Effect of bath temperature on the magnetic and mechanical properties of nanostructured FePtP hard magnetic films

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In this study we have fabricated FePtP films by electrodeposition technique. High quality of deposit with low cost is the advantage of this technique. Magnetic thin films are extensively used in various electronic devices including high density recording media and Micro Electro Mechanical System (MEMS) devices. The surface morphology, crystalline structure, grain size and magnetic properties of the plated films prepared at various current densities, bath temperature and concentration of phosphorous source material (NaH_2PO_2) have been compared. This results shows that the structural & magnetic properties of this thin film depends on the phosphorus content in the film. But the phosphorus content depends on bath temperature and concentration of phosphorous source material (NaH_2PO_2) . When the bath temperature increases the phosphorus content decreases and hence coercivity increases. Also coercivity increases after annealing. Reasons for variation in magnetic properties and structural characteristics were discussed.

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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 [1-5] there has been growing interest in developing electroplated, nanostructured soft and hard magnetic materials[6,7] for microactuators, micromotors and microswitches . The possibilities of these electroplated materials, retaining hard and soft magnetic properties up to several microns thickness, give researcher opportunity to explore them for micro fabrication of MEMS devices. Recently, much effort is being made to electrodeposit materials of the group of L10 ordered alloys, like FePt [8,9] and CoPt [9,10] because they exhibit a significantly higher uniaxial magneto crystalline 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[11}. Various FePt and CoPt based ternary alloys have been considered for meeting the challenges of improved corrosion resistance and lower stress with superior hard magnetic properties.

In the present study we investigated in detail the effects phosphorus on electrodeposited magnetic FePtP films at various bath temperature and current density. Also we discussed their structural and magnetic characterization.

2. Experimental details

A copper substrate of size 1.5 x 5.0 cm as cathode and stainless steel of same size as anode were used for galvanostatic electrodeposition experiments. Current for electrodeposition was passed from a regulated direct current unit. Analytical reagent grade chemicals were used to prepare baths. An adhesive tape was used to mask off all the substrate except the area on which deposition of film was desired. Each substrate was buffed for removing scratches in a mechanical polishing wheel using a buffing cloth coated with aluminium oxide abrasive. Buffed substrates were degreased using acetone. Before electrodeposition these substrates were electrocleaned in an alkaline electrocleaning bath. The bath contained sodium hydroxide: 7.0 g/l; sodium carbonate: 20.0g/l; trisodium phosphate:9.0g/l and sodium metasilicate: 24.0g/l. The bath was operated at 70^0 C and current density applied was 3.0 A/dm^2 . After electrocleaning the substrates were rinsed in distilled water. Electrodeposition was carried out on the cleaned substrates using different temperature, current density and time of deposition.

FePtP films were electrodeposited on polycrystalline Cu substrate from a single bath containing: H_2PtCl_6 :0.02M, $(NH_4)_2SO_4$: 0.1 M , $FeSO_4$: 0.2M, NaH_2PO_2 : 0.2M and 0.4M The solution pH was adjusted to 3 by adding a small amount hydrochloric acid. Electro-deposition was carried out with varying current densities bath temperature and concentration of NaH_2PO_2.

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. The integral film composition was measured by energy dispersive X-ray spectroscopy(EDX), the EDX detector(EDAX system method. Adhesion of the film was tested by bend test (bending the film with substrate to 180^0) and by scratch test (draw equal lines by pin and paste an adhesive tape over the scratch and pull it. If the film comes with tape then adhesion is poor). These tests are widely used in the field of electroplating [Murphy and Frost (2006)]

3. Results and discussion

3.1 Surface analysis

3.1.1 Morphological observation

Microstructures of electrodeposited FePtP films obtained from various bath temperatures like 30^0C, 50^0C and 70^0C and various concentrations of NaH_2PO_2 were examined using scanning electron microscope. The backscattered electron image revealed a finely granular structure of FePtP electrodeposits as shown in Fig. 1. Examination of the micrographs indicated that initially, the deposit obtained from 0.2 M NaH_2PO_2 with high bath temperature crystallites are smaller and granular. The uniform grains through out the entire region have been noticed with a perfect crystal structure. But the deposit obtained from 0.4 M NaH_2PO_2 crystallites are bigger and low granular

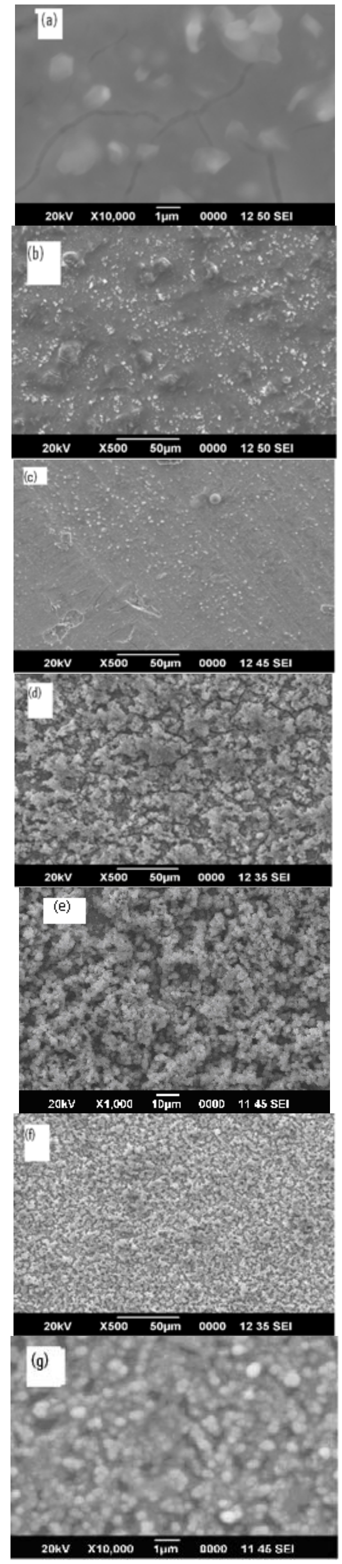


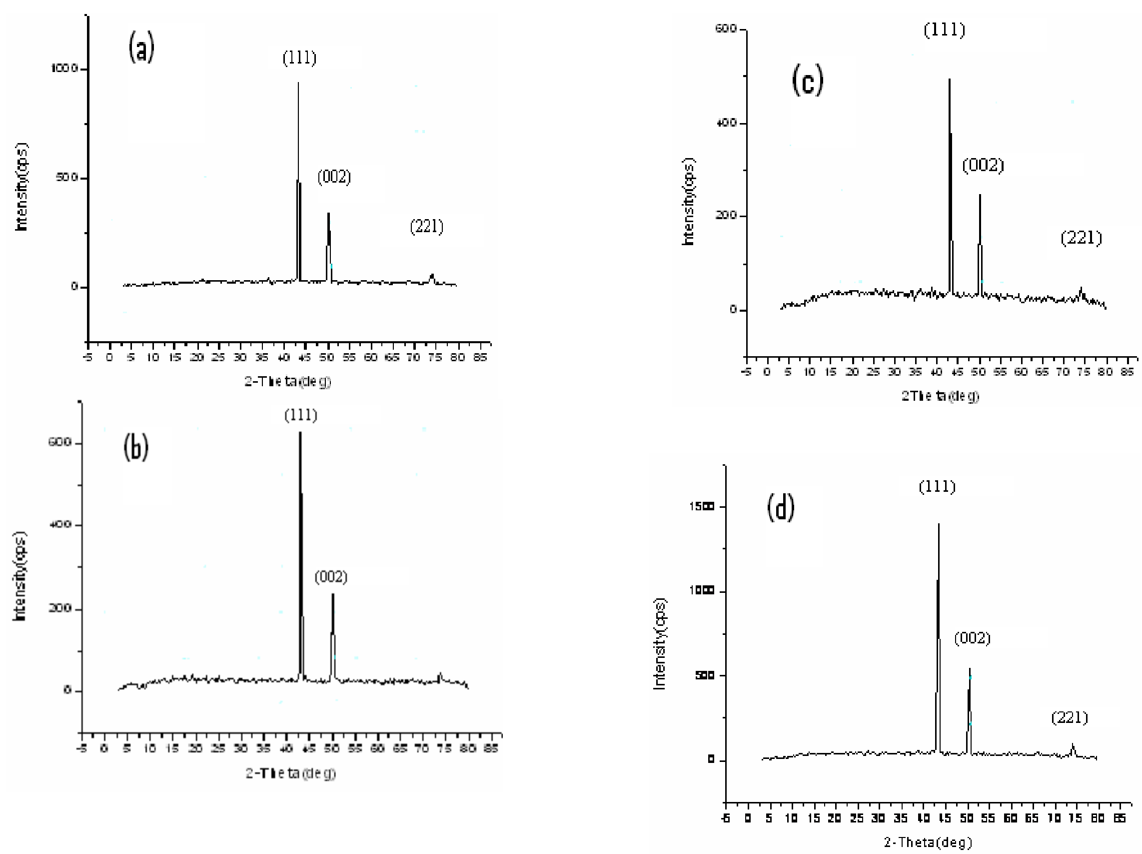
Fig. 1. SEM images of FePtP films electrodeposited for 60 min at the current density 6 mA/cm^2 and bath temperatures (a)30^0c, (b)50^0c , (c)70^0c with NaH_2PO_2 (0.2mol/L) and (d) 30^0c, (e)50^0c , (f)70^0c with NaH_2PO_2 (0.4mol/L) , (g) sample (b) annealed at 155^0C in vacuum for 30 min.

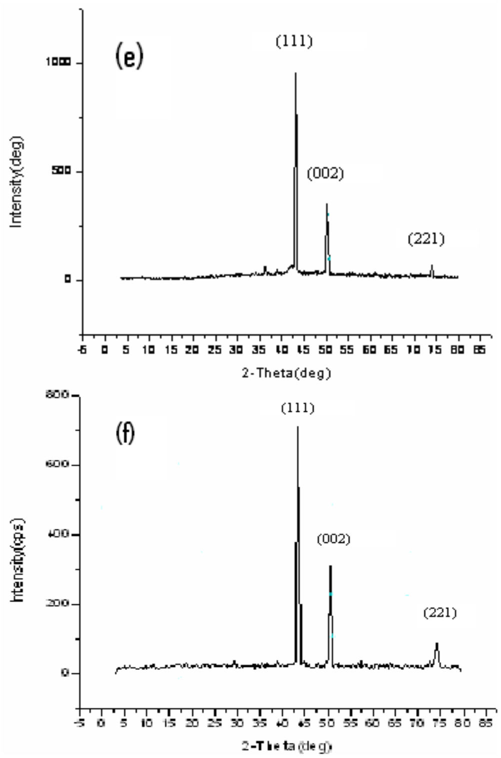
3. 1. 2 Structural analysis

Electrodeposited FePtP films were subjected to XRD studies. The X-ray wavelength used was 1.5406 A^0 of Cu Kα radiation. Films obtained from various bath temperatures like 30^0C, 50^0C and 70^0C and various concentrations of NaH_2PO_2 were studied for their structural characteristics as shown in Fig 2. FePt films had face centered tetragonal structure and exhibited (111) plane predominantly. The (111) plane peak is shifted in all XRD patterns because of phosphorous . In the presence of phosphorous few low intensity peaks like (002) and (221) were also observed because of the formation intermetallic FePtP compound(fct) during electrodeposition.Stress of the films were calculated from XRD pattern using the formula: Youngs modulas= stress/strain and presented in Table 1. FePtP film prepared from low concentration of NaH_2PO_2 and high bath temperature acts as a grain refiner and stress reliver. But on increasing concentration of NaH_2PO_2 stress is also increased.

Table 1. Effect of temperature on the structural and mechanical properties of FePtPfilm electrodeposited at 6 mA cm^{-2} for 30 minutes.

NaH_2PO_2 (M)	Bath temperature ^{0}C	Crystalline size (nm)	Stress (M Pa)	Vickers hardness (VHN)
0.2	30	39	168	320
	50	35	152	341
	70	29	140	369
0.4	30	43	179	312
	50	38	163	335
	70	33	151	348





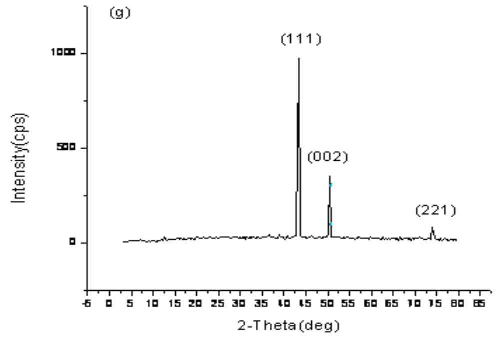


Fig. 2. XRD patterns of FePtP films electrodeposited for 60 min at the current density 6 mA/cm^2 and bath temperatures (a)30^{0}c, (b)50^{0}c, (c)70^{0}c with NaH_2PO_2 (0.2mol/L) and (d) 30^{0}c, (e)50^{0}c, (f)70^{0}c with NaH_2PO_2 (0.4mol/L), (g) sample (b) annealed at 155^{0}C in vacuum for 30 min.

Table 2. Effect of NaH_2PO_2 and bath temperature on the structural and mechanical properties of FePtP film electrodeposited at 6mA cm^{-2} after annealing at 155^{0}C for 30 minutes.

NaH_2PO_2 (M)	Bath temperature ^{0}C	Crystalline size (nm)	Stress (M Pa)	Vickers hardness (VHN)
0.2	30	34	150	333
	50	29	137	355
	70	24	124	380
0.4	30	39	160	321
	50	32	149	345
	70	29	140	360

Crystallite sizes of the deposited film swere calculated from XRD pattern using the formula i.e., crystalline size= 0.9λ/βcosθ .These values clearly show that the crystallite size of the FePtP deposit by electro-deposition process are in nano scale. The crystallite size of the deposits are given in Table 1. This analysis reveals the effect of phosphorous on the crystallite size of the deposit. The stress and crystallite size of the FePtP films decreases after annealing the samples at 155^{0}C for 30 minutes in vacuum. It is given in Table 2.

3.2 Mechanical properties

Adhesion of the film with the substrate is tested by bend test and scratch test. It showed that the film is having good adhesion with the substrate. Hardness of these films was examined using a Vicker's hardness tester by the diamond intender method. The results are reported in Table 1. The results shows that hardness increases with increasing bath temperature. This may be due to lower stress associated with FePtP film. Hardness of the film decreases when concentration of increases because of high stress.

3.3 Elemental analysis

Elements present in the film were analyzed by energy dispersive X-ray spectroscopy (EDX) and the results showed that the films obtained from high temperatures have low phosphorus content and their magnetic properties are high.

3.4 Magnetic properties

Magnetic properties of electrodeposited films were studied using Vibration Sample Magnetometer. Magnetic properties are strongly dependent on bath temperature and annealing. The coercivity of electrodeposited FePtP films increased with increase in bath temperature. Table 3 presents the results of electrodeposition of FePtP and their magnetic properties. The bath used for deposition was solution with NaH_2PO_2: 0.2 M. From the results it was observed that on increasing the current density and bath temperature coercivity and remanent values are increasing, whereas magnetic saturation values were decreasing. Also coercivity increases after annealing.

Electrodeposition were carried out from an electrolyte with 0.4 M NaH_2PO_2. The deposited samples were subjected to thickness and magnetic studies. The results are presented in Table 4.

Table 3. Effect of NaH_2PO_2 (0.2M), current density and bath temperature on magnetic properties of electrodeposited FePtP films.

Current density (mA/cm^2)	Temperature ^0C	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)
2	30	.89	.04	350
	50	.85	.05	470
	70	.8	.07	600
4	30	.81	.06	500
	50	.76	.08	700
	70	.72	.11	900
6	30	.75	0.08	700
	50	.71	0.12	950
	70	.65	0.19	12500

The deposits had low remanent and coercive values, which were very low compared to the values obtained for 0.2 M NaH_2PO_2. This is because of the higher phosphorus content in the deposit, which affects the magnetic properties of the deposit. Also coercivity increases after annealing the samples at 155^{0}C for 30 minutes in vacuum and is given in Table 5. From these results it was found that, the magnetic saturation decreases when coercivity and remanent increases. The above phenomenon confirms that the FePtP deposits are of hard magnetic nature. Also these films have good adhesion with the substrate and their crystalline sizes are in nano scale.

Table 4. Effect of NaH_2PO_2 (0.4M), current density and bath temperature on the magnetic properties of electrodeposited FePtP films

Current density (mA/cm^2)	Temperature ^0C	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)
2	30	.92	.03	300
	50	.87	.04	440
	70	.82	.05	540
4	30	.87	.05	470
	50	.81	.06	600
	70	.75	.09	800
6	30	0.82	0.06	600
	50	0.77	0.09	780
	70	0.72	0.15	1050

Table 5. Effect annealing of on the magnetic properties of electrodeposited film at the current density 6 mA/cm^2 .

Current density (mA/cm^2)	Temperature ^0C	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)
0.2	30	.71	0.14	1200
	50	.68	0.17	1650
	70	.62	0.21	2300
0.4	30	0.72	0.13	1100
	50	0.69	0.16	1520
	70	0.65	0.19	2010

4. Conclusions

FePtP film having good hard magnetic properties can be electrodeposited from a bath containing the following composition: H_2PtCl_6 :0.02M, $(NH_4)_2SO_4$: 0.1 M , $FeSO_4$: 0.2M, NaH_2PO_2 : 0.2M at the current density 6 mA cm^{-2} . Increase in the concentration of phosphorous will decrease the hard magnetic properties. This method using a novel bath when compared to vapor deposition methods, opens an alternative route for the production of FePtP films that may be useful for MEMS applications . In the low temperature bath the film character is changed i.e it showed soft magnetic character because of high concentration of phosphorus. It also increases the film stress, which is a cause for cracked film. The high temperature bath films have lowe stress and high coercivity which are used in MEMS devices. Hardness of the film also increases in higher bath temperature films. After annealing the samples at 155^0C for 30 minutes in vacuum coercivity increases.

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