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INFLUENCE OF PHOSPHOROUS AND UREA ON THE MAGNETIC AND MECHANICAL PROPERTIES OF NANOSTRUCTURED FEPTP FILMS

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Abstract: The properties of hard magnetic FePtP films electrodeposited in the presence of urea as additive and phosphorous acid as a precursor with varying concentrations were studied with respect to thickness of the films. Films were electrodeposited in various current densities in order to get different thickness and uniform deposits. Elemental composition of the films was obtained using energy dispersive X-ray spectroscopy. Vibrating sample magnetometric studies indicate that additives have favourable impact on the magnetic properties of these films. Structural and surface analysis was carried out using X-ray diffractometry and scanning electron microscopy, respectively. Reasons for variation in magnetic properties and structural characteristics are discussed. Hardness and adhesion of the films were also studied.

Keywords: Electrodeposition; FePtP; hard magnetic films; additives; magnetic properties

1. Introduction

Electrodeposition of hard magnetic films attracts increasing interest for application as micromagnets in microelectromechanical systems or in the field of high density magnetic data storage. The advantages of electrodeposition over physical deposition methods are numerous: no need of vacuum equipment, easier handling, higher deposition rates, which all yields a cheaper and more efficient deposition.

With the progress in the field of Micro ElectroMechanical System (MEMS) technologies [1-4] there has been growing interest in developing electroplated, nanostructured soft and hard magnetic materials [5,6] for microactuators, micromotors and microswitches. The possibilities of these electroplated materials, retaining hard and soft magnetic properties up to several microns thickness, gives researches opportunity to explore them for micro fabrication of MEMS devices. Recently, much effort is being made to electrodeposit also materials of the group of L10 ordered alloys, like FePt [7,8] and CoPt [9,10], because they exhibit a significantly higher uniaxial magnetocrystalline anisotropy. As the formation of the L10 phase is kinetically hindered at room temperature, post-annealing of the films is necessary. Electrodeposited and post-annealed FePt and CoPt films can reach coercivities exceeding 1T [9,10].

In the present study we investigated in detail the effects of electrodeposition conditions on the magnetic properties of FePtP films. The influence of concentration of urea and phosphorous source material in the bath was investigated. Also we discussed their structural and magnetic characterization.

2. Experimental details

FePtP films were electrodeposited on polycrystalline Cu substrate from a single bath containing : H_2PtCl_6 : 0.02 M, $(NH_4)_2$ SO_4 : 0.1 M, $FeSO_4$: 0.2 M. Hereafter the above bath composition will be referred to as bath A. Then 0.2M and 0.4M of phosphorous acid (H_3PO_3) and 2.5 and 5.0 gl^{-1} of organic additive like urea were added in this bath and their effect on the properties of FePtP films were investigated. The solution pH was adjusted to 3 by adding a small amount of either sulfuric acid or hydrochloric acid. Films are deposited using dc plating in the current densities varying from 2-6 mA cm^{-2} at 60 minutes.

The thickness of the deposits was tested using digital micrometer (Mitutoyo, Japan). Magnetic properties of deposited films were studied using vibrating sample magnetometry. In this technique the material under study was contained in a sample holder, which was centered in the region between the pole pieces of a laboratory magnet. A slender vertical sample rod connects the sample holder with a transducer assembly. The transducer converts a sinusoidal alternating current drive signal into a sinusoidal vertical vibration of the sample rod. Coils mounted on the pole pieces of the magnet pick up the signal resulting from the sample motion. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were used to study the structure and morphology of these magnetic films, respectively. From XRD data crystallite size of the deposited FePtP and film stress were calculated. Percentage of elements such as Fe, Pt and P present in the deposits were obtained as follows. For elemental analysis FePtP film was electrodeposited on stainless steel substrate to ensure easier peeling off of the film. After deposition the film was peeled of from the substrate. It was dissolved in 3:1 v/v of H_2SO_4 and HNO_3 and the percentage composition was obtained using energy dispersive X-ray spectroscopy (EDS). Hardness of the deposit was obtained using Vicker's hardness tester using diamond intender method. Adhesion of the film was tested by bend and by scratch test. These tests are widely used in the field of electroplating [11].

3. Results and Discussion

3.1. Thickness and Magnetic properties

Table 1 shows the effect of concentration of H_3PO_3, urea and current density on the thickness and magnetic properties of FePtP films obtained under different experimental conditions. The thickness of the film increased with increase in current density. The concentration of H_3PO_3 or urea did not have much effect on thickness. However, the magnetic properties of the film were found to increase with the current density. The morphology of the film was found to be poor when no urea was added in the electrodeposition bath.

The effect of addition of urea into the bath-A along with H_3PO_3 was investigated. With the addition of low concentration of urea the deposit characteristics as well as its magnetic properties

improved significantly. Under the best conditions involving addition of 0.2 M of H_3PO_3 and 2.5 g l^{-1} of urea at a current density of 6.0 mA cm^{-2} and time of deposition 60 minutes, the thickness of the film was found to be 6.2 μm with coercive and remanent values of 3000 Oe and 0.25 Am^2 [experiment.number:6] respectively. The high coercivity obtained in FePt after annealing [12] is obtained in this case without annealing. With further increase in H_3PO_3 concentration the thickness of the films found to be 5.8 μm with coercive and remanent values of 1000 Oe and 0.12 Am^2 [18].

Table 1. Effect of H_3PO_3 and Urea on the thickness and magnetic properties of FePtP films electrodeposited from bath-A.

Bath Additive		Current density (mA/cm^2)	Thickness of deposit (μm)	Magnetic saturation (Am^2)	Remanent (Am^2)	Coercivity (Oe)	Squareness	Experiment number
H_3PO_3 (M)	Urea (gl^{-1})							
0.2	0	2	4.2	.78	.05	600	.07	1
		4	5	.71	.11	850	.10	2
		6	5.8	.64	.16	1000	.17	3
	2.5	2	4.7	.88	.14	1200	.18	4
		4	5.6	.83	.20	1900	.25	5
		6	6.2	.8	.25	3000	.27	6
	5	2	5.1	.89	.15	900	.17	7
		4	5.7	.84	.17	1330	.22	8
		6	6.3	.81	.21	1650	.26	9
0.4	0	2	4.1	.80	.04	500	.06	10
		4	4.9	.75	.09	650	.17	11
		6	5.9	.72	.13	850	.11	12
	2.5	2	4.5	.94	.11	800	.13	13
		4	5	.92	.13	980	.19	14
		6	6.4	.87	.15	1300	.23	15
	5	2	4.8	.98	.09	650	.10	16
		4	5.3	.95	.10	770	.14	17
		6	5.8	.91	.12	1000	.18	18

Increase in magnetic properties of the films is mainly due to urea. The electrodeposited films were uniform and bright. The urea molecules thus are found to have leveling effect, which ensures uniform orientation of crystals during electrodeposition. With increasing the concentration of H_3PO_3 and urea magnetic properties of the films decreased. This was because of the stress present in the films, which was caused by the inclusion of decomposed products of additives.

3.2. Structural analysis

Electrodeposited FePtP films were subjected to XRD studies. The X-ray wavelength used was 1.5405 Å of Cu K_α radiation. Films obtained from experiment number 3,6,9,12,15 and 18 of Table 1 were studied for their structural characteristics. These data were compared with Joint committee for powder diffraction_studies data. FePtP films had faced centered tetragonal structure and exhibited (111) plane primarily. (111) plane peaks in the data for films obtained from experiment number 9 and 18 were shifted because of the film stress. It was known that film stress will shift XRD peaks [13]. Stress of the films were calculated from XRD data using the formula, i.e., Youngs modulus = stress / strain. The results are shown in Table 2. Stress was low for film obtained from a bath contained 2.5 g l^{-1} of urea. It increased with increasing the concentration of urea to 5.0 g l^{-1}. This was due to the incorporation of decomposed products of additive into the film. Crystallite sizes were also low for films obtained from 2.5 g l^{-1} urea. These were calculated from XRD data using the formula i.e., crystallite size equal $0.9\lambda/\beta\cos\theta$ (Scherrer equation), where λ is the wavelength of X-ray radiation, β is the peak full-width at half-height and θ is the diffraction angle. Crystallite sizes thus obtained were in the nano scale and it was shown in Table.2.

Electrodeposited FePtP films obtained from experiment number 3,6,9,12,15 and 18 of Table 1 were subjected to SEM. The micrographs are presented in Fig.1. In general microstructure of the FePtP was affected by the percentage of phosphorus content. The film with very low concentration of phosphorus, Fig. 2b and e appeared to have a crevice pattern. The film obtained from a bath contained 5.0 g l^{-1} was cracked through substrate due to stress of the film as shown in Fig. 1c and f. It was also observed in Table 2 that film obtained from bath contained 5.0 g l^{-1} of urea had high stress.

Table 2: Effect of H3PO3 and Urea on the structural and mechanical properties of FePtP film electrodeposited from bath-A.

H_3PO_3 (M)	Urea (gl^{-1})	Crystalline Size(nm)	Stress (MPa)	Vickers Hardness (VHN)	Film composition(mass%) Fe	Pt	P
0.2	0	35	148	380	54.5	29.5	16
	2.5	28	133	391	56.8	33.1	10.1
	5	31	140	360	55.1	31.6	13.3
0.4	0	39	157	358	55.5	26.6	17.9
	2.5	30	148	370	57.4	30.1	12.5
	5	34	153	350	56.6	28	15.4

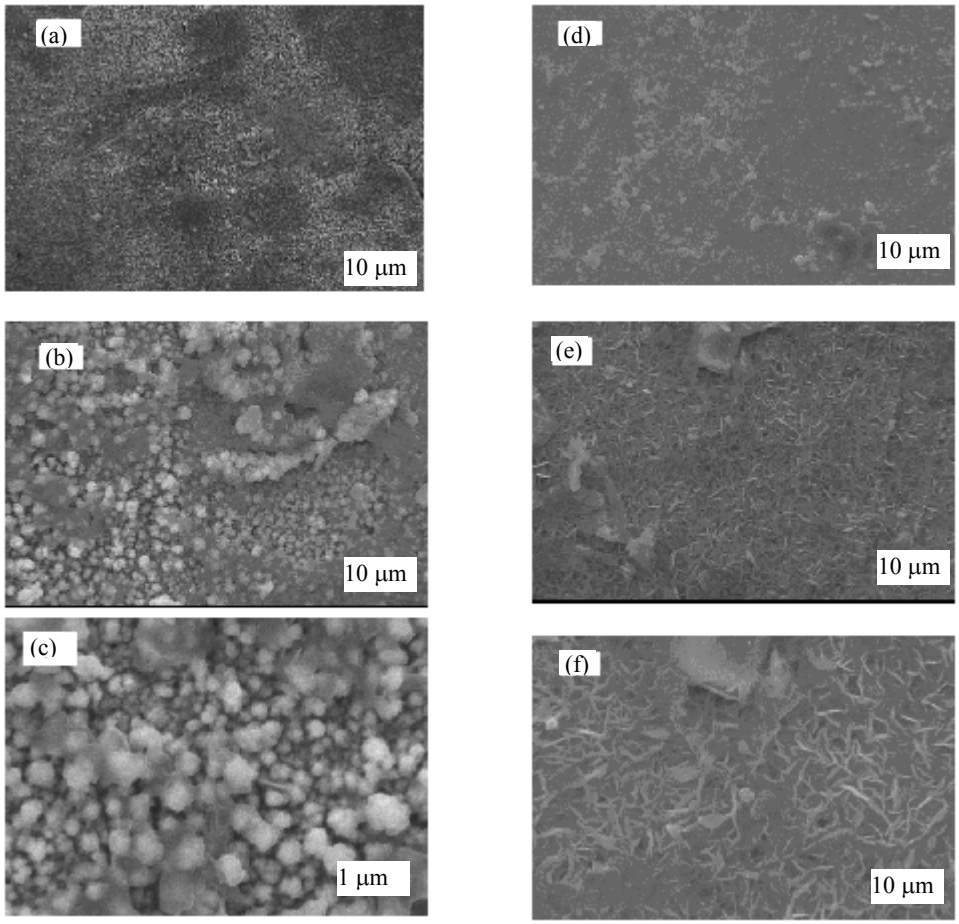

Fig. 1. SEM images of FePtP films from bath A with (a) H_3PO_3: 0.2M, urea: 0 gl^{-1}, (b) H_3PO_3: 0.2M, urea: 2.5 gl^{-1}, (c) H_3PO_3: 0.2M, urea: 5.0 gl^{-1} (d) H_3PO_3: 0.4M, urea: 0 gl^{-1} , (e) H_3PO_3: 0.4M, urea: 2.5 gl^{-1}, (f) H_3PO_3: 0.4M, urea: 5.0 gl^{-1}.

3.3. Mechanical properties

FePtP films, which were selected for XRD and SEM studies, were tested for their Vicker's hardness number. The results are reported in Table 2. Higher concentration of urea in the bath decreased the hardness of the film. It was due to the stress present in the film, which caused cracks in the structure. Adhesion of the film with the substrate was found to be good.

3.4. Elemental analysis

Table 2 presents the results of EDS. It was observed that all the films obtained from various baths had less than 18 % phosphorous. Even with low phosphorous content the films showed high magnetic properties. This was due to the addition of urea in the bath, which improved the crystalline structure of FePtP films.

4. Conclusions

A FePtP film with high hard magnetic properties can be obtained by galvanostatic electrodeposition process. The bath required for electrodeposition contained H_2PtCl_6 : 0.02M,

$(NH_4)_2\ SO_4$: 0.1 M , $FeSO_4$: 0.2M, H_3PO_3 : 0.2 M and urea : 2.5 g l^{-1}. The current density for the deposition was 2.0–6.0 mA cm^{-2}. Addition of urea increased the coercive value of the film. The high coercive value obtained in this work was 2900 Oe. This is because the urea molecules are found to have leveling effect, which ensures uniform orientation of crystals during electrodeposition. 5.0 g l^{-1} of urea was found to be the optimum concentration in the bath in order to obtain a FePtP film with improved magnetic, structural and mechanical properties.

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