TITLE: Microstructure and Magnetic Properties of Co-CoO Nanocomposite Films

Mat. Res. Soc. Symp. Proc. Vol. 674 © 2001 Materials Research Society

Microstructure and Magnetic Properties of Co-CoO Nanocomposite Films

Jae-Young Yi, G. A. Hirata* and M. L. Rudee
Material Science and Engineering, University of California, San Diego,
La Jolla, CA 92093, U.S.A.
*CCMC-UNAM, Ensenada, B.C., 22860, Mexico

ABSTRACT

The effect of exchange anisotropy on nanosize Co particles was studied in Co-CoO nanocomposite thin films for possible applications for magnetic storage media. XRD analyses showed nanosize hcp Co particles and (111) textured CoO phase. A broken columnar structure was observed in cross-section TEM images. Very large room temperature coercivity (~1 kOe) was observed and believed to be due to a shape effect and possible local exchange coupling. Large exchange anisotropy at low temperatures and linear type temperature dependence were explained by finite size effects and thermal relaxation of the CoO particles. A slow decrease of thermoremanent moment (TRM) with temperature and large TRM at room temperature indicated that the exchange anisotropy significantly modified the anisotropy energy barrier of the Co crystallites in the CoO matrix. The results indicated that the exchange anisotropy could be used to stabilize nanosize ferromagnetic particles.

INTRODUCTION

The particle sizes of magnetic storage media in computer hard disk drives continuously decrease to satisfy the demand of higher areal density. Reducing the sizes is important not only for smaller bit size but also for high signal to noise ratio. As particle size decreases thermal stability becomes a critical issue. The thermal stability is addressed by the ratio of anisotropy energy to thermal energy [1,2]. There have been many different approaches to improve the thermal stability [3,4,5]. Basically they are based on how to increase the magnetocrystalline anisotropy energy in order to enhance the overall energy barrier against thermal fluctuation. In this study, exchange anisotropy was explored as an additional anisotropy source. We investigated this effect on nanosize ferromagnetic particles. The exchange anisotropy was observed when ferromagnetic (FM) materials were coupled to antiferromagnetic (AFM) materials through a field cooling process. Exchange anisotropy could enhance the magnetic stability of fine ferromagnetic particles by exchange coupling. Meiklejohn and Bean, discoverers of the exchange anisotropy, were first to mention that the exchange anisotropy constant could be the same order of magnitude as the crystalline anisotropy of cobalt for a specific case [6]. So far most studies were conducted in FM/AFM bilayer or multilayer systems because of the simplicity of the structure and the ease to formulate the results. Since exchange anisotropy has a interfacial characteristic and a fine particle has a large surface area, it would be interesting to investigate the exchange anisotropy in fine particle systems.

EXPERIMENTS

Co-CoO composite films were prepared by co-sputtering from separate Co and CoO targets. CoO is antiferromagnetic material and the Néel temperature is 297 K. Co-SiO_2 films were also deposited as a reference system. Prior to deposition the base pressure was better than 5×10^{-7} Torr and Ar pressure was kept at 2 mTorr during sputtering process. The sputtering power of each target was carefully controlled to obtain desired Co volume fractions. The films were deposited onto Si substrates at room temperature. The microstructure of the films was investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The magnetic properties were measured using an alternating gradient force magnetometer (AGM) and a superconducting quantum interference (SQUID) magnetometer.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns (Co K_α, λ=1.7902 Å, 1.8 kW) of the Co-CoO films with different Co volume fractions. The relative intensities of Co and CoO were gradually changed as the volume fractions of each phase were changed. As for the CoO phase only (111) peak was observed, indicating textured structure along the direction. As the volume fraction of the Co phase increased, three peaks were developed. They were identified as hcp Co phase. No evidence of fcc Co phase was found. The Co and CoO crystallite sizes were calculated from XRD peak broadening using the Scherrer formula after correcting for instrumental broadening. As the Co volume fraction increased from 31 % to 51 % the Co particle sizes increased from 34 Å to 62 Å whereas the CoO particle sizes decreased from 105 Å to 68 Å. Typically particle sizes are proportional to the volume fraction in a granular structure.

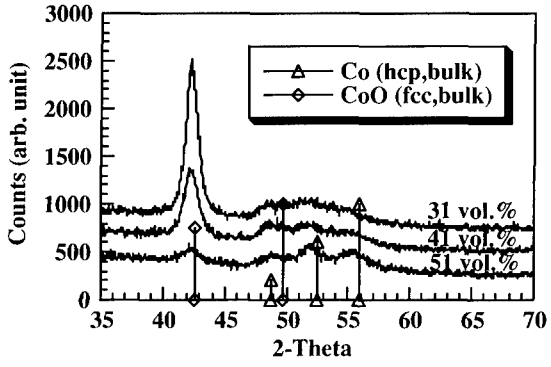
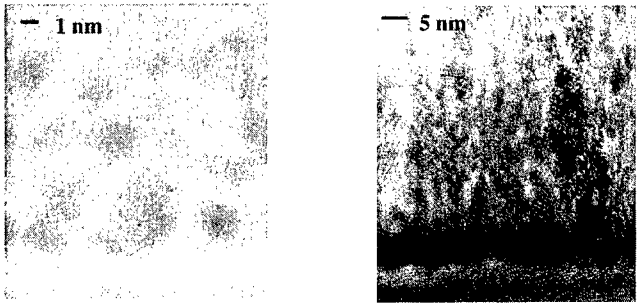


Figure 1. XRD patterns of the Co-CoO specimens with different Co volume fractions. The patterns are vertically shifted for clarification.

Figure 2-(a) and (b) show TEM cross-section images of the Co-SiO_2 and Co-CoO film, respectively. Spherical Co particles surrounded by SiO_2 matrix were observed in the Co-SiO_2 film. However, for the Co-CoO film, because both Co and CoO are crystalline phases, it was difficult to distinguish one from the other. In general columnar type structures were observed. From tilting experiments in the TEM, it was believed that each column was consisted of Co and CoO crystallites rather than one phase.



(a) (b)

Figure 2. Cross-section TEM images of (a) Co-SiO_2 and (b) Co-CoO films.

Figure 3 shows magnetic hysteresis loops of the Co-SiO_2 and Co-CoO films measured at room temperature using AGM. Both films had about 30 volume percent of Co. The Co-SiO_2 film exhibited no coercivity and zero remanant magnetization, indicating superparamagnetic behavior of the Co particles. However the Co-CoO film showed unusually large coercivity, about 1 kOe.

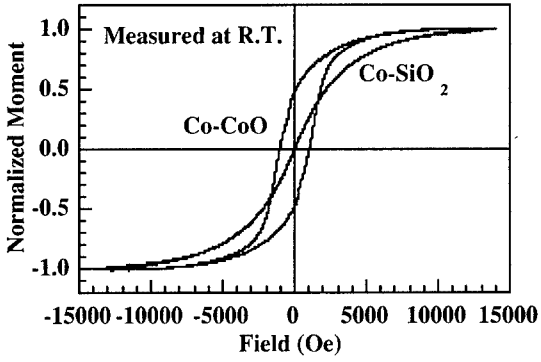


Figure 3. Magnetic hysteresis loops of the Co-SiO_2 (29 vol.% Co) and Co-CoO (31 vol.% Co) films.

One of possible explanations is a shape effect. As seen in TEM images the crystallites in the Co-CoO film appeared to be slightly elongated normal to the film plane. This would provide shape anisotropy to Co particles in the CoO matrix. Another possible source would be local exchange coupling of the Co particles to the CoO matrix. Even if exchange anisotropy is not expected at room temperature (Néel temperature of CoO is 293 K.), the Co particles could be locally exchange coupled to the CoO matrix. This had the same effect as increasing the volume of the particles. Therefore more energy would be required to rotate the magnetization of the Co particles.

To examine exchange anisotropy, the Co-CoO films were cooled down in a 5.5 T field from room temperature to 10 K. Large loop shifts were observed in all the Co-CoO films. Figure 4 shows the exchange anisotropy fields (H_e) as a function of temperature of the Co-CoO films with different Co volume fractions. The 31 vol. % of Co specimen exhibited the largest H_e at all temperatures and the H_e decreased as the Co volume fractions increased. The H_e almost linearly decreased with temperature in all compositions and vanished at lower temperatures than the Néel temperature of bulk CoO. This was a very different observation than the observation in the Co/CoO bilayer structure. In the Co/CoO bilayer structure TRM decreased with temperature below 100 K but remained at a constant value up to 200 K, and then decreased to zero at room temperature [7]. Finite size effects were considered as a possible mechanism for our observation. In the Co-CoO composite films, the CoO particle sizes were calculated to be about 68 ~ 105 Å. In this size range, due to the lack of internal structure, some of surface spins of the CoO particles would not be fully compensated and this would be attributed to the exchange anisotropy [8,9]. The continuous decrease of the H_e as a function of temperature can be understood by the superparamagnetic blocking and relaxation phenomena of the finite size CoO crystallites.

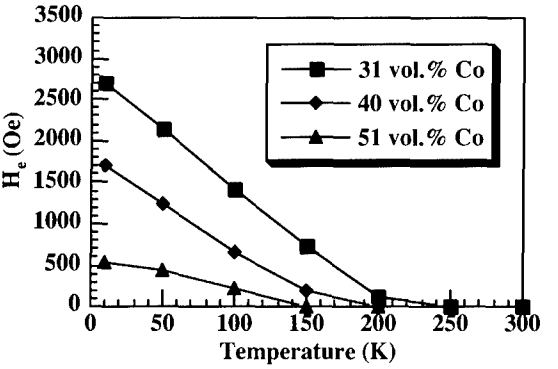


Figure 4. Exchange anisotropy field (H_e) of the Co-CoO films as a function of temperature.

The thermoremanent moment (TRM) and reverse TRM (R-TRM) of the Co particles was measured to investigate the relative effects of anisotropy and thermal energy. The moments were measured in zero field as temperature increased, after field cooling (+6 T) the specimens from 390 K to 10 K. Figure 5 shows the TRM and R-TRM curves of the Co-SiO_2 and Co-CoO

films. For the Co-SiO_2 film the effective anisotropy energy barrier is mostly due to the volume magnetocrystalline anisotropy. Since the Co particle sizes were estimated only ~30 Å at this volume fraction, the magnetization of the particles were easily disturbed by thermal energy, showing zero magnetization above 70 K. However, the Co-CoO film with the same amounts of Co exhibited very different behavior. The exchange anisotropy significantly modified the overall anisotropy energy barrier so that the Co particles seemed to have more resistance to thermal fluctuation.

To examine unidirectional characteristics of the exchange anisotropy, so called, reverse TRM (R-TRM) curves were also measured. In these measurements, after field cooling the specimen in a positive direction (+6 T) in the same way as the TRM measurement, the field direction was reversed to -6 T, then the magnetization was measured with temperature. If the system is dominated by uniaxial anisotropy, TRM and R-TRM curves should be the same except for the sign (+ or -) regardless of the cooling field direction. As expected the curves from the Co-SiO_2 film were exactly symmetric along a temperature axis, indicating the anisotropy energy barrier of the Co crystallites in the SiO_2 matrix had a uniaxial characteristic. Obvious differences in TRM and R-TRM indicate that unidirectional exchange anisotropy significantly altered the anisotropy energy barrier.

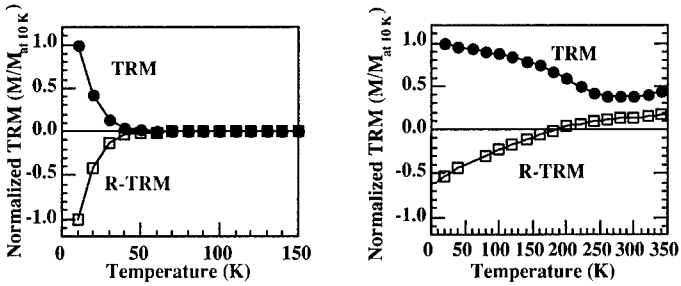


Figure 5. Normalized TRM and R-TRM curves of the (a) Co-SiO_2 and (b) Co-CoO films.

CONCLUSION

The effects of exchange anisotropy on the nanosize Co particles were studied in sputter deposited Co-CoO films. A very large coercivity (~1kOe) was observed at room temperature. Finite size effects of the CoO particles were introduced to explain linear type temperature dependence of the H_e, and lower blocking temperature than T_N. Large TRM and asymmetric TRM and R-TRM curves indicate that the exchange anisotropy modified the anisotropy energy barrier of the Co particles in the CoO matrix.

This research was supported by NSF Grant DMR-9400439.

REFERENCES

1. P. L. Lu and S. H. Charap, *J. Appl. Phys.* **75**, 5768 (1994)
2. P. L. Lu and S. H. Charap, *IEEE Trans. Magn.* **30** (6), 4230 (1994)
3. A. Moser and D. Weller, *IEEE Trans. Magn.* **35** (5), 2808 (1999)
4. D. Weller and A. Moser, *IEEE Trans. Magn.* **35** (6), 4423 (1999)
5. D. Weller, A. Moser, L. Folks, M. E. Best, Wen Lee, M. F. Toney, M. Schwickert, J. -U. Thiele, M. F. Doerner, *IEEE Trans. Magn.* **36** (1), 10 (2000)
6. W. H. Meiklejohn and C. P. Bean, *Phys. Rev.* **105** (3), 904 (1957)
7. K. Takano, R. H. Kodama, A. E. Berkowitz, W. Cao and G. Gareth, *Phys. Rev. Lett.* **79**, 1130 (1997)
8. L. Néel, *Comp. Rend. Acad. Sci.* **252**, p. 4075 (1961); **253**, p. 9, 203 (1961); **254**, 598 (1962)
9. W. J. Schuele and V. D. Deetscreek, *J. Appl. Phys.* **33** (3), suppl., 1136 (1962)