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MAGNETIC PROPERTIES OF UREA DOPED NANOCRYSTALLINE FePtP FILMS

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Abstract. This paper reports a unique approach to the fabrication of FePtP films by electroplating technique which is especially interesting due to its low cost, high throughput and high quality of deposit. Effect of concentration of urea in the presence of sodium hyphophosphite was studied. Vibration sample magnetometric studies indicate that has favourable impact on the magnetic properties of these films. Elemental composition of the molecules was studied using energy dispersive X-ray spectroscopy. The result shows that the phosphorous content was found to be less than 10%. Morphology and structural properties were carried out using scanning electron microscopy and X-ray diffractometry. Reasons for variation in magnetic properties and structural characteristics are discussed. Mechanical properties such as residual stress, hardness and adhesion of the films were also studied.

1. Introduction

Magnetic micro-electro-mechanical-systems (Magnetic MEMS) present a new class of conventional MEMS devices with great potential for science and applications. Using the same technology as for MEMS and incorporating magnetic materials as the sensing or active element offer new capabilities and open new markets within the information technology, automotive, biomedical space and instrumentation. Magnetic MEMS are based on electromagnetic interactions between magnetic materials and active (coils) or passive magnetic field sources -permanent magnets [1]. Moreover, they are less susceptible to malfunction when subjected to adverse environments such as dust and humidity [2].

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 [3]. Numerous studies have been carried out to develop hard magnetic films of this material due to potential application in high-density recording media and microelectromechanical systems [4,5]. The elecrodeposited FePt samples showed a much smoother hysteresis loop than CoPt. The reason for this behaviour is due to the fact that the composition ratio may vary within a small range throughout the nanowires during electrodeposition [6]. The important magnetic properties of hard magnetic materials are remanent, coercivity and magnetic saturation. Electodeposited hard magnetic materials consist of heterogeneous alloys. Generally, hard magnetic alloys are iron based because fct-structured iron-platinum has a high magneto crystalline anisotropy [7]. As the formation of the $L1_0$ 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 [8]. The three phases present in FePtP alloy have a beneficial effect on the magnetic properties, i.e., FePt for the anisotropy, PtP_2 for

pinning the magnetic domain wall, and the Fe-rich Fe-P phase for enhancing the magnetization and their optimal combination can be a useful design tool for high performance magnets [9].

In the present study we investigated in detail the effects of concentration of urea on the magnetic, structural and mechanical properties of FePtP films.

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 gl^{-1}; sodium carbonate: 20.0 gl^{-1}; trisodium phosphate: 9.0 gl^{-1}, and sodium metasilicate: 24.0 gl^{-1}. 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: 0.2 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 0.2 M and 0.4 M of sodium hypophosphite (NaH_2PO_2) and 2.5 and 5.0 gl^{-1} of urea were added in this bath and their effect on the properties of FePtP films was 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 and stress of the deposited FePtP films were calculated. Percentage of elements such as Fe, Pt and P present in the deposits were 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 [10].

3. Results and discussion

Thickness and magnetic properties. Table 1 summarizes the effect of concentration of NaH_2PO_2 and urea on the thickness and magnetic properties of FePtP films obtained under different experimental conditions by varying the current density. In the absence of urea the thickness of the film increased with increase in current density. However the electrodeposited film had relatively poor magnetic properties. For example the best coercive and remanent obtained in the absence of urea were found to be 135,289 Am^{-1} and 0.19 Am^2 [experiment number 3] respectively.

Table 1. Effect of NaH_2PO_2 and urea on the thickness & 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 (Am^{-1})	Experiment number
NaH_2PO_2 (M)	Urea (gl^{-1})						
0.2	0	2	2.9	0.8	0.07	47,746	1
		4	4.2	0.72	0.13	83,564	2
		6	5	0.65	0.19	135,289	3
	2.5	2	5.5	0.88	0.18	123,353	4
		4	6.2	0.83	0.22	175,078	5
		6	6.8	0.78	0.27	250,667	6
	5.0	2	5.1	0.91	0.16	83,556	7
		4	5.7	0.88	0.17	143,796	8
		6	6.3	0.83	0.23	198,951	9
0.4	0	2	2.8	0.82	0.06	41,200	10
		4	3.8	0.75	0.11	63,662	11
		6	4.7	0.72	0.15	93,556	12
	2.5	2	5.2	0.94	0.13	71,620	13
		4	5.8	0.92	0.15	97,543	14
		6	6.4	0.87	0.18	143,350	15
	5.0	2	4.8	0.98	0.11	43,683	16
		4	5.3	0.95	0.12	63,662	17
		6	5.8	0.91	0.14	105,232	18

In general NaH_2PO_2 addition was found to have little effect on the thickness of the film. On increasing the concentration of NaH_2PO_2 from 0.2 to 0.4 M, the coercivity was found to decrease from 135,289 Am^{-1} (experiment number 3) to 93,556 Am^{-1} (experiment number 12). The morphology of the film however was found to be poor when no urea was incorporated in the electrodeposition bath.

The effect of addition of urea into the bath A along with NaH_2PO_2 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 NaH_2PO_2 and 2.5 gl^{-1} of urea at a current density of 6 mA cm^{-2} and time of deposition 60 minutes the thickness of the film was found to be 6.8 μm with coercive and remanent values are 250,667 Am^{-1}, 0.27 Am^2 (experiment number 6) respectively. With further increase in urea concentration the thickness, coercive and remanent values were found to decrease significantly.

Increase in magnetic properties of the films is mainly due to urea. The urea molecules thus are found to have leveling effect, which ensures uniform orientation of crystals during electrodeposition. On increasing the concentration of NaH_2PO_2 and urea magnetic properties of the films decreased. It was because of the stress present in the films, which was caused by the inclusion of decomposed products of additives.

In general thickness and magnetic properties (coercivity and remanence) of the films were increased with increase in current density. It is shown in Fig. 1a-1c. Magnetic saturation

level of the films was decreased with increase in current density as shown in Fig. 1d. It is also observed from Fig. 1b that films deposited from a bath contained 2.5 gl^{-1} of urea and 0.2 M of NaH_2PO_2 has high coercivity. The coercivity obtained in this case is more than coercivity obtained in FePt after annealing [11], i.e. instead of annealing, using urea as additive high coercivity is attained.

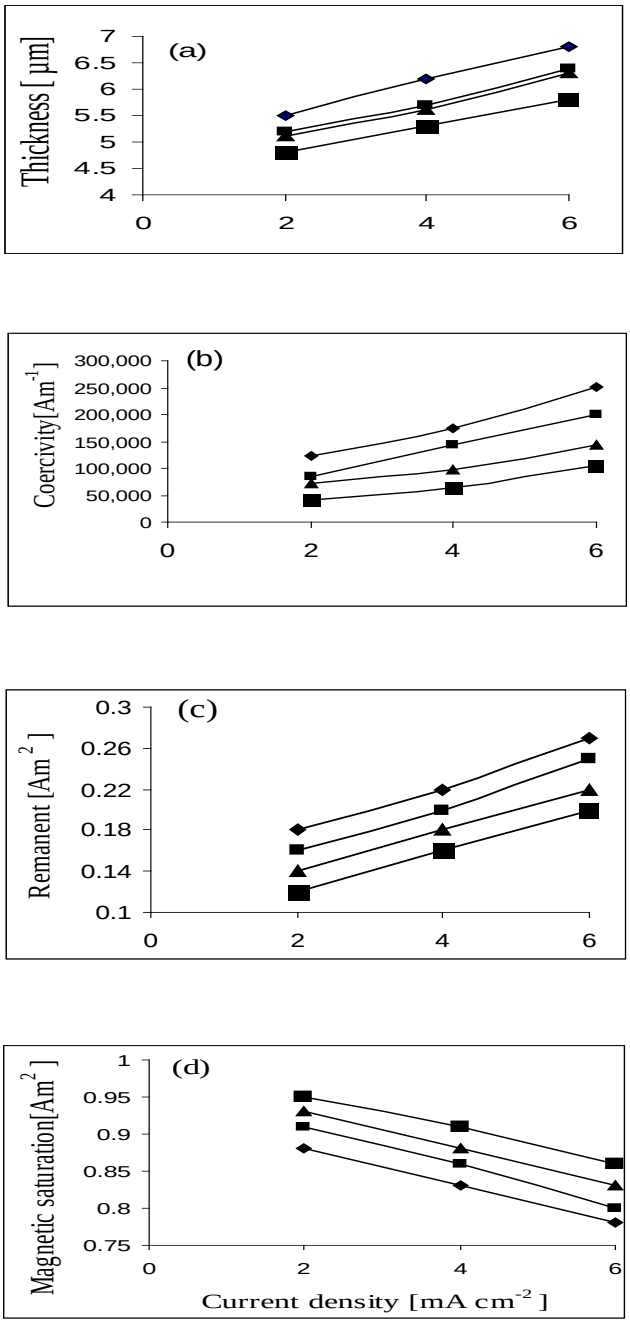

Fig. 1. Effect of current density on thickness, coercivity, remanent and magnetic saturation of FePtP films electrodeposited from bath A with urea: (▪) NaH_2PO_2: 0.2 M; urea: 2.5 gl^{-1}, (■) NaH_2PO_2: 0.2 M; urea: 5.0 gl^{-1}, (▲) NaH_2PO_2: 0.4 M; urea: 2.5 gl^{-1}, (■) NaH_2PO_2: 0.4 M; urea: 5.0 gl^{-1}.

Structural analysis. Electrodeposited FePtP films were subjected to XRD studies. The X-ray wavelength used was 1.54439 Å of Cu Kα radiation. Films obtained from experiment numbers 3, 6, 9, 12, 15 and 18 of Table 1 were studied for their structural characteristics and they are presented in Fig. 2. The data obtained from the XRD pattern were compared with the standard data and were found to have face centered tetragonal structure and exhibited (111) plane predominantly. But the plane peak is slightly shifted in all XRD patterns due to residual stress. In the case of films and metals XRD peaks will be shifted because of the stress of the material [12]. Few low intensity peaks like (002) and (221) were also observed. Stress of the films were calculated from XRD pattern peak using the formula i.e., Young's modulas = stress/strain and presented in Table 2. FePtP film produced from a bath with low concentration of urea has low stress and this is due to uniform crystal orientation during electro-deposition. Hence it may be noted that low concentration of urea acts as a grain refiner and stress reliever. But on increasing concentration of urea, film stress is also increased. This is due to inclusion of decomposed product in the film from the additive when its concentration is higher.

Table 2. Effect of NaH_2PO_2 and urea on the structural and mechanical properties of FePtP film electrodeposited at 6 mA cm^{-2} for 60 minutes.

NaH_2PO_2 (mol/L)	Urea (gl^{-1})	Crystalline Size(nm)	Stress (MPa)	Vickers Hardness (VHN)	Film composition (mass%)		
					Fe	Pt	P
0.2	0	29	140	389	24.6	66.6	8.8
	2.5	23	130	398	25	68.8	6.2
	5 .0	30	145	360	24.8	67.5	7.7
0.4	0	33	151	370	25.5	64.5	10
	2.5	30	140	390	26.5	65.2	8.3
	5.0	35	160	350	2 5.4	65.4	9.2

Crystallite size of the deposits were calculated from the XRD pattern using the formula: crystallite size=$0.9\lambda/\beta\cos\theta$. The calculated values clearly show that the crystallite size of the FePtP deposit obtained by electrodeposition is in a nano scale and it is shown in Table 2.

Morphological observation. Electrodeposited FePtP films obtained from experiment numbers 3, 6, 9, 12, 15 and 18 of Table 1 were subjected to SEM. The micrographs are presented in Fig.3. In general microstructure of the FePtP was affected by the percentage of phosphorous content.

The film deposited without organic additive was cracked because of phosphorous content as shown in Fig. 3a and 3d. Figures 3b and 3e proved that the film with very low concentration of phosphorous appeared to have crevice pattern. The film obtained from a bath contained 5.0 gl^{-1} urea was cracked through substrate due to stress of the film in Fig. 3c and 3f. It was also observed in Table 2 that film obtained from bath contained 5.0 gl^{-1} of urea had high stress. Stress measurements from the XRD pattern also support this result.

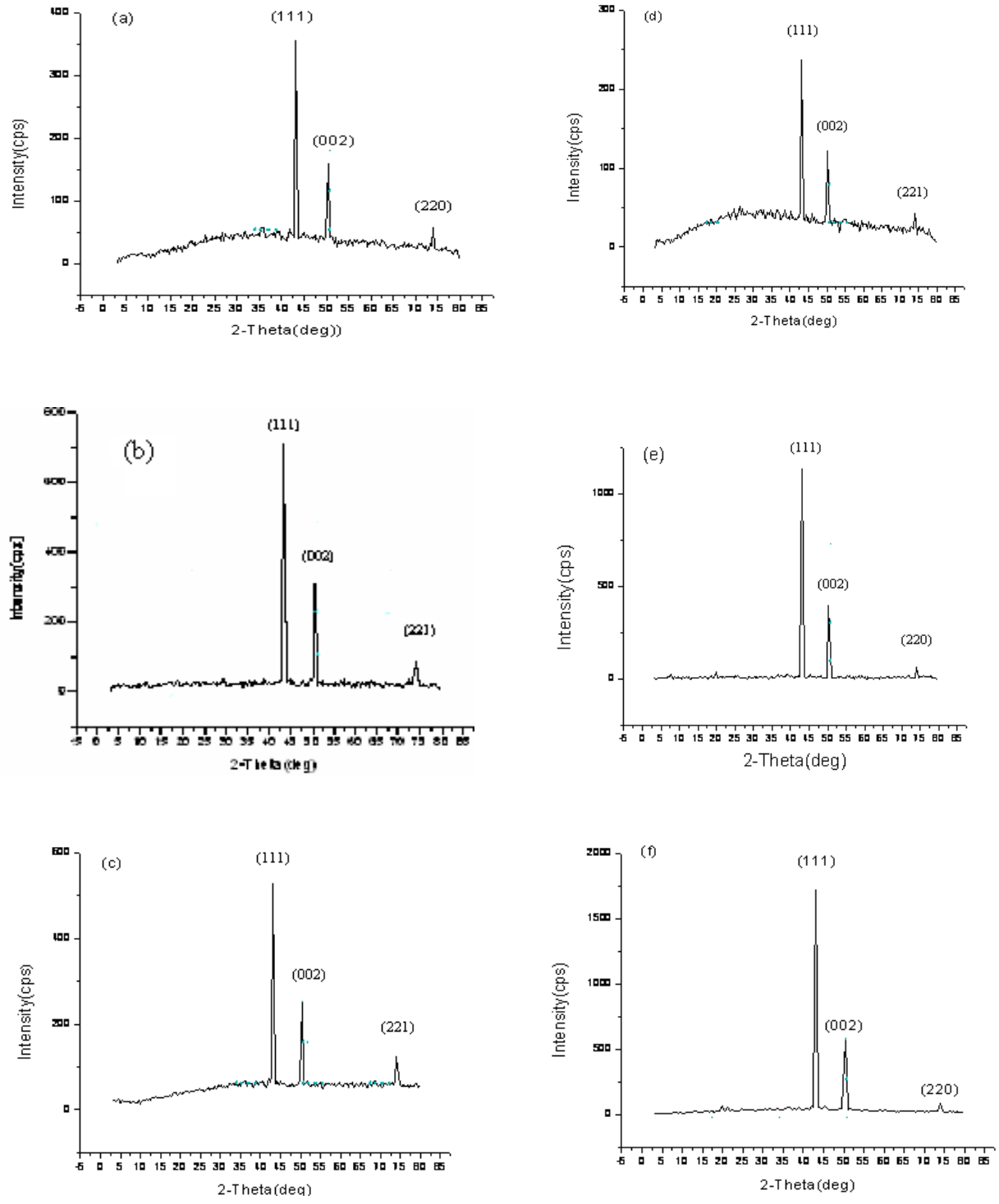

Fig. 2. XRD patterns of FePtP films electrodeposited for 60 min at 6 mA/cm^2 from bath A with (a) NaH_2PO_2: 0.2 M, urea: 0 gl^{-1}, (b) NaH_2PO_2: 0.2 M, urea: 2.5 gl^{-1}, (c) NaH_2PO_2: 0.2 M, urea: 5.0 gl^{-1}, (d) NaH_2PO_2: 0.4 M, urea: 0 gl^{-1}, (e) NaH_2PO_2: 0.4 M, urea: 2.5 gl^{-1}, (f) NaH_2PO_2: 0.4 M, urea: 5.0 gl^{-1}.

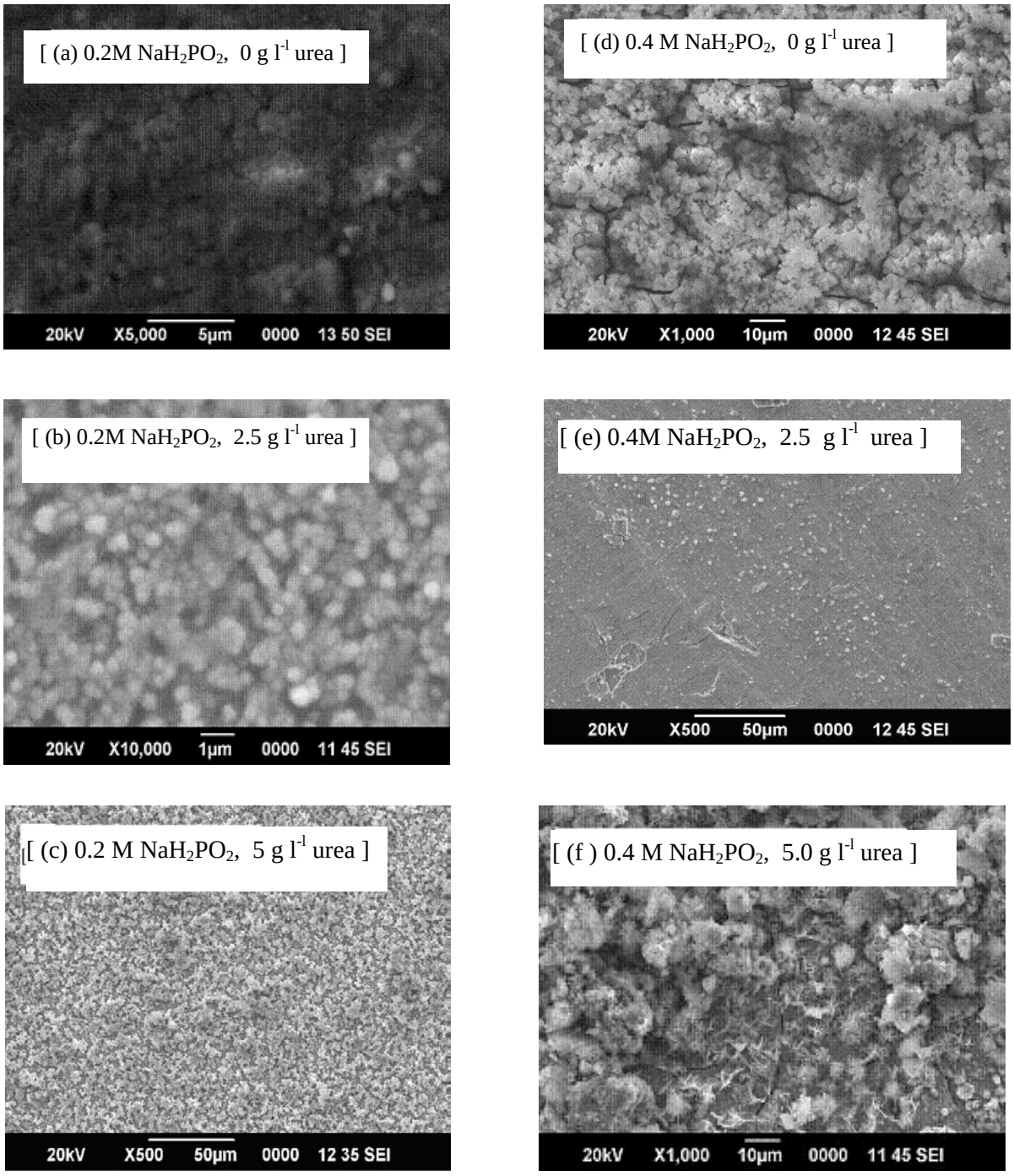

Fig. 3. SEM images of FePtP films electrodeposited for 60 min at 6 mA/cm^2 from bath A.

Mechanical properties. Electrodeposited 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.

Elemental analysis. Table 2 also presents the results of EDS. It was observed that all the films obtained from various baths had low phosphorous. Even with low phosphorous

content the films showed high magnetic properties. It was due to the addition of urea in the bath which improved the crystalline structure of FePtP films.

4. Conclusion

This experiment was carried out to investigate the magnetic properties of nanostructured FePtP films. It was found that high quality magnetic properties with high coercivity were obtained by doping urea in lower concentration. This is because the urea molecules are found to have leveling effect which ensures uniform orientation of crystals during electrodeposition. Coercivity of the films significantly decreases by increasing the concentration of urea. Hardness of the films is decreased because of increase in urea concentration. It also increases the film stress which is a cause for cracked film. As these types of magnetic films are used in MEMS devices they should have minimum stress. 2.5 gl^{-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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References

[1] D. Niarchos // *Sensors and Actuators A: Physical* **109** (2003) 166.
[2] C.H. Ahn, M.G. Allen // *IEEE Trans. Ind. Electron*. **45** (1998) 866.
[3] R. Skomski, J.M.D. Coey, *Permanent Magnetism* (Institute of Physics, Bristol, 1999).
[4] J.W. Judy, R.S. Muller // *IEEE J. Microelectron. Syst.* **6** (1997) 249.
[5] T.M. Selvakumari, R.N. Emerson , S. Ganesan // *Am. J. Appl. Sci.* **6** (2009) 1175.
[6] Y.H. Huang, H. Okumura, G.C. Hadjipanayis // *J. Appl. Phys.* **91** (2002) 6869.
[7] V.V. Bondar, M.M. Mel'nikova, Y.M. Polukarov, In: *Electrodeposition of metals and alloys*, ed. by N.E. Khomutov (IPST Press, Jerusalem, 1969) p.71.
[8] K. Leistener, J. Thomas, B. Schlorb, M. Weisheit, L. Schultz, S. Fahler // *Appl. Phys. Lett.* **85 (**2004) 3498.
[9] A.A. Kundig, N. Abe, M. Ohnuma, T. Ohkubo, H. Mamiya, K. Hono *// Appl. Phys. Lett.* **85** (2004) 789.
[10] M. Murphy, P.N. Frost (Eds.), *Metal Finishing*; *68th Guide Book and Directory* **98** (2006) 372.
[11] T.M. Selvakumari, R.N. Emerson**,** S. Ganesan // *Int. J. Pure and Appl. Phys.* **5** (2009) 165.
[12] I.C. Noyan, J.B. Cohen, *Residual Stress Measurement by Diffraction and Interpretation* (Spinger-Verlag, New York, 1987).