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SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE FePtP FILMS

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In this work we have synthesized FePtP films using sodium hypophosphite as source material for phosphorous. 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. The results shows that the structural & magnetic properties of this thin film depends on the phosphorus content in the film. When the bath temperature increases the phosphorus content decreases & 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

In recent years, the well-known hard magnetic material FePt has received a lot of attention due to its high magneto-crystalline anisotropy. Potential application areas of FePt include high density magnetic storage and their use as micromagnets in micro-electromechanical systems (MEMS) [1-5]. 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 electrodeposits also materials of the group of L10 ordered alloys, like FePt[8,9] and CoPt[10,11], 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

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.

The thickness of the deposits was tested using digital micrometer (Mitutoyo, Japan). Magnetic properties of deposited films were studied using vibrating sample magnetometry. 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 film and its stress were calculated. The integral film composition was measured by energy dispersive X-ray spectroscopy(EDAX). Hardness of the deposit was obtained using Vicker's hardness tester using diamond intender 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 Magnetic properties

Magnetic properties of electrodeposited films were studied using Vibration Sample Magnetometer. Magnetic properties are strongly dependent on bath temperature. The coercivity of electrodeposited FePtP films increased with increase in bath temperature. 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 1. 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. The above phenomenon confirms that the FePtP deposits are of hard magnetic nature. The coercivity increases after annealing the samples at 155^0C in vacuum for 30 minutes and is shown in Table 2.

Table 1: Magnetic properties of FePtP films

NaH_2PO_2 (M)	Temperature ^0c	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)
0.2	30 50 70	.75 .71 .65	0.08 0.12 0.19	700 950 1550
0.4	30 50 70	0.82 0.77 0.72	0.06 0.09 0.15	600 780 1050

Table 2. Magnetic properties of FePtP films after annealing at 155^{0}C

NaH_2PO_2 (M)	Temperature ^{0}c	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)
0.2	30 50 70	0.71 0.68 0.62	0.14 0.17 0.21	1200 1650 2400
0.4	30 50 70	0.72 0.69 0.65	0.13 0.16 0.19	1100 1520 2010

3.2 Surface analysis

3.2.1. Morphological observation

Microstructures of electrodeposited FePtP films obtained from various bath temperatures like 30^{0}C, 50^{0}C and 70^{0}C 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.

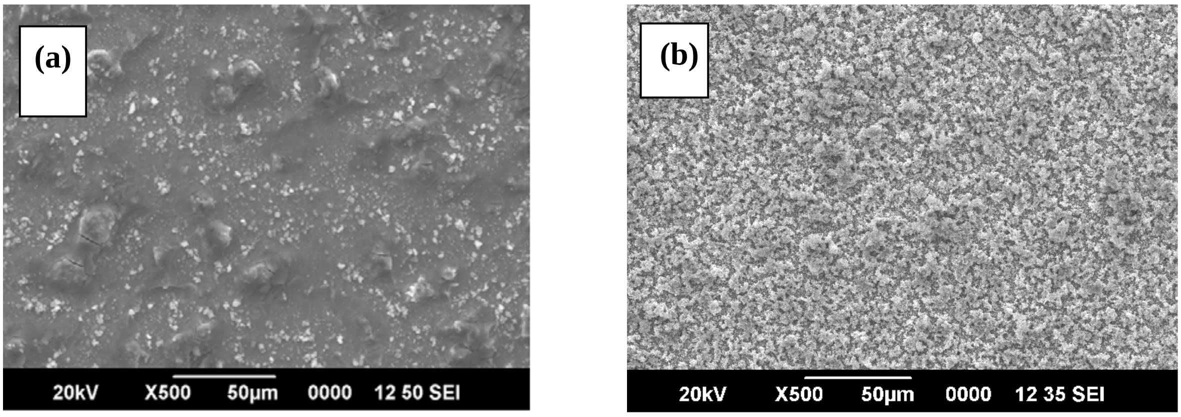

Fig. 1. Microstructures of FePtP films at (a) NaH_2PO_2 : 0.2 M and (b) NaH_2PO_2 0.4 M

3.2.2 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^{0}C, 50^{0}C and 70^{0}C and various concentrations of NaH_2PO_2 were studied for their structural characteristics as shown in Fig 3. FePtP 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 3. 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 attentiveness of NaH_2PO_2 stress is also increased.

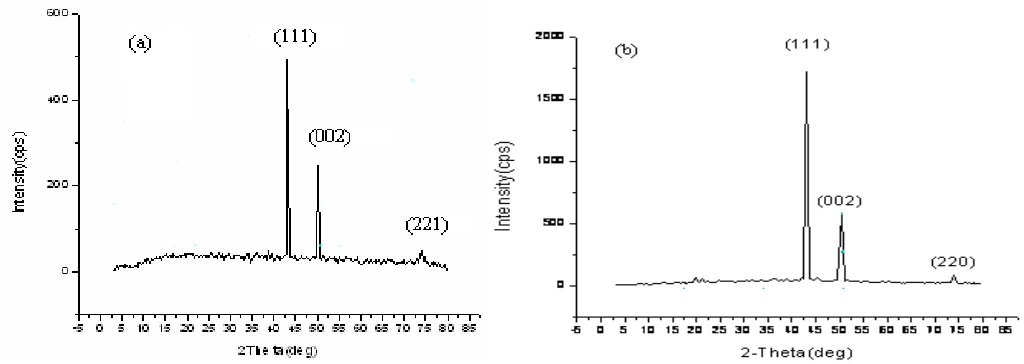

Fig. 2. XRD pattern for FePtP films of (a) NaH_2PO_2: 0.2 M and (b) NaH_2PO_2: 0.4 M

Crystallite sizes of the deposited films were calculated from XRD pattern using the formula i.e., crystalline size= $0.9\lambda/\beta\cos\theta$ .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 3. This analysis reveals the effect of phosphorous on the crystallite size of the deposit. The structural properties of FePtP films after annealing the samples at 155^{0}C in vacuum for 30 minutes and is shown in Table 4.

Table 3. Structural and mechanical of FePtP films

NaH_2PO_2 (mol/L)	Bath temperature ^{0}C	Crystalline Size(nm)	Stress (MPa)	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

Table 4. Structural and mechanical properties of FePtP films after annealing at 155^{0}C.

NaH_2PO_2 (M)	Bath temperature	Crystalline Size(nm)	Stress (MPa)	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

3.3 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 3 and 4. 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.

3.4 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.

4. Conclusions

We have presented the first report of continuous electrodeposited FePtP films. FePtP film having good hard magnetic properties are electrodeposited from a bath containing the following composition: H_2PtCl_6 :0.02M, $(NH_4)_2$ SO_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

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