

THE INFLUENCE OF MICROSTRUCTURE ON THE MAGNETIC PROPERTIES IN NANOSTRUCTURED COPT L₁₀ THIN FILMS

S. JEONG, M.E. MCHENRY, and D.E. LAUGHLIN

Data Storage Systems Center, MSE Department, Carnegie Mellon University, Pittsburgh, PA, 15213, sjeong@andrew.cmu.edu

ABSTRACT

We have applied the Neel's spin pair potential model to model the dependence of magnetocrystalline anisotropy on the long range order parameter. We have produced CoPt nanoscale thin films, with and without an immiscible second phase, by RF and DC magnetron sputtering. These thin films showed a shoulder in their magnetic hysteresis, indicative of a disordered soft magnetic phase for samples annealed above 600 °C while it was barely detectable in 500-600 °C annealed samples. A (111) texture is observed in as-deposited and annealed films is identified as one of the possible contributions to the lower coercivity squareness S^* and perpendicular magnetic properties. Micromagnetic calculations confirmed a poor exchange interaction, identified rotational energy barriers and inferred that the ordered region was not fully ordered. The initial stage of ordering clearly showed a discontinuous type transformation.

INTRODUCTION

CoPt and FePt thin films have potential applications in extremely high density recording (EHDR)¹ where their large anisotropy energy density provides a barrier to thermally activated switching of the magnetization (superparamagnetism). It is well known that the Co-based HCP phase will exhibit significant thermal decay for sizes below 10 nm and superparamagnetic response below 7 nm^{1,14}. Because of the high magnetocrystalline anisotropy, L₁₀ materials is predicted to be thermally stable down to the 2-3 nm size range. However, increasing the anisotropy results in increasing the intrinsic anisotropy field, H_K , and consequently the coercive field, H_c , making it difficult to write magnetic information. It is important to determine the optimum anisotropy field and resulting coercivity, considering both the issues of writing and the thermal stability, simultaneously. If the coercivity can be effectively varied through control of the magnetocrystalline anisotropy, it would be applicable to the future media. In the case of L₁₀ materials, when they are completely ordered, the coercivity can reach over 1 T.¹⁸ However for recording media applications, we must adjust and control this intrinsic coercivity so as to attain a reasonable writing coercivity.

In the light of the above arguments, it is of interest to investigate L₁₀ materials since their magnetic properties can be tailored by choice of annealing temperature, time and composition³. Prior studies have involved bulk L₁₀ materials and correlation of the magnetic properties and their microstructures. However, many unsolved questions remain and the study of thin film L₁₀ materials is in its infancy. Recent studies of CoPt L₁₀ films (based on TEM measurements) showed (111) texture and heterogeneous transformation ordering kinetics^{2,6}. These authors discussed exchange coupling between the magnetically hard L₁₀ phase and remaining soft disordered phase. In bulk CoPt, it is known that the coercivity mechanism can be attributed to domain pinning due to anti-phase domains (APBs) and twins⁴. This might be different in the nanoscale polycrystalline thin films where we could assume the films to be a single domain assembly with neighbors coupled by relatively weak intergranular interactions. It is known that

the exchange interaction is sensitive to atomic configurations, therefore, the grain boundary could have a weakened exchange interaction compared with bulk materials.

In this article, we have attempted to relate the magnetocrystalline anisotropy energy density to the long range order parameter, applying spin pair model. We've synthesized CoPt alloy thin films with and without immiscible second phases at the grain boundaries. A micromagnetic model was used to explain how the microstructure would influence the magnetic properties. Based on previous studies, our experimental and simulated results, we will discuss the possible relationship between the microstructure and magnetic properties in the nanoscale thin films.

EXPERIMENTAL PROCEDURE

CoPt alloy films were deposited on the silicon (100) wafers or smooth glass substrates by the RF or DC magnetron sputtering. The base pressure before sputtering was 5×10^{-7} torr. The sputtering pressure of Ar gas was 1-5mtorr. Sputtering was performed in the power range of 20 – 100 W. Alloy targets (CoPt, 50 at%) or chips were used to produce the thin films. The purity of metal sources was better than 99.9%. Post annealing process was performed by RTA (rapid thermal annealing) in an Ar atmosphere for 5-7 minutes. Magnetic properties were measured using VSM (Vibrating Sample Magnetometry), and AGFM (Alternating Gradient Force Magnetometry) in the fields up to 1.4 T or by SQUID magnetometry in fields up to 5 T. Structural analysis was made using X ray diffractometer (Cu-K α , 35kV, 20mA). The chemical composition of the films was measured by X-ray fluorescence or EDS.

RESULTS AND DISCUSSION

A. Spin-pair Potential Model for L₁ Anisotropy

We have applied the Neel's spin pair potential model to model the strong uniaxial intrinsic anisotropy and explain the dependence of a long range order parameter on the intrinsic magnetocrystalline anisotropy in CoPt. This is used to explain the dependence of coercivity on thermal treatment. This is a phenomenological theory explains the surface anisotropy based on symmetry breaking ideas.^{8,10} The premise of this model is that anisotropy due to symmetry breaking and magnetostriction at surface or interfaces are connected quantitatively^{7,8,10}. In this localized moments model, the elementary internal energy of the spin pair can be expanded in a series of Legendre polynomials, as

$$W(r, \psi) = g(r) + l(r)(\cos^2 \psi - \frac{1}{3}) + q(r)(\cos^4 \psi - \frac{6}{7} \cos^2 \psi - \frac{3}{35}) + \dots \quad (1)$$

Where r is the distance between atoms and ψ is the polar angle between the bond and spin direction S . The common direction of the spins is determined by the exchange interaction. The first term, $g(r)$, which is spatially isotropic, corresponds to the exchange interaction. The second term is called the dipole-dipole interaction term. The magnitude of $l(r)$ is much larger than $q(r)$. therefore, in this study, we neglect from the third term. Magnetic anisotropy is calculated by summing over all spin pairs included in a unit volume of the crystal. Since the pair energy for distant pairs is small, we consider only the nearest neighbors. In an A-B binary system, considering AA, AB, BB atomic pairs and applying above assumptions, this internal energy per unit volume can be expressed as:

$$E_a = \frac{1}{2} N \sum_j^{NN=12} l_j (\cos^2 \psi_j - \frac{1}{3}) = \frac{1}{2} \left[N_\alpha \sum_j^{NN=12} l_j (\cos^2 \psi_j - \frac{1}{3}) + N_\beta \sum_j^{NN=12} l_j (\cos^2 \psi_j - \frac{1}{3}) \right] \quad (2)$$

Here, $N_\alpha = N_\beta = N/2$, $l = l(r, \xi, C)$. N_α , N_β and N are the number of atoms per unit volume in α , β site and the total number of atoms per unit volume, respectively. ξ is the long range order parameter and C is the atomic fraction of A element. The anisotropy constant K_u can be expressed in terms of the long range order parameter ξ and the composition, as $E_a = K_u \sin^2 \alpha_3 + \text{const}$ ---- (3)

$$\text{where } K_u(\xi, c) = N/4 \left[\frac{4l_{\alpha-\beta}(\xi, c)}{1+\Delta^2} (2\Delta^2 - 1) + (l_{\alpha-\alpha}(\xi, c) + l_{\beta-\beta}(\xi, c)) \right], \Delta = c/a$$

From this relationship, we can predict the variation of anisotropy constant with the degree of order and composition.

The $L1_0$ structure has alternating layer of Co and Pt. It is known that Pt can be spin polarized in CoPt alloys¹⁶, though its moment is small. When completely disordered, the second order or dipole term makes no contribution to the anisotropy. However, in the ordered state or partially ordered state, the second term does not disappear and contributes to the uniaxial anisotropy. This is true for geometries in which we do not consider strain. In a strained state, $l(r)$ can be expanded in terms of the bond strain. The values of $l(r)$ for Co-Co, Pt-Pt, Co-Pt can be deduced from magnetostriction coefficients or from first principles calculated values by J. M. MacLaren^{11,12}. Also a consideration is the fact that the lattice parameter of the CoPt alloy depends on the composition. Here then, $l(r)$ could have different values at each composition differing from the bulk values.

In the theory of phase transformations, $L1_0$ type ordering is classified as a first order. Therefore, above an instability line, it would exhibit a discontinuous transition involving nucleation processes. It has been reported that the transformation will occur on an ordering path with a lower energy barrier and a metastable structure based on $L1_0$ symmetry with (1) a non-equilibrium c/a ratio or (2) a non-equilibrium order parameter⁴. Also it has been proposed that ordered regions are not fully ordered in the initial stage of the transformation¹³ and do not possess their maximum possible degree of tetragonality. The dependence of the anisotropy constant on annealing time and temperature can be attributed to these reasons and thus might be very sensitive to composition and degree of order due to the quadratic and linear dependences of K_u on ξ and composition, respectively. Our calculations can be useful in interpreting previous and present experimental results and the scatter of coercivity data.

B.Experimental and Simulation Results

Our preliminary results on CoPt alloy films synthesized by putting Co and Pt chips on a SiO_2 target showed degraded magnetic properties below 10 nm thickness. This can be attributed to several reasons. The composition of the sputtered thin films were 54 at% Pt by EDS and X-ray fluorescence analysis. However, a small thickness dependence of the composition was detected. Other reasons could include oxidation during sputtering or slow kinetics.

Further investigation of the magnetic properties was carried out for CoPt thin films produced using 50 at%Pt alloy target. The deposited alloy composition was 54 at% Pt and thickness ranged from 5 to 40 nm. X-ray analysis revealed random (111) texture with a tendency toward more random texture with increasing SiO_2 . For the same thickness, the addition of SiO_2 contributes to the peak broadening probably due to non-uniform strain or smaller grains. The samples annealed below 600 °C by RTA for 7 minutes do not show any shoulder in their hysteresis curve suggesting highly exchange coupled grains (Figure 2.(b)). ΔM showed larger peaks with decreasing annealing temperature. This confirmed an increasing grain isolation during the grain growth process or oxidation of surface layer with increasing the annealing temperature. As the annealing temperature is increased, the hard phase comes out discontinuously, giving rise to a

shoulder in the hysteresis curve. Both in-plane and perpendicular coercivities of films were almost the same, suggesting a spin rotation mechanism¹⁹. Ordering starts at 500 °C, and coercivities increase from below hundred Oe to the higher values depending on the thermal treatments. The coercivities abruptly increased from around 1000 Oe to 7000 Oe, between 600 °C and 650 °C. The saturation magnetization, M_s decreases with increasing annealing temperature (as deposited $M_s \cong 700$ emu/cc). This reduction might be due to tracing a minor loop or the dependence of M_s on order parameter.

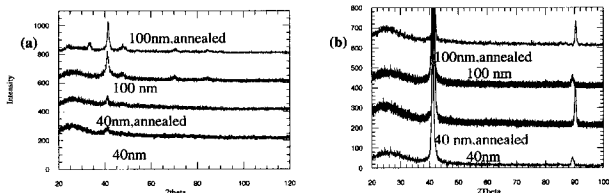


Figure 1. XRD analysis of (a) $(\text{Co}_{46}\text{Pt}_{54})_{90} - (\text{SiO}_2)_{15}\text{vol}\%$ (b) $\text{Co}_{46}\text{Pt}_{54}$: RTA 700°C

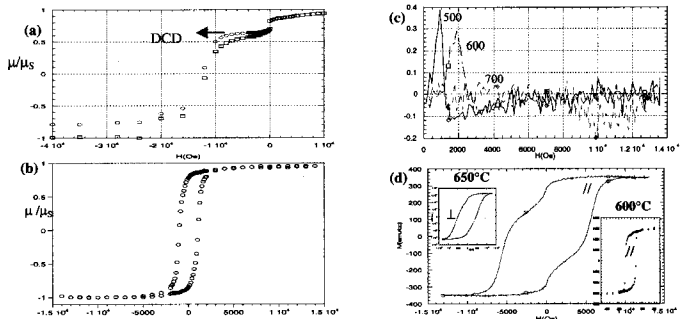


Fig.2 (a) $\text{Co}_{46}\text{Pt}_{54}$, 20nm, 700°C by RTA, 7min, in-plane; (b) same as (a) but 550°C RTA, in-plane; (c) $\Delta M/M_r$, $\text{Co}_{46}\text{Pt}_{54}$ 550, 600, 700°C by RTA 7min, 20nm; (d) $\text{CoPt-SiO}_2(30\text{vol}\%)$, 10nm, RTA 600($H_c=905$ Oe), 650 °C, 7min, // : in-plane, \perp : perpendicular

It has been reported that the ordering at 500 - 600 °C from disordered phase is 'discontinuous' while the annealing over 600 °C promotes a 'continuous' transformation in bulk CoPt ¹³. Our experiments for the nanoscale thin films showed a shoulder in the hysteresis loop for samples annealed by RTA to temperatures above 600 °C. The shoulder disappears with increasing annealing time. The samples annealed by RTA below 600 °C, do not show a shoulder at the initial stage and have much higher squareness, S and S^* , values presumably due to enhanced exchange coupling. SiO_2 addition shows a nearly similar behavior (Figure 2(d)) except for a reduced exchange interaction inferred from the ΔM curve.

(111) texture results in magnetic easy axes, 36° out of plane has a nearly identical reversal process to the 3-D random distribution, based on the simple Stoner-Wohlfarth model. Consequently, both textures result in the low squareness, S^* , since most of the irreversible switching occurs after a large amount of rotation before the coercive field is reached (Figure 3(a)). Due to the intergranular coupling, texture effects may be lessened (higher S^* and S), however, inappropriate texture could still be a possible reason for low S^* . Introduction of magnetostatic interactions yield similar results, however, its effects will be lessened when there is the substantial increase of K_u (decrease of M_s/H_k) based on the previous micromagnetic studies. To identify the reversal process in more depth at the initial stage of ordering, a numerical simulation of the magnetization reversal process was performed using a 2-d nanostructured array model of the interacting single domain assembly. These were performed varying the ordered fraction and considering the intergranular interaction in terms of magnetostatic interaction and exchange coupling between the grains. A detailed description of micromagnetic calculation can be found in references 14 and 17. The previously observed grain sizes had a large variation, so we've used a size ranging from 10 to 60nm in our model. These values are all smaller than the domain wall width, δ_w (around 72 nm) of the soft disordered phase (for the ordered $L1_0$ phase: $\delta_w \sim 10\text{nm}$)¹⁵. In each grain, the magnetocrystalline anisotropy is assumed to be uniaxial and the ordered tetragonal phase can be assumed to have non-equilibrium uniaxial anisotropy, as discussed above, which could range from $\sim 10^5$ to 10^7 erg/cc. Even though this model has limitations (due to the possibility of an incoherent reversal mechanism (exchange length $l_{ex} \ll$ particle size), co-existence of two phases and structural variants within a grain and uniform particle size assumptions), we can easily visualize the mechanism of the reversal process qualitatively. Although there exists a significant fraction of the soft phase, it is hardly detectable due to intergranular exchange coupling. Even if we remove the remaining soft phase by long time annealing, the resulting large anisotropy is not favorable in the recording media applications.

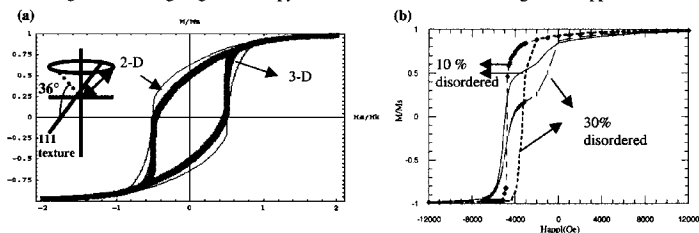


Fig.3 (a)Stoner-Wohlfarth model for 3-D random, 2-D random ,(111) texture of easy axis distributions(Cornical); (b)one of the micromagnetic simulation results containing soft phase 10%, 30% with and without effective exchange coupling $A^*=0.4 \times 10^{-11}\text{J/m}$ (h_{exchange} (normalized by H_k)= $A^*/KD^2=C^*=0.1$), D (particle size) =10nm, M_s common to both phases(=500 emu/cc), partially ordered phase assumed, $K_1 = 4 \times 10^6$ and $K_{1,\text{disordered}} \approx 6 \times 10^5$ erg/cc. Easy axis : 3-D random.

CONCLUSION

We have related the dependence of the magnetocrystalline anisotropy to the long range order parameter in CoPt thin films. CoPt thin films deposited by RF or DC magnetron sputtering showed 'discontinuous' type transformation during the annealing procedure and consequently a

disordered magnetically soft phase – retained. The (111) texture observed is not favorable for the longitudinal recording. A strong in-plane orientation must be induced using the underlayer to increase the S^* which is related to ‘transition parameter’ in the longitudinal recording media.

APPENDIX

P (Probability of A atom occupying α site) : P_A^α , C : Atomic fraction of A atom. (C_A)

$$N_A^\alpha + N_B^\alpha = 0.5N, N_A^\beta + N_B^\beta = 0.5N, N_A^\alpha + N_A^\beta = N_A, N_B^\alpha + N_B^\beta = N_B$$

$$\text{USING, } P = P_A^\alpha = N_A^\alpha / N_\alpha, P_B^\alpha = N_B^\alpha / N_\alpha, P_A^\beta = N_A^\beta / N_\beta, P_B^\beta = N_B^\beta / N_\beta, C_A = C, C_A + C_B = 1,$$

$$C_A / C_B \leq 1 (= C_A \leq 0.5), \text{Then, } P_B^\alpha = 0.5 - P, P_A^\beta = C - P, P_B^\beta = 0.5 - P_A^\beta = 0.5 - C + P, \text{Therefore,}$$

$$l_{\alpha-\alpha} = P_A^\alpha P_A^\alpha l_{A-A} + 2 \cdot P_A^\alpha P_B^\alpha l_{A-B} + P_B^\alpha P_B^\alpha l_{B-B} = P^2 l_{A-A} + 2P(1-P)l_{A-B} + (1-P)^2 l_{B-B}$$

$$l_{\alpha-\beta} = P_A^\alpha P_A^\beta l_{A-A} + (P_A^\alpha P_B^\beta + P_B^\alpha P_A^\beta) l_{A-B} + P_B^\alpha P_B^\beta l_{B-B}$$

$$= P(2C - P)l_{A-A} + [P(P - 2C + 1) + (1 - P)(2C - P)]l_{A-B} + (1 - P)(P - 2C + 1)l_{B-B}$$

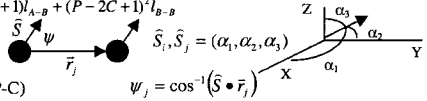
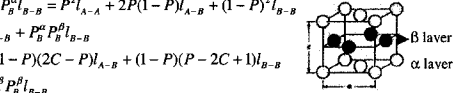
$$l_{\beta-\beta} = P_B^\beta P_B^\beta l_{A-A} + 2 \cdot P_A^\beta P_B^\beta l_{A-B} + P_B^\beta P_B^\beta l_{B-B}$$

$$= (2C - P)^2 l_{A-A} + 2(2C - P)(P - 2C + 1)l_{A-B} + (P - 2C + 1)^2 l_{B-B}$$

$$\xi = \frac{N_A^\alpha + N_B^\beta}{N} - \frac{N_A^\beta + N_B^\alpha}{N}$$

$$\xi: \text{Long range order parameter } \xi = 2(P - C)$$

$$P = P_A^\alpha = \xi/2 + C \Rightarrow \text{Plug this term into above equations, Then we get } l = l(\xi, C).$$



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