Mater. Res. Soc. Symp. Proc. Vol. 961 © 2007 Materials Research Society 0961-O01-06

Annealing Study of $(Co/Pd)_N$ Magnetic Multilayers for Applications in Bit-Patterned Magnetic Recording Media

Chunsheng E.[1], James Rantschler[1], Shishan Zhang[2], T. Randall Lee[2], Darren Smith[3], Dieter Weller[4], Sakhrat Khizroev[5], and Dmitri Litvinov[1,6]
[1]Electrical & Computer Engineering, University of Houston, Houston, TX, 77204
[2]Chemistry, University of Houston, Houston, TX, 77204
[3]Materials Engineering, University of Houston, Houston, TX, 77204
[4]Seagate, Fremont, TX, 94538
[5]Electrical Engineering, University of California - Riverside, Riverside, CA, 92521
[6]Chemical & Biomolecular Engineering, University of Houston, Houston, TX, 77204

ABSTRACT

This work presents an annealing study of high-anisotropy $(Co/Pd)_N$ magnetic multilayers designed for bit-patterned medium recording applications. Magnetic multilayers were deposited by magnetron sputtering at 2.5mT argon pressure at room temperature and annealed at different temperatures (up to 250°C) for up to 2 hours in atmosphere and in vacuum. Depending on the annealing time, the samples annealed in atmosphere exhibited two distinct modes of magnetization reversal. In samples annealed for a time shorter than some critical time, t_c, where t_c is a function of the annealing temperature, the magnetization reversal occurs by domain wall injection and propagation. In samples annealed for times longer then t_c, the magnetization reversal mode switches to magnetization rotation. Using XPS, it is found that the transition is accompanied by the formation of oxidizes at the grain boundaries leading to exchange decoupling of the grains. In samples annealed at higher temperatures, the increases of the coercivity of as high as 30 times the coercivity of as prepared samples are observed. Significantly, annealing in vacuum showed only small modification of magnetic properties as manifested by relatively minor modifications of vertical M-H loops and unchanged morphology of domain patterns in ac demagnetized state.

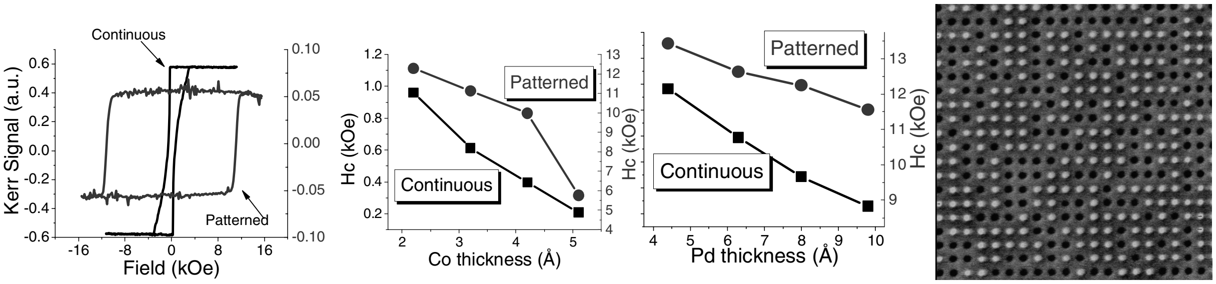
INTRODUCTION

High magnetic anisotropy multilayer thin films such as $(Co/Pd)_N$ and $(Co/Pt)_N$ have been studied extensively as candidates for recording layers in magnetic and magneto-optical recording schemes including bit-patterned medium [1-4]. Perpendicular magnetic anisotropy in these multilayers results from the interfacial effects between Co and Pd layers; the control of these interfaces being at the focus of material development. Various parameters control the quality of the interfaces including stress due to lattice mismatch. During annealing, the mobility of the atoms increases, which can result in intermixing of Co and Pd atoms at the interfaces, the relaxation of lattice stress, or both depending on the annealing conditions. Den Broeder et. al. [5] reported that when $(Co/Pd)_N$ multilayer films are annealed at 350 ºC for up to 8 hours, the uniaxial anisotropy constant K_U, the remnance ratio Mr/Ms and coercivity H_C decrease monotonically with the annealing time. The changes in K_U, M_r/M_S and H_C have the same trends for $(Co/Pd)_N$ multilayer exposed to ion irradiation [6]. Under these annealing conditions, effects due to intermixing at Co/Pd interfaces dominate. On the other hand, Yamane et. at. [7] reported that if annealed in ambient atmosphere, oxygen may diffuse into the grain boundaries and oxidize Co. Co oxides, such as Co_3O_4, may lead to exchange-decoupling of the grains such that domain wall propagation during magnetization reversal is inhibited.

In this work, evolution of magnetic properties of $(Co/Pd)_N$ multilayer thin films under relatively low temperature annealing is presented. The changes in magnetic properties are correlated to the changes in multilayer microstructure.

EXPERIMENT

$(Co/Pd)_N$ magnetic multilayers were deposited using magnetron sputtering at 2.5mT argon pressure at room temperature onto thermally oxidized silicon wafers (500nm oxide thickness). The base pressure was better than 1×10^{-8} Torr. A 20nm Ta seed deposited by RF magnetron sputtering was used to promote strong intergranular exchange coupling [8]. 30 bi-layer multilayers were used with the thicknesses of Co and Pd layers of 3.2Å and 6.3Å, respectively, optimized for application in bit-patterned medium (to achieve the high coercivity following pattering as illustrated in **Figure 1**).



(a) (b) (c) (d)

Figure 1: (a) Easy axis M-H loops for continuous and patterned Co(3.2Å)/Pd(6.3 Å) multilayer films; (b) cobalt and (c) palladium thickness dependence of easy axis coercivity; (d) MFM image of corresponding bit-patterned medium. 200nm islands on a 500nm pitch were used.

$(Co/Pd)_n$ multilayers were atmosphere annealed at 150 ºC, 200ºC and 250ºC for up to 2 hours. Magnetic properties were characterized using polar magneto-optical Kerr effect (MOKE) magnetometer. Surface morphology and magnetic domain structure of AC demagnetized films were mapped using atomic force microscopy and magnetic force microscopy, respectively. Crystal structure was characterized using X-ray diffraction.

XPS measurements [9] are carried out at room temperature in a PHI Model 5700 X-Ray Photoelectron Spectrometer with an Al Kα X-ray source. After an initial survey scan, high resolution scans are obtained for energy ranges of 765-815 eV for the Co 2p electron shell, 330-350 eV for the Pd 3d electron shell, and 280-300 eV for the C 1s electron shell. The energy analyzer was operated in the constant energy mode at 23.5 eV pass energy and all of the narrow spectra were scanned with step size of 0.1 eV. Peak fitting is used to quantitatively determine the binding energies and compositions for each sample.

DISCUSSION

The coercivity, H_C, as a function of annealing time is shown in Figure 2a. In multilayers annealed at 150 ºC, the H_C increased by ~10% after 2h annealing. At 200ºC, H_C, increased about

30 times within 2 hours, indicating significant microstructure modification of the films. At 250ºC, a rapid increase in Hc followed by a gradual decrease is observed.

The transition of the switching modes can be inferred from the angular dependence of the remnant switching field Hsw_0 [10-13]. Remnant coercivity differs from remnant switching field only at high angles and is used in this study. In Figure 2b, the remnant coercivity is plotted as a function of θ, the angle between the applied field and the sample plane normal, for samples annealed at 250ºC for 0, 5, 15, 65, and 125 minutes. The as prepared sample fits to the 1/cos(θ) relation, indicating a dominant domain nucleation and domain wall motion switching mode [13]. The samples annealed for 65 and 125 minutes, on the other hand, have a minimum of remnant H_C around 30º, manifesting the magnetization reversal through rotation.

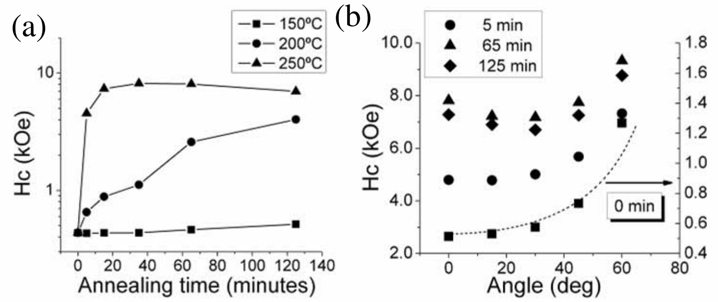
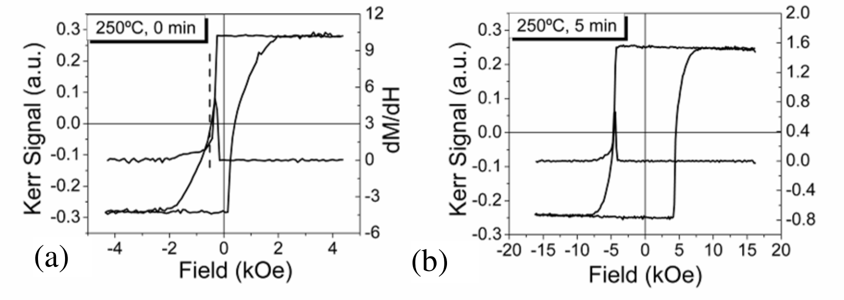


Figure 2: (a) Coercivity as a function of annealing time for Co/Pd multilayer thin film annealed at 150ºC, 200ºC and 250ºC. (b) Angular dependence of remnant coercivity of unannealed sample and samples annealed at 250ºC.

The hysteresis loops and dM/dH curves for samples annealed at 250 ºC for 0, 5, 15 and 125 minutes are illustrated in Figure 3. The as prepared sample shows a typical two-phase domain nucleation/domain wall motion switching mode. The dM/dH curve is not symmetric about H_C. It peaks where the nucleation takes place and the domains expand the fastest. Annealed for 5 minutes, the sample shows a hysteresis loop similar to the unannealled sample, only broader. The shape of the hysteresis loop is still characterized with two-phase switching, indicating that the reversal mode is still domain nucleation and domain wall motion. The sample annealed for 15 minutes shows a transition mode. The slope of the reversal branch is reduced compared to the fresh and 5 minutes samples. The dM/dH curve is not symmetric about H_C. While the peak is still closer to the nucleation edge, the pulse width is much wider than those of the fresh sample and the sample annealed for 5 minutes. The hysteresis loop for the sample annealed for 125 minutes shows a totally different shape; the dM/dH curve is symmetric about and peaks at H_C, and it fits well to the Gaussian function, indicating a single phase magnetization reversal mode.



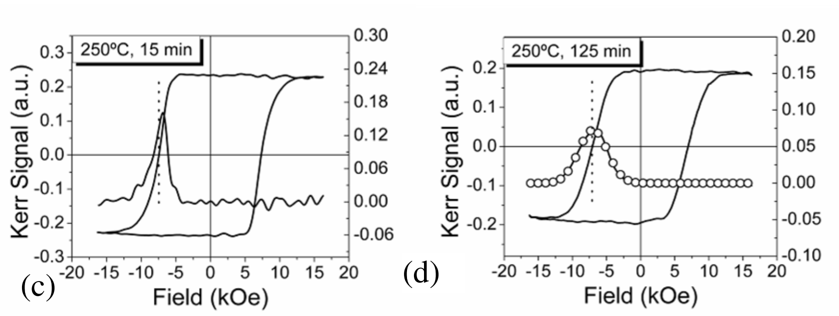


Figure 3: Hysteresis loops and dM/dH curves of sample 2 annealed in ambient atmosphere at 250 ºC for (a) 0min, (b) 5min, (c) 15min and (d) 125min.

The XRD scanned rocking curves and normalized curve-fitted rocking curves are plotted in Figure 4. A decrease in FWHM of as deposited sample and sample annealed for 5 minutes indicates a texture improvement, which is coincident with the magnetic hardening observed in hysteresis loop of Figure 2a and 2b.

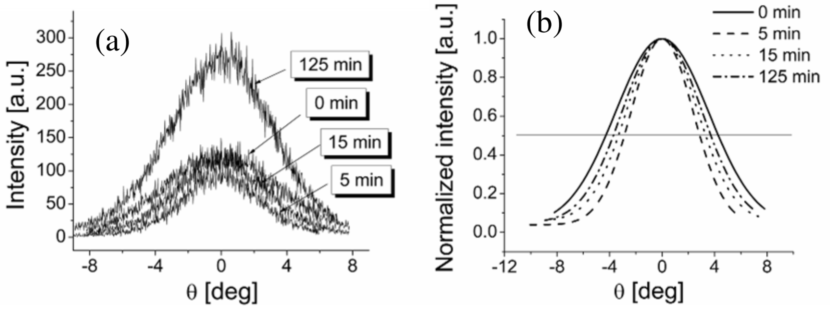
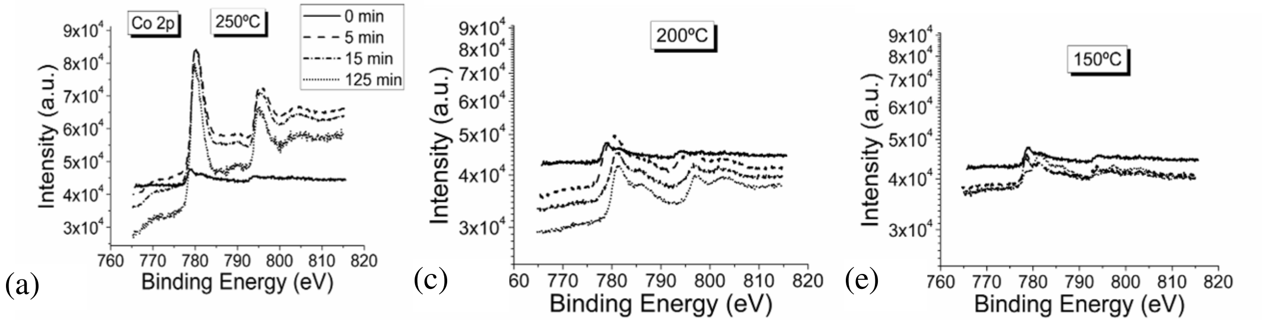


Figure 4: (a) Scanned XRD rocking curves and (b) normalized and curve-fitted rocking curves of samples annealed at 250 ºC for 0min (solid line), 5min (dashed line) 15min (dotted line) and 125min (dash dot dot line).

In Figure 5a, Co 2p spectra from XPS measurements are plotted for the samples annealed at 250ºC for 0, 5, 15 and 125 minutes. The signal intensity is much stronger for the annealed samples than the un-annealed sample, indicating the movement of Co atoms to the near surface region along the grain boundaries upon annealing. Figure 5b shows the Pd 3d spectra of the same samples. The signal intensity decreases with the increasing of annealing time. This observation further supports the movement of Co to the outer surface. As comparisons, Co 2p and Pd 3d spectra for samples annealed at 200ºC and 150ºC are plotted in Figure 5c-f. As we can see in Figure 4a, 4c and 4e, the Co 2p peaks shift to higher binding energy as the annealing time increases, revealing the formation of Co-oxides. Co-oxides effectively exchange decouple the grains, which prohibits the domain wall propagation between the grains. This explains the different switching modes of the samples annealed for 0 and 5 minutes from annealed for 125 minutes. The sample annealed for 15 minutes is a transition between these two modes.



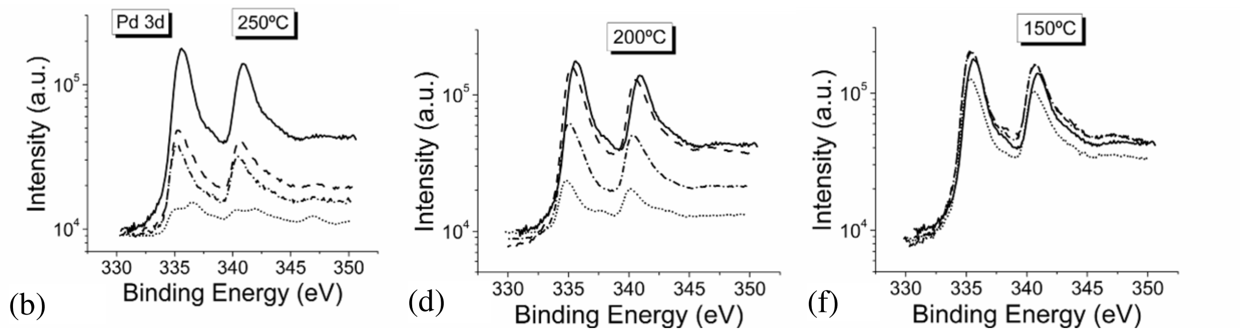


Figure 5: XPS spectra for sample 2 annealed for 0 min (solid line), 5 min (dash line), 15min (dash dot line) and 125 min (short dot line). (a) Co 2p, 250ºC (b)Pd 3d, 250ºC (c) Co 2p, 200ºC (d) Pd 3d, 200ºC (e) Co 2p, 150ºC and (f)Pd 3d, 150ºC

The effects of forming Co oxides at the grain boundaries on the domain patterns are illustrated in Figure 6, where the MFM images of the AC demagnetized states for 0, 5, 15 and 125 minutes samples are shown. The domain patterns reveal a transition from long range ordering to short range ordering. VSM measurements indicate that the Ms decreased from 526emu/cc to, 463emu/cc, 265emu/cc and 229emu/cc, as annealed for 5 min, 15 min and 125 min, respectively. Therefore, the transition of domain patterns is likely not caused by minimizing the magnetostatic energy, but rather is attributed to the reduction of the intergranular exchange coupling.

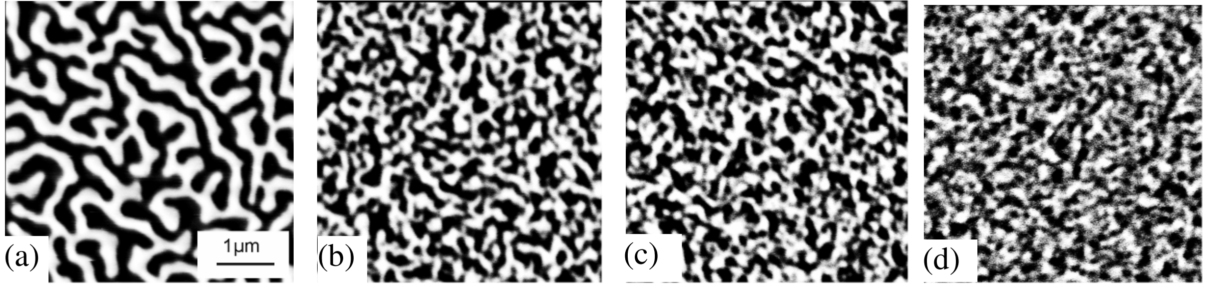


Figure 6: MFM images of ac demagnetized states of samples annealed at 250 ºC in air for (a) 0min, (b) 5min, (c) 15min and (d) 125min. 5μm by 5μm scan. Switching from long range ordering to short range ordering as annealing time is observed.

In contrast to annealing in atmosphere, samples annealed in vacuum exhibit relatively small changed of magnetic properties as can be seen from the vertical M-H loops and dM/dH curves for the samples annealed in vacuum at 250 ºC for 5, 15 and 125 minutes (shown in Figure 7). Also, MFM images of ac demagnetized samples presented in Figure 8 show no evidence of domain morphology modification.

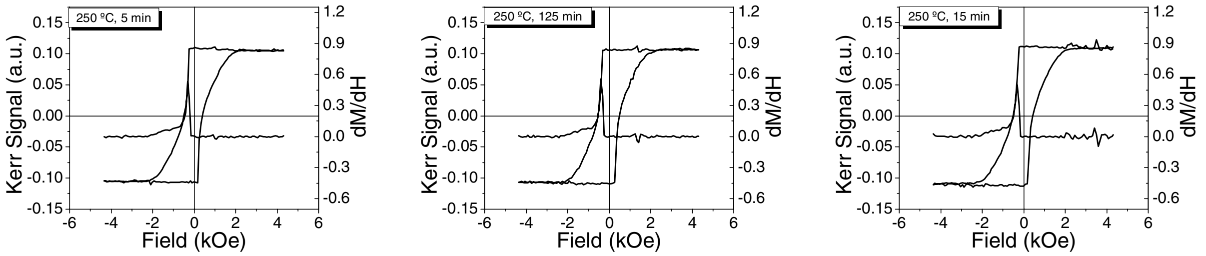


Figure 7: Hysteresis loops and dM/dH curves of sample 2 annealed in vacuum at 250 ºC for (a) 0min, (b) 5min, (c) 15min and (d) 125min.

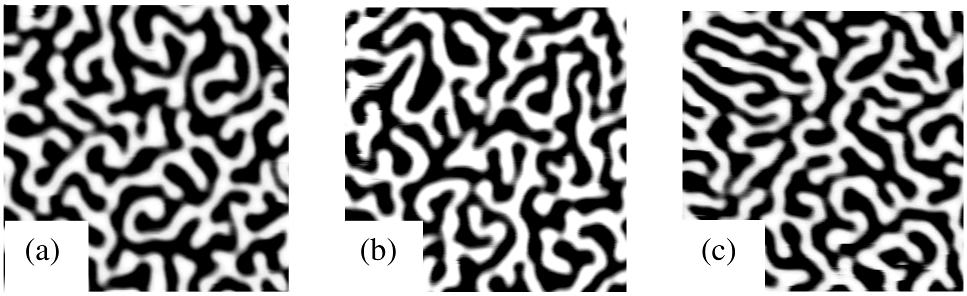


Figure 8: MFM images of ac demagnetized states of samples annealed at 250 ºC in vacuum for (a) 5min, (b) 15min, (c) 125min. 5µm by 5µm scan.

CONCLUSIONS

(Co/Pd)n multilayer thin films were atmosphere annealed for 0, 5, 15, 35, 65 and 125 minutes at 150ºC, 200ºC, and 250ºC. The coercivity H_C was observed to increase before, and decrease after an optimum annealing time at 250ºC. There is a transition of the magnetization reversal mode from two-phase domain nucleation and domain wall motion to a single phase rotation for the annealed samples. Before this transition, the magnetic hardening is due to lattice relaxation and enhancement in the interfacing anisotropy. H_C keeps increasing in the transition region, where the formation of oxides at the grain boundaries effectively reduces exchange coupling between grains and inhibits the propagation of domain walls. This also leads to the switching from long range ordering to the short range ordering of the magnetization as illustrated by the AC demagnetized domain patterns.

ACKNOWLEDGMENTS

This work was supported by the grants from National Science Foundation (ECS-0404308, ECS-0421255, ECS-0401297), Information Storage Industry Consortium, and AFOSR.

REFERENCES

[1] C. F. Brucker, "High-Coercivity Co/Pd Multilayer Films By Heavy Inert-Gas Sputtering," *J. Appl. Phys.*, vol. 70, pp. 6065-6067, 1991.
[2] D. Weller, A. Moser, L. Folks, M. E. Best, W. Lee, M. F. Toney, M. Schwickert, J. U. Thiele, and M. F. Doerner, "High K-u materials approach to 100 Gbits/in(2)," *IEEE Trans. Magn.*, vol. 36, pp. 10-15, 2000.
[3] G. Hu, T. Thomson, C. T. Rettner, and B. D. Terris, "Rotation and wall propagation in multidomain Co/Pd islands," *IEEE Trans. Magn.*, vol. 41, pp. 3589-3591, 2005.
[4] V. Parekh, E. Chunsheng, D. Smith, A. Ruiz, J. C. Wolfe, P. Ruchhoeft, E. Svedberg, S. Khizroev, and D. Litvinov, "Fabrication of a high anisotropy nanoscale patterned magnetic recording medium for data storage applications," *Nanotechnology*, vol. 17, pp. 2079-2082, 2006.
[5] F. J. A. Denbroeder, D. Kuiper, and H. J. G. Draaisma, "Effects of Annealing and Ion-Implantation on the Magnetic-Properties of Pd/Co Multilayers Containing Ultrathin Co," *IEEE Trans. Magn.*, vol. 23, pp. 3696-3698, 1987.
[6] A. D. C. Viegas, L. F. Schelp, and J. E. Schmidt, "Magnetostriction in Ar(+)Implanted and Annealed Co/Pd Multilayers," *IEEE Trans. Magn.*, vol. 31, pp. 4106-4108, 1995.

[7] H. Yamane, Y. Maeno, and M. Kobayashi, "Annealing Effects on Multilayered Co/Pt and Co/Pd Sputtering Films," *Appl. Phys. Lett.*, vol. 62, pp. 1562-1564, 1993.

[8] D. Litvinov, T. Roscamp, T. J. Klemmer, M. Wu, J. K. Howard, and S. Khizroev, "Co/Pd multilayers for perpendicular recording media," *Materials Research Society Symposium Proceedings*, vol. 674, pp. T3.9, 2001.

[9] Z. Simsa, J. Zemek, J. Simsova, P. Dehaan, and C. Lodder, "Kerr Rotation and Xps Spectra of Co/Pd Multilayers," *IEEE Trans. Magn.*, vol. 30, pp. 951-953, 1994.

[10] K. R. Coffey, T. Thomson, and J. U. Thiele, "Angular dependence of the switching field of thin-film longitudinal and perpendicular magnetic recording media," *J. Appl. Phys.*, vol. 92, pp. 4553-4559, 2002.

[11] T. C. Ulbrich, D. Makarov, G. Hu, I. L. Guhr, D. Suess, T. Schrefl, and M. Albrecht, "Magnetization reversal in a novel gradient nanomaterial," *Phys. Rev. Lett.*, vol. 96, 2006.

[12] M. P. Sharrock and J. T. McKinney, "Kinetic Effects in Coercivity Measurements," *IEEE Trans. Magn.*, vol. 17, pp. 3020-3022, 1981.

[13] R. H. Victora, "Predicted Time-Dependence of the Switching Field for Magnetic-Materials," *Phys. Rev. Lett.*, vol. 63, pp. 457-460, 1989.