

Electrodeposited FePt Films

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Abstract—A novel bath for electrodepositing FePt films was developed and films were electrodeposited on copper substrates with thickness up to 0.45 μm . The magnetic and structural properties of the films were measured. The films developed 0.3-T coercivity after annealing at 400 °C and formed the $L1_0$ FePt phase. Films are shiny and smooth. Morphology was found to be affected by the annealing process.

Index Terms—Electrodeposition, films, $L1_0$ FePt, magnetization.

I. INTRODUCTION

THE face-centered tetragonal FePt phase, known as the $L1_0$ phase, is of interest for permanent magnet applications due to its excellent intrinsic magnetic properties ($\mu_0 M_s = 1.43$ T, $K_1 = 6.6$ MJ/m³) and corrosion resistance [1]. Numerous studies have been carried out to develop hard magnet films of this material due to potential application in high-density recording media and microelectromechanical (MEMS) systems [2]. Most of these studies have used sputtering, vapor deposition, or laser ablation. Thin-film samples typically show coercivities between 1–2 T [3]–[8] while bulk samples typically show coercivity values of 0.5 T [9]. Only recently, Huang *et al.* have electrodeposited nanowires of FePt in a porous anodized aluminum disk from a single bath [10] in despite of the remarkable progress on electrodeposited CoPt films [11]–[13]. Here, we present the first report in the literature of the preparation of continuous FePt films by electrodeposition from a novel bath and we also present their structural and magnetic characterization.

II. EXPERIMENTAL DETAILS

FePt films were electrodeposited on polycrystalline Cu substrates from a single bath containing 1 mmol/l H_2PtCl_6 , 0.1 mol/l Na_2SO_4 and 0.1 mol/l FeSO_4 . 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 factory calibration of 205 ± 5 mV. All potentials are quoted with respect to this reference electrode. Solutions were prepared from 100 ml deionized water. Cu substrates were used as working electrodes and cut out from 99.9% pure copper foil 0.5 mm thick into 5×5 mm squares. These substrates were coated on one

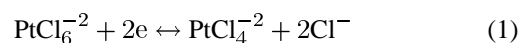
side with varnish and connected to a 1-mm copper wire. Just before electrodeposition, the substrates were dipped into a 10% H_2SO_4 solution to remove any oxide layers and then dipped into deionized water. Fresh solutions were vigorously stirred in open atmosphere at room temperature and the deposition took place immediately after inserting the substrate into the bath. The deposition was controlled using an EG&G model 263A potentiostat.

Composition of the samples was determined by energy dispersive X-ray spectroscopy (EDX) and morphology was examined using a scanning electron microscopy (SEM). The crystalline structure was investigated by X-ray diffraction (XRD) with Cu K_α radiation and a 0.02° step. Magnetic properties were measured in a 5-T superconducting quantum interference device (SQUID) magnetometer and the thickness was evaluated in an atomic force microscopy (AFM) in the contact mode.

Films were deposited with thickness of about 0.45 μm . As-deposited films were amorphous and therefore subjected to annealing at temperatures between 400 and 700 °C under vacuum of 10^{-6} torr. The annealing process consists of heating up a furnace to the desired temperature, inserting the sample into the furnace at a temperature for the annealing time, then removing the sample and leaving it to cool down to room temperature, all under vacuum.

III. RESULTS AND DISCUSSION

Platinum is electrodeposited from a complex ion PtCl_6^{-2} in two consecutive steps on the working electrode



The standard reduction potentials for the reactions (1) and (2) are 0.52 and 0.54 V quoted relative to Ag–AgCl reference electrode [14]. As Pt is more noble than copper, we observed that the deposition of Pt takes place even without applying a potential to the electrochemical cell. The standard potential for Fe^{+2} reduction is -0.669 V. In this case, we have selected the concentration of Fe^{+2} (0.1 mol/l FeSO_4) in order to have Fe deposition governed mainly by reaction kinetics and the concentration of PtCl_6^{-2} (1 mmol/l $\text{H}_2\text{PtCl}_6^{-2}$) in order to have Pt deposition in the mass transport regime. By measuring the thickness of the film in an AFM and taking account of the integrated charge, we estimated the current efficiency. Values of about 5% at -0.7 V and 23% at -1.1 V were found.

Pt content in the films was found to vary almost linearly around -0.9 V as shown in Fig. 1. Films were shiny and homogeneous. EDX analysis showed distinct and very low intensity Cl peaks (<1 at.%) which comes from PtCl_6^{-2} complex ion. After the reduction of this complex ion the concentration

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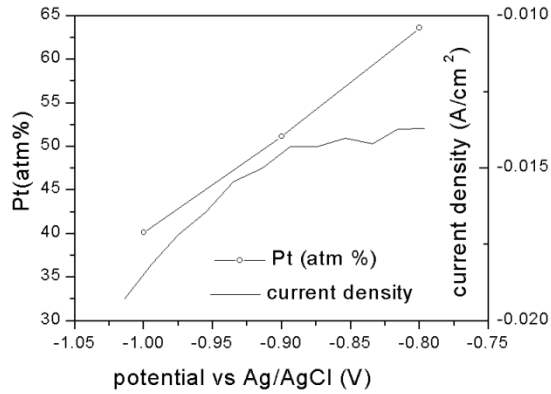


Fig. 1. Pt content as a function of the overpotential and current density applied to the electrochemistry cell.

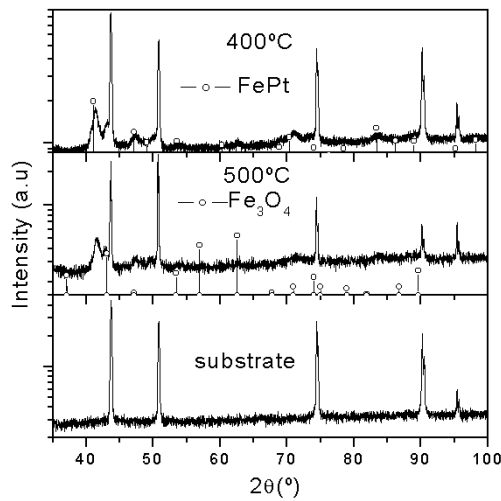


Fig. 2. XRD of FePt films annealed at 400 °C, 500 °C, and Cu substrate. Films electrodeposited at -0.9 V.

of Cl^- increases on the surface of the working electrode; therefore, some of these ions are likely to be trapped by the depositing material.

Films electrodeposited at -0.9 V with a total charge of 2.4 C showed a thickness value of $0.45 \mu\text{m}$ when plated over an area of 0.25 cm^2 . This gives a rate of $0.75 \mu\text{m C}^{-1} \text{ cm}^{-2}$ that was verified between 0.6 to 2.4 C.

The diffraction pattern of as-deposited films at -0.9 V showed only a broad amorphous hump. Films subjected to annealing developed a combination of ordered $L1_0$ FePt phase and a minor amount of Fe_3O_4 as shown in Fig. 2. The optimized annealing time that leads to greater amounts of $L1_0$ FePt in the annealed samples at 400 °C is 20 min, and at 500 °C it is 10 min. Samples subjected to long annealing (60 min.) showed severe cracking that partially or totally peeled the film off the substrate. Fig. 3 shows the initial development of cracking in samples annealed at 400 °C for 20 min. It is likely that these cracks are due to internal stress in the films which may come from gases absorbed during the deposition such as H_2 and O_2 .

Magnetic measurements are shown in Fig. 4. The samples annealed at 500 °C exhibit coercivity of 0.2 T and the shape

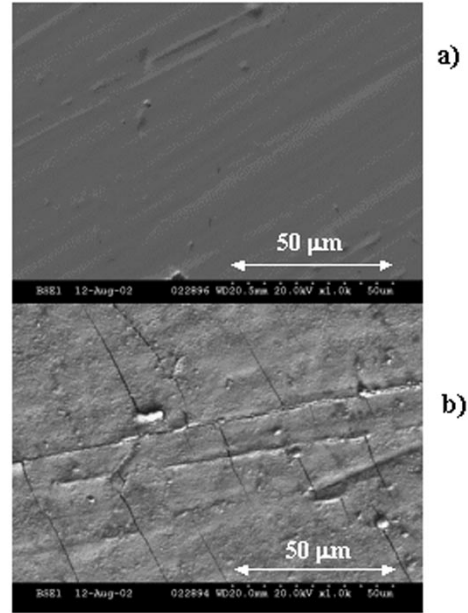


Fig. 3. SEM of sample (a) before and (b) after annealing at 400 °C for 20 min.

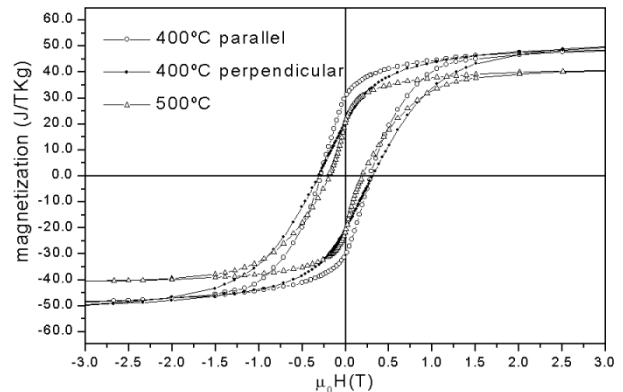


Fig. 4. Room temperature hysteresis loops of FePt films annealed 400 °C and 500 °C.

of the magnetization curve suggests the presence of two-coupled phases where the major presence of the lower coercivity phase tends to reduce the coercivity when compared to samples annealed at 400 °C which show a higher coercivity (0.3 T) and better loop shape. Coercivity values in the present study are smaller than reported for FePt thin films (1–2 T) [3]–[8] and close to both values of FePt bulk (0.5 T) [9] and electrodeposited CoPt thin films (0.5 T) [11]. Saturation magnetization 50 J/Tkg ($\mu_0 M_s = 0.95 \text{ T}$) is in agreement with reported values for bulk samples produced by cold deformation [15]. The remanence ratio σ_r/σ_s calculated for this sample is 0.65, suggesting the existence of intergrain exchange interaction among the fine grains. The samples are magnetically isotropic.

IV. CONCLUSION

We have presented the first report of continuous electrodeposited FePt film. The $L1_0$ FePt phase was developed after annealing at 400 °C, resulting in 0.3-T coercivity. This

method using a novel bath, when compared to vapor deposition methods, opens an alternative route for the production of FePt films that may be useful for MEMS applications.

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