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Electrodeposition of coercive L1₀ FePt magnets

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ABSTRACT

We report the preparation, characterization of structure and magnetic properties of electrodeposited L1₀ FePt films with high coercivity. Equiatomic as-deposited films are nanocrystalline, soft and magnetically isotropic. The transition from the disordered to the ordered phase was studied by varying the annealing time and annealing temperature. The as-deposited nanocrystalline deposits were treated in forming gas and developed the tetragonal L1₀ structure only at temperatures above 500 °C. The coercivity increases with both annealing temperature and time reaching a value of 1.5 T at 900 °C. The magnetization reversal mechanism was identified as nucleation type from the initial magnetization curve of a thermally demagnetised sample.

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1. Introduction

The recent development of hard magnets has been driven by potential applications of thin films in high-density recording media and of thick films in microelectromechanical (MEMS) systems [1]. Integration emerges as an important requirement for both applications. For demonstrating functionality, discrete magnetic components cut out from sintered bulk [2,3] or sputtered NdFeB [4] films have been used as parts in devices such as rotors for micromotors and deformable magnetic mirrors for adaptive optics [5]. Among the various techniques currently being exploited for integration, electrodeposition shows advantages over vacuum deposition, sputtering and high temperature sintering techniques for thick films because it is fast, relatively inexpensive and operates at room temperature. Face-centred tetragonal FePt with the L1₀ structure should be considered as a candidate material due to its excellent corrosion resistance and intrinsic magnetic properties ($\mu_0 M_s = 1.43$ T, $K_1 = 6.6$ MJ m⁻³) in the bulk form [6], as it can be readily electroplated.

FePt films have mostly been prepared using sputtering, vapor deposition or pulsed laser deposition (PLD). Thin continuous FePt films typically show coercivities between 1–2 T after annealing [7–12], while bulk samples typically show coercivity values of 0.5 T [13]. Recently, Shima et al [14] reported coercivities as high as 7 T at room temperature (10.5 T at 5 K) in ultrathin films obtained by co-sputtering of Fe and Pt, which is associated with the formation of isolated nanoparticles. Their substrate was MgO (001) and they carried out deposition at 780 °C. The combination of epitaxial growth and particle isolation led to high out-of-plane anisotropy in samples with 5 nm nominal thickness. The coercivity fell to 4.0 T as the thickness was increased to 40 nm, which is well above the reported bulk value. Weisheit et al. [15] obtained similar results using PLD as a preparation route. They reported room temperature coercivities as high as 5.6 T for a 40 nm thick film. Films were prepared on substrates made of glass with an MgO (001) seed layer at a deposition temperature of 800 °C. The authors also found that the films grew epitaxially and formed well-separated nanoparticles.

Electrodeposition of continuous L1₀ films [16,17] or nanowires [18,19, 20] are potential alternatives to sputtered and PLD deposition for MEMS applications as thick structures can be obtained. Here, we report a detailed study of the microstructural evolution and magnetic properties of electrodeposited L1₀ FePt films with varying annealing temperature and annealing time. We also identified the magnetization switching mechanism from initial magnetization curves on thermally demagnetized samples.

2. Experimental Methods

FePt films were electrodeposited from a single bath containing 1 mM H₂PtCl₆, 0.1 M Na₂SO₄ and 0.1 M FeSO₄. The solution pH was adjusted to 2.9 by adding a small amount of either sulfuric acid or hydrochloric acid. The counter electrode was a 6-mm diameter by 50-mm long graphite rod and the reference electrode was Ag/AgCl saturated with KCl with a factory calibration of 205 ± 5 mV. All potentials are quoted with respect to this reference electrode.

All solutions were prepared in 100 ml of deionized water. FePt alloys were electrodeposited onto Ag substrates. The substrates were cut out from a 50 μm thick foil into 6 mm x 6 mm electrodes and contacted to a copper wire, the substrates and Cu wire was varnished leaving an area of 5 mm x 5 mm on which a film was electrodeposited. Prior to electrodeposition, the substrates were dipped into a 10 vol. % H₂SO₄ solution to remove any impurities on the surface and then washed in deionized water. Fresh solutions were vigorously stirred in an open atmosphere at room temperature and the deposition took place immediately after inserting the substrate into the bath. The deposition was controlled using an EG&G model 263A potentiostat.

Annealing was carried out at 500–900 °C in a tube furnace in a constant flow of forming gas, a H₂-Ar (5 vol.% H₂) mixture. The temperature was ramped from room temperature (RT) to the annealing temperature at a constant rate (40 °C min⁻¹), the annealing was then carried out for 20–120 min before cooling to RT at 40 °C/min. The crystalline structure was investigated by X-ray diffraction (XRD) with Cu K_α radiation and a 0.03° step size. The film thickness was evaluated from cross-section imaging in an SEM. Composition was characterized using electron microscopy coupled with EDX analysis. Magnetic properties were measured using a 5 T SQUID magnetometer (Quantum Design) at room temperature.

3. Results and discussion

The dependence of the composition of electrodeposited Fe-Pt on plating potential can be understood by considering three regions: platinum rich, alloy modulation and iron rich. At more positive potential ($V > -0.6$ V vs Ag/AgCl), Pt preferentially plates and the film composition ranges from 95 to 99 at. % Pt, which is associated with the fact that Pt is more noble than Fe. A second region ($-1.0 < V$ vs Ag/AgCl < -0.6 V) is the alloy modulation region, where the

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composition is very sensitive to the applied potential. In this region the deposition of Pt is mass-transport limited, whereas Fe deposition is limited by kinetics. We observed that by adjusting the applied potential, a controlled composition with typical slope of about 125 at. % Pt/Volt is achieved. Smooth and shiny films are obtained in this range of potentials. The iron rich region (V vs. $\text{Ag}/\text{AgCl} < -1.2$), is weakly sensitive to applied potential because both Pt and Fe deposition are mass-transport limited. In this region, film composition is about 5 at. % Pt. The deposits in the iron-rich region are spongy and powdery. At large overpotentials, there is also an undesirable reaction taking place, which is the hydrogen evolution reaction ($2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$). Hydrogen evolution is responsible for changes in pH in the vicinity of the electrode and formation of bubbles, which may block surface nucleation sites, producing a rough or powdery deposit. Stirring helps to remove the bubbles from the surface of the electrode. We focus on samples with nearly equiatomic composition obtained from plating at potentials of -0.9 V vs. Ag/AgCl .

Ag electrodes were chosen as substrates because they do not form any alloy with either Fe or Pt, which contrasts with Cu which forms cubic $\text{Cu}(\text{Pt})$ and CuFe phases. Nearly equiatomic FePt films electrodeposited onto the Ag substrates were annealed in a forming gas atmosphere.

The phase evolution of FePt films was studied by varying the annealing temperature and annealing time at temperatures ranging from $500 \text{ }^\circ\text{C}$ to $900 \text{ }^\circ\text{C}$ for a period of up to 2 hours. The X-ray diffraction patterns of nearly equiatomic FePt films annealed at different temperatures are shown in Fig. 1. All the as-deposited samples were found to be nanocrystalline showing a broad peak at the [111] reflections (figure 1a). A grain size of 11–14 nm, was estimated using the Scherrer formula. This diffraction pattern matches the disordered cubic FePt pattern (shown at the bottom of the figure). There was little structural difference between the samples annealed at $500 \text{ }^\circ\text{C}$ and the as-deposited films. At $650 \text{ }^\circ\text{C}$, tetragonal FePt starts to form and there is considerable grain growth. The phase transformation is evident from the appearance of the [200] reflection, and sharpening of the [111] peak clearly shows grain growth. At $800 \text{ }^\circ\text{C}$ and $900 \text{ }^\circ\text{C}$, there were further changes in the structure accompanied by the appearance of the [002], [201], [112], [220] and [202] reflections.

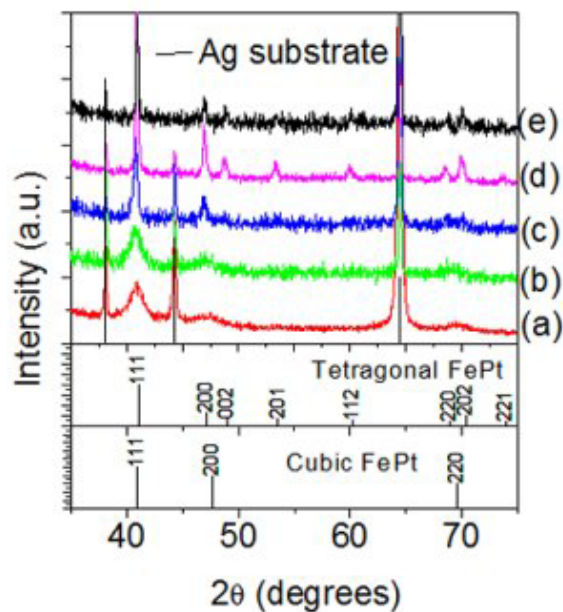


Figure 1. X-ray diffraction patterns of $0.45 \mu\text{m}$ thick FePt films (a) as-deposited and annealed at (b) $500 \text{ }^\circ\text{C}$, (c) $650 \text{ }^\circ\text{C}$, (d) $800 \text{ }^\circ\text{C}$ and (e) $900 \text{ }^\circ\text{C}$ for 2 hours. X-ray pattern for the ordered tetragonal and disordered cubic FePt phases are shown at the bottom of the figure.

The annealing time was varied from 30 to 120 min, as shown in Fig. 2, while the temperature was kept at $800 \text{ }^\circ\text{C}$. As can be seen, the formation of the tetragonal phase starts at an early stage of the annealing process at $800 \text{ }^\circ\text{C}$. Significant grain growth indicated by a sharp [111] peak is already present in samples annealed for 30 min. Also, the [002], [201], [112], [220] and [202] reflections clearly show the tetragonal L1_0 FePt phase. As the annealing time is increased to 60 min and 120 min no further evolution of the structure could be observed. The effect of the annealing time is similar to the annealing temperature; at longer annealing times and higher temperatures the tetragonal FePt phase is formed. From the width of the peaks, the grain size is estimated to be $> 60 \text{ nm}$.

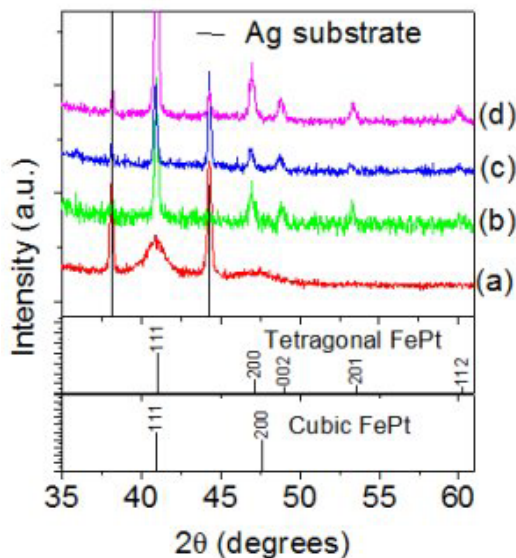


Figure 2. X-ray diffraction patterns of $0.45 \mu\text{m}$ thick FePt electrodeposited films (a) as-deposited and annealed at $800 \text{ }^\circ\text{C}$ for (b) 30 min, (c) 60 min and (d) 120 min. Below, the X-ray pattern for the ordered tetragonal and disordered cubic FePt phases.

All nearly equiatomic as-deposited FePt films were magnetically soft and isotropic with coercivities smaller than 5 mT. The dependence of the magnetic properties on the annealing temperature and annealing time was also investigated. Room-temperature magnetization measurements of FePt electrodeposited on Ag substrates after annealing at different temperatures are shown in Fig. 3. The samples annealed at $650 \text{ }^\circ\text{C}$ show a small contribution from a soft magnetic phase, presumably disordered cubic FePt, in the magnetization curve. The initial magnetization curve of samples annealed at temperatures ranging from $650 \text{ }^\circ\text{C}$ to $900 \text{ }^\circ\text{C}$ (fig. 3) is characteristic of a nucleation-type magnet. In this case, reversed nuclei cannot grow to form larger domains until a critical reverse nucleation field is reached, after which a large change in magnetization takes place. Room temperature magnetization curves measured for samples annealed at all temperatures show that L1_0 FePt deposits are magnetically isotropic, which is line with the polycrystalline nature of the deposits revealed by the XRD results (Fig. 1 and Fig. 2). As a result of the large anisotropy, the magnetization is unsaturated in a field of 5 T.

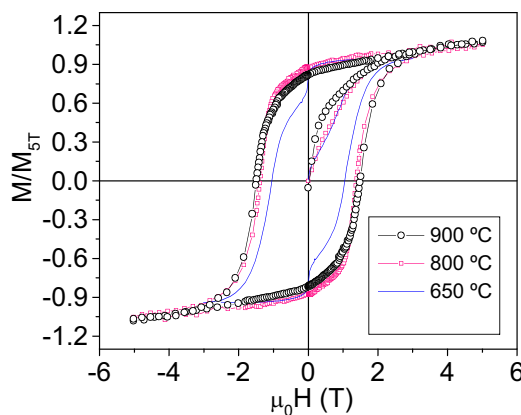


Figure 3. Room-temperature magnetization measurement of $0.45 \mu\text{m}$ thick FePt films annealed at $650 \text{ }^\circ\text{C}$, $800 \text{ }^\circ\text{C}$ and $900 \text{ }^\circ\text{C}$ for 2 hours.

The dependence of the coercivity on the annealing time and temperature of FePt films is shown in Fig. 4. At $800 \text{ }^\circ\text{C}$, coercivity quickly increases and reaches a plateau of 1.4 T after 20 min annealing. Samples annealed at low temperature ($500 \text{ }^\circ\text{C}$ for 2 hours) show the same coercivity of as-deposited samples. Coercivity only starts to develop at an annealing temperature higher than $600 \text{ }^\circ\text{C}$, then it increases sharply and reaches 1.5 T at a temperature of $900 \text{ }^\circ\text{C}$. The coercivity dependence on the annealing time and annealing temperature

can be understood in terms of the phase transition from the disordered phase to the ordered phase. For short annealing times and lower temperatures the phase formation is far from complete, accounting for the small coercivities, associated with the disordered cubic FePt phase. As the annealing time and temperature are increased, the phase formation approaches completion and the coercivity reaches a maximum value 1.5 T at 900 °C. The magnetization in 5 T of films annealed at 800 °C is 1.05 T which agrees with values reported in the literature for polycrystalline films [17,21, 22].

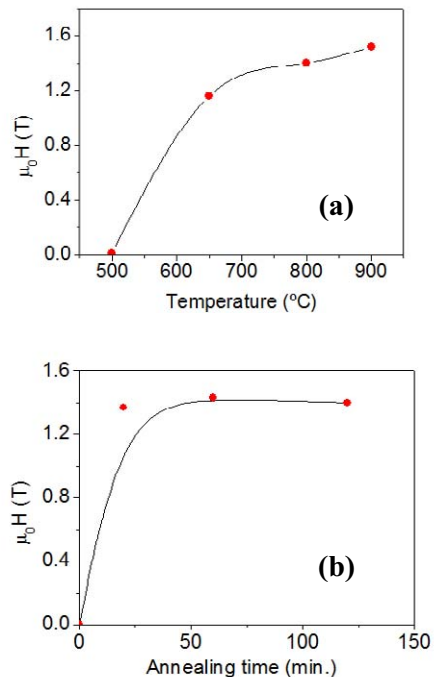


Figure 4. Coercivity dependence of nearly equiatomic 0.45 μm thick FePt films on the (a) temperature for 120 min and (b) annealing time at 800 °C in H_2 atmosphere.

4. Conclusion

We have prepared and characterized electrodeposited L1_0 FePt films. As-deposited films are magnetically isotropic, nanocrystalline and soft. The L1_0 tetragonal phase was achieved after annealing in forming gas at temperature above 500 °C. Both annealing temperature and annealing time favour the formation of the L1_0 tetragonal phase. Equiatomic FePt films show coercivities of 1.5 T after annealing at 900 °C for an annealing period of two hours. The use of Ag contributes to the formation of the L1_0 phase as it acts an inert substrate, which does not form any alloy with Pt nor Fe, thereby does not interfere with the composition of the FePt alloys. Initial magnetization curves indicate that the magnetically isotropic FePt films can be fairly easily magnetized to give a magnetization of about half the saturation value. The FePt may find application in MEMS devices especially if the annealing temperature can be reduced to a value that is compatible with CMOS circuitry.

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