties.

The choice of the thickness of Co–Zr–O layers, x, and the thickness of $\mathrm{ZrO_2}$ layers, y, is based on the following ideas: First, x should be small enough so that in each Co–Zr–O layer, the columnar structure does not have an opportunity to develop. Second, y should be large enough for $\mathrm{ZrO_2}$ to form continuous interlayers and prevent the continuation of any nascent columnar formation; and it also should be small enough to allow adjacent Co–Zr–O layers to be magnetically coupled. Tests with other layer thicknesses were consistent with these hypotheses.

IV. CONCLUSION

Co–Zr–O films deposited on sloping surfaces have been investigated. Observed stripe domains and degradation of soft magnetic properties are ascribed to the shadowing effect associated with the oblique deposition. Substrate bias and multilayer structure were used to attempt to compensate for the shadowing effect.

For small slope angles, a low substrate bias was effective, whereas a high bias caused separate growth of Co and Zr–O oxide columns which leads to even worse magnetic properties.

For large-angle depositions, utilizing a multilayer Co–Zr–O/$\mathrm{ZrO_2}$ structure is a more efficient approach to overcome the shadowing effect and regain good soft properties. Insertion of thin oxide layers prevented the development of columnar structure through film thickness.

We conclude that, for micro-inductive devices using cobalt-based core films and having significant sloping portions, it is beneficial to utilize a laminated structure for the core films. For deposition on flat, planar substrates, either single-layer or multilayer structures can work well.

ACKNOWLEDGMENT

This work was supported by AF Contract #FA8650-05-C-7201, GEGR PO#700118315, and by the National Insitute of Standards and Technology (NIST) under Grant 60NANB2D0120.

REFERENCES

[1] S. Ohnuma, H. Fujimori, S. Mitani, and T. Masumoto, "High-frequency magnetic properties in metal-nonmetal granular films," *J. Appl. Phys.*, vol. 79, pp. 5130–5135, 1996.
[2] S. Ohnuma, H. J. Lee, N. Kobayashi, H. Fujimori, and T. Masumoto, "Co-Zr-O nano-granular thin films with improved high frequency soft magnetic properties," *IEEE Trans. Magn.*, vol. 37, no. 4, pp. 2251–2254, Jul. 2001.
[3] S. Ohnuma and T. Masumoto, "High frequency magnetic properties and GMR effect of nano-granular magnetic thin films," *Scripta Mater.*, vol. 44, pp. 1309–1313, 2001.
[4] Y. Sun, W. Li, P. Dhagat, and C. R. Sullivan, "Perpendicular anisotropy in granular Co–Zr–O films," *J. Appl. Phys.*, vol. 97, no. 10, p. 10N301, 2005.
[5] T.-S. Kim, K. Suezawa, M. Yamaguchi, K.-I. Arai, Y. Shimada, and C.-O. Kim, "Properties of high resistivity CoPdAlO film for possibility of application to RF integrated inductor," *IEEE Trans. Magn.*, vol. 37, no. 4, pp. 2255–2257, Jul. 2001.
[6] C. R. Sullivan, "Microfabrication of magnetic components for high frequency power conversion," Ph.D. thesis, Univ. California, Berkeley, 1996.
[7] S. Prabhakaran, Y. Sun, P. Dhagat, W. D. Li, and C. R. Sullivan, in *Proc. 36th IEEE Power Electron. Specialists Conf.*, 2005, pp. 1513–1519.
[8] Y. Murayama, "Micromagnetics on stripe domain films. I. critical cases," *J. Phys. Soc. Jpn.*, vol. 21, no. 11, pp. 2253–2266, 1966.
[9] A. Hubert and R. Schäfer, *Magnetic Domains: The Analysis of Magnetic Microstructures*. Berlin, Germany: Springer-Verlag, 1998, pp. 298–303.
[10] P. Zou, W. Yu, and J. A. Bain, "Influence of stress and texture on soft magnetic properties of thin films," *IEEE Trans. Magn.*, vol. 38, no. 5, pp. 3501–3520, Sep. 2002.
[11] M. Ohring, *Materials Science of Thin Films*, 2nd ed. New York: Academic, 2002, pp. 504–515.
[12] R. E. Jones Jr., J. Williams, L. Spector, and C.-J. Lin, "Magnetic properties of NiFe sputtered on sloping surfaces," *IEEE Trans. Magn.*, vol. 31, no. 6, pp. 3817–3819, Nov. 1995.
[13] S. Wang and J. Hong, "Magnetic and microstructural characterization of FeTaN high saturation materials for recording heads," *IEEE Trans. Magn.*, vol. 35, no. 2, pp. 782–787, Mar. 1999.
[14] J. Hong and S. Wang, "Microstructures of FeTaN films in the neck region of magnetic recording heads," *IEEE Trans. Magn.*, vol. 37, no. 4, pp. 3039–3042, Jul. 2001.

Manuscript received April 1, 2007; revised August 28, 2007. Corresponding author: C. R. Sullivan (e-mail: charles.r.sullivan@dartmouth.edu).