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Analysis of grain size in FePt films fabricated using remote plasma deposition

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Abstract

Remote plasma sputtering (RPS) offers a high degree of control over the sputtering parameters used to deposit thin metallic films and has demonstrated a capability to control the media grain size distribution. Narrow grain size distributions remain a key requirement for future magnetic media. Here we report a comprehensive magnetometry, X-Ray diffraction and transmission electron microscopy study of how RPS affects the grain size distribution of continuous, non-segregated L1₀ FePt thin films. These provide a model medium for heat-assisted magnetic recording and more generally for spintronic devices such as magnetoresistive random access memory and spin torque oscillators, where very high perpendicular magnetocrystalline anisotropy is required. Varying the target DC bias voltage, which in RPS can be tuned independently of the plasma generation, produces no meaningful, statistical change in average grain size, 6.5 ± 0.1 nm, for as-deposited, disordered FePt. Annealing at 800°C creates the well-ordered L1₀ phase but results in an increased average grain size of 8.3 - 13.6nm, and a significantly wider grain size distribution of 6.4 - 8.5nm. These results show that whilst RPS is capable of producing well-ordered L1₀ FePt thin films, it does not offer an advantage in controlling the grain size of FePt, as reported in other thin film systems.

Keywords: FePt; thin films; remote plasma sputtering; grain size distribution; x-ray diffraction; transmission electron microscopy

1 Introduction

Materials with high perpendicular magnetocrystalline anisotropy (PMA) are an essential component of many rapidly developing technologies. These include spin-transfer torque magnetoresistive random access memory (STT-MRAM) [1, 2], spin torque oscillators (STOs) [3] and energy assisted magnetic recording [4, 5]. High PMA materials can be used as efficient polarising layers, to bias synthetic anti-ferromagnetic reference layers and to maintain the thermal stability of stored data as device footprints continue to shrink.

Energy assisted magnetic recording systems will require media with high PMA together with small, well controlled grain sizes in order to meet the challenge of increased storage areal densities [5]. The grain size in magnetic storage media gives an upper bound on the storage density, since increased storage capacities require small grain sizes to maintain sufficient signal-to-noise ratio (SNR) on readout [6]. In addition, the grain size distribution must be tightly controlled to a maximum of $\pm 10\%$ of the grain size [7] in order to allow reliable switching under the thermal/magnetic write field [8]. Ordered L1₀ FePt thin films with PMA of $\sim 4 \times 10^7$ erg/cm³ are the leading contender to satisfy these requirements for heat assisted magnetic recording systems (HAMR) with storage capacities in excess of 1 Tbit/in² [9, 10]. The high PMA found in ordered L1₀ FePt permits small grain sizes of < 5 nm whilst retaining thermal stability [7, 8].

Remote plasma sputtering (RPS), also known as high target utilization sputtering (HiTUS) [11], offers an alternative sputtering technique capable of finer process control than conventional magnetron systems [12, 13, 14]. Here the plasma generation is decoupled from the sputtering process so that the target DC bias voltage and acceleration of the Ar⁺ ions can be controlled independently of the plasma generation, allowing a greater degree of control of the sputtering process. In addition, by generating the plasma remotely and guiding it to the target material, the target is sputtered uniformly over its entire surface area. This approach is far more efficient than magnetron sputtering, where the plasma is generated locally at the target surface and sputtering is confined to a thin circular track by the magnetic field of the magnetron gun. Consequently, it also makes it a cost effective solution for the

deposition of expensive materials such as Pt. Varying the ion impact energy, through tuning of the target DC bias voltage, has been shown to influence the average grain size in certain materials [12, 13], providing a method of producing thin films with controlled grain size. RPS has also been shown to allow the tuning of the anisotropy of multilayer materials through control of interfacial mixing [14]. Here, we investigate the effect on grain size and grain size distribution when non-segregated FePt films are deposited using RPS at different target DC bias voltages. Estimates of the average grain size and distribution for as-deposited and annealed FePt thin films are determined using Scherrer analysis of XRD data and through grain identification from transmission electron microscopy (TEM) images.

2 Methods

2.1 Thin film Deposition & Characterization

FePt thin films were deposited by RPS on to MgO (001) substrates using a PlasmaQuest HiTUS system attached to a Lesker vacuum chamber. The films, of thickness of 10nm, were deposited from a Fe₅₀Pt₅₀ at% alloy target at an RF power of 1kW for three target DC bias voltages of 200V, 600V, and 1000V. The chamber base pressure was better than 8×10^{-9} mbar and an Ar pressure of 3×10^{-3} mbar was used throughout the deposition. All sputtering was carried out at ambient temperature with no deliberate substrate heating. The as-deposited FePt films were in the expected fcc disordered phase [15, 16], so post annealing of the thin films was performed to induce the required L1₀ phase. The films were annealed in a conventional tube furnace at 800°C for one hour in an Ar/10%H₂ reducing atmosphere to minimize oxidation. The magnetic and structural properties of the films were analyzed both before and after annealing.

Magnetic properties were measured using a MicroSense Model 10 vector vibrating sample magnetometer (VSM), which allows a (maximum) 2T magnetic field to be applied in different geometries to enable the in-plane and out-of-plane hysteresis loops to be measured, from which saturation magnetization (M_s) and coercivity (H_c) can be determined. The anisotropy field was determined through the extrapolation of the hard axis loop. All VSM measurements were performed at room temperature.

The presence of the desired $L1_0$ ordered phase in the films was determined from XRD data produced using a Philips X'Pert Pro X-ray Diffractometer with a Cu anode operating at 1.2kW providing K_α radiation at a wavelength of $1.5418\text{\AA}$. The diffractometer was equipped with a Nickel filter and an X'Celerator 1D silicon strip detector. Scans were taken with a 2θ between 20° and 55° at 0.0334° intervals with a measurement time of 80 seconds per point. Due to the instrument configuration available a large background contribution was present from the MgO substrate making it difficult to determine the $L1_0$ order parameter directly from the ratio of the (001) and (002) peaks. Consequently, ordering in the films was determined by the presence of fcc FePt (200) and $L1_0$ FePt (001) and (002) peaks in the XRD data. In an ordered film we expect to observe strong, high intensity $L1_0$ FePt (001) and (002) peaks along with a significantly reduced intensity fcc FePt (200) peak [17]. Grain sizes were estimated from the XRD data using the Scherrer equation [18, 19]. In order to determine the parameters required for the Scherrer equation, Gaussian curves were fitted to the peaks in the XRD data from which values for the full-width half-maximum (FWHM) and peak position were determined. In the case of the disordered FePt phase the fcc FePt (200) peak was used, whereas in the case of the ordered, $L1_0$, phase the $L1_0$ FePt (001) peak was used. A shape factor of 0.9 was assumed [18].

2.2 Transmission Electron Microscopy (TEM)

TEM was used to determine the average grain size and distribution for the as-deposited and annealed films. In order to image the samples it was necessary to reduce the thickness of the MgO substrate to electron transparency. Here a process of mechanical polishing using an Allied High Tech Multiprep automatic polishing machine was employed. This uses a variation on the tripod polishing technique [20], required for preserving the crystallinity of the samples, and also avoids the surface amorphization associated with ionic polishing. Samples were polished to a wedge shape orientated approximately 30° to the cubic crystal lattice planes of the substrate in order to avoid fracturing and crumbling of the delicate wedge tip. The wedge had a relatively large angle of inclusion of 3° in both x and y directions to further reinforce the sample. The instruments used for the TEM measurements were equipped with a LaB_6 source, and an accelerating voltage of 200kV was used for all measurements. The as-deposited samples were imaged with a Phillips CM200 TEM and the annealed

samples with a FEI Tecnai T20 TEM. Selected area electron diffraction (SAED) patterns were produced to identify key material features. The samples were tilted a few degrees off-axis to eliminate diffraction contrast from the MgO substrate. Grains were identified from dark field TEM images using the machine-learning algorithm *Trainable Weka Segmentation* in ImageJ [21], which provides a semi-automatic, objective, reproducible method for consistently analyzing all images using the same classifier. Feret's diameter [22] was used as a convenient measure of the grain size, and a minimum area threshold of 7nm^2 was applied to reduce false positives. Histograms of the grain size distribution were produced and fitted with lognormal distributions. The mean grain size and a measure of the width of the grain size distribution were calculated from the fitted parameters. Uncertainties in the fitting process, specifically from the difference between the data and the ideal model, are larger than the standard error of each distribution.

3 Results and discussion

The magnetic and structural properties of the as-deposited and annealed films were analyzed using VSM, XRD and TEM. The magnetic properties were found from hysteresis loop measurements using the VSM. Chemical ordering in the films was determined from the XRD data and both XRD and TEM were used to estimate the average grain size and, in the case of TEM, the grain size distribution.

3.1 Magnetic and X-Ray characterization

Figure 1 (a) shows the in-plane and out-of-plane hysteresis loops for the as-deposited, and Figure 1(b) shows the hysteresis loops after annealing, for the film deposited using a target DC bias voltage of 600V. Similar results (not shown) were observed for the other films. Figure 1(c) shows the conventional θ - 2θ XRD data where the scattering vector is perpendicular to the plane of the film for the as-deposited and annealed films, with the key angles representing the XRD peaks of interest identified.

Figure 1: In-plane and out-of-plane hysteresis loops for the (a) as-deposited and (b) following annealing at 800°C, for the FePt thin film deposited at a target DC bias voltage of 600V. (c) shows the conventional θ -2 θ XRD data for the as-deposited and annealed FePt thin film deposited at a target DC bias voltage of 600V.

The hysteresis loops for the as-deposited films exhibit an in-plane anisotropy, which is expected for FePt thin films in the disordered fcc phase. This is confirmed by the presence of a strong fcc FePt (200) peak and the absence of L₁₀ FePt (001) and (002) peaks in the XRD data. Following annealing, the hysteresis loops show that a strong PMA has developed as explained by the XRD data which shows high intensity L₁₀ FePt (001) and (002) peaks and no fcc FePt (200) peak, indicating that we have developed the desired L₁₀ phase following annealing. The saturation magnetization of $M_s \approx 700 \text{ emu/cm}^3$ for the annealed film is lower than might be expected for bulk FePt, but a reduced M_s is commonly observed in thin films [23]. Following annealing, all films had an anisotropy field $>40 \text{ kOe}$ as is clearly evident for the 600V sample from Figure 1 (b). However, the large uncertainties in extrapolating the hard axis data preclude making a reasonable estimate of the actual value of the anisotropy field.

3.2 Grain size analysis

In the case of XRD data the average height of the crystallites, and hence average grain size, can be calculated using Scherrer analysis. The average grain sizes for the as-deposited and annealed films determined using Scherrer analysis are shown in Figure 2(a). Although the films were nominally 10nm thick, the calculated grain size varies between 8.3nm and 10.1nm for the annealed film, which is mostly smaller than the assumed films thickness. As such thin films exhibit only single grains in the out-of-plane direction [24], this suggests the presence of disordered material, maybe due to oxidation of the top surface in atmosphere after annealing, and/or oxygen migration from the MgO substrate during annealing. The thickness of the well ordered magnetic material within the film is therefore potentially less than the total film thickness, which could account for a lower than expected measured film magnetization. For our thin film geometry XRD is a surface reflectivity technique and is only sensitive to dimensions in the out-of-plane direction, hence, TEM was used as a direct measurement of lateral grain size, which can be compared against grain size estimates produced from Scherrer analysis of the XRD data. Representative dark field images were taken of each sample for grain size analysis, shown in Figure 3 (a) and (c) for the case of the film deposited using a target DC bias voltage of 600V. The SAED patterns, Figure 3 (b) and (d), evidence the good crystalline quality of the samples. The emergence of the highlighted (100) spots after annealing in Figure 3 (d) show a clear epitaxial relationship with the cubic crystal MgO substrate, and confirm the presence of the desired $L1_0$ crystal structure in the FePt demonstrated in the XRD data. Double diffraction spots are visible due to the bi-layer crystalline structure of the sample where the MgO substrate and the FePt thin film have slightly different lattice parameters. The TEM images reveal a preferential direction for the annealed samples, where grains of FePt can be seen to form lines, visible left to right across in Figure 3 (c), which is attributed to terracing formed by the MgO cut angle always present in single crystal substrates [25].

Figure 2: (a) Average grain size as a function of target DC bias voltage calculated using Scherrer analysis of the XRD peaks (dash-dot) and TEM analysis (dashed) for the as-deposited (squares) and annealed (diamonds) thin films. (b) the width of the grain size distribution determined from TEM analysis for the as-deposited (squares) and annealed films (diamonds).

Figure 3: Representative TEM Images for the (a) as-deposited and (c) annealed, along with SAED patterns for the (b) as-deposited and (d) annealed, for the FePt thin film deposited at a target DC bias voltage of 600V

From the dark field TEM images the grains were identified and outlined using the segmentation algorithm (see Figure 3 (a) and (c)), from which a normalized probability distribution of grain sizes was determined, as shown in Figure 4, for the as-deposited and annealed films at the three target DC bias voltages. A lognormal curve was fitted to each distribution and the average grain size and width of the grain size distribution were determined from the fitted curve.

Figure 4: Grain size distributions for as-deposited (a)-(c) and annealed (d)-(f) thin films for target DC bias voltages of 200V (a) and (d), 600V (b) and (e), and 1000V (c) and (f). Solid line indicates the best-fit curve used to extract the average grain size and width of the grain size distribution.

The calculated average grain sizes are shown in Figure 2 (a) and the width of the distribution in Figure 2 (b) for the as-deposited and annealed films. There is little difference in the average grain size calculated from the XRD data and measured from the TEM image in the as-deposited case. Both approaches predict small grain sizes with an XRD average of 6.3 ± 0.1 nm (for the vertical grain size as determined from Scherrer analysis) and a TEM average of 6.7 ± 0.2 nm (for the lateral grain size). For the as-deposited films equiaxed grains can be expected, and the good agreement between TEM and XRD suggests that for these films both techniques give an accurate measurement of grain size in the material. The TEM analysis further allows the grain size distribution to be determined, which is quite large with an average width of 2.4 ± 0.1 nm.

After annealing, both approaches show a significant increase in the grain size at all target DC bias voltages suggesting that the grains have grown both vertically and laterally. The TEM analysis measured a much larger increase in lateral grain size compared to XRD Scherrer analysis of the vertical grain size. The XRD average vertical grain size varied between 8.3 ± 0.3 nm and 10.1 ± 0.3 nm, whilst the TEM average lateral grain size varied between 11.4 ± 0.5 nm and 13.6 ± 0.6 nm. Grain growth during annealing is limited in the vertical direction by the thickness of the film, whereas the lateral grain size is less constrained. No systematic behavior was observed for different DC bias voltages, with small differences attributed to film-to-film variation. In addition, the width of the grain size distribution is seen to increase by over a factor of three after annealing, reaching values between 6.4 ± 0.7 nm and 8.5 ± 1.2 nm.

The average grain size for the as-deposited films show no dependency on the target DC bias voltage. However, the greatest increase in average grain size after annealing is for a target DC bias voltage of 600V, with the smallest average grain size being observed at a low target DC bias voltage of 200V.

4 Conclusion

RPS has been investigated as a method of controlling the grain size of non-segregated, prototype FePt thin films. The additional parameter space this technique

offers has been explored to investigate possible advantages for a variety of applications. Surprisingly, considering the advantages demonstrated in other materials, there is no evidence that the grain size in FePt can be controlled by depositing using RPS. Our results demonstrate a lack of correlation between DC target voltage and grain size, indicating that the properties of this media are robust to such variation of fabrication conditions. In the as-deposited, non-ordered state the combined average grain size is shown to be 6.5 ± 0.1 nm, but the films exhibit a large grain size distribution of 2.4 ± 0.2 nm on average. Annealing at high temperature (800°C) results in the creation of the desired L1_0 phase. However, whilst well ordered films with high PMA can be produced using RPS, the resulting grains are large, varying between 8.3 and 13.6 nm depending on the target DC bias voltage used. More significantly, a major increase in the width of the grain size distribution is observed from 2.2nm to 8.5nm, or 35% to 63% of the measured average grain size, for the thin film deposited at a target DC bias voltage of 600V. We conclude that whilst RPS offers a route to producing ordered L1_0 FePt thin films, it does not offer an advantage in controlling the grain sizes and producing small, controlled grain size distributions in such thin film materials.

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