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Effect of Saccharin on the Mechanical and Magnetic Properties of Electrodeposited CoMnP Thin Film Alloys

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Abstract

CoMnP alloy films were synthesized by electrodeposition technique. The electrochemical deposition technique is especially interesting due to its low cost, high throughput and high quality of deposit. Magnetic thin films are extensively used in various electronic devices including high density recording media and micro electromechanical systems (MEMS). Electrodeposition being cost effective, in the present work cobalt based magnetic films was deposited electrochemically and deposition characteristics were studied. Effect of concentration of organic additives saccharin in the presence of the sodium hypophosphite was studied. Structural and magnetic properties were investigated by X-ray diffractogram (XRD) and Scanning electron Microscope (SEM) respectively. The content of Co, Mn and P was analyzed using Energy Dispersive X-Ray Spectroscopy (EDS) technique. The hysteresis loops of the CoMnP alloy films were measured by a vibrating sample magnetometer (VSM) and studies showed that organic additive has altered the magnetic properties of the films. The reason for the change in magnetic properties and structural characteristics because of the additive were discussed. Mechanical properties such as hardness and adhesion of the films were also examined and reported.

Keywords: CoMnP thin films, organic additive Saccharin , EDS, XRD, SEM.

Introduction

The importance of electrodeposition as a fabrication technology in the electronic industry is large and growing. [1-4]. Development of microelectromechanical

systems [MEMS] and magnetic recording devices requires hard magnetic films with both high coercivity and remanence [5]. Electrodeposited magnetic thin films are important in computer read/ write heads and MEMS because of their fiexibility, capability, quality and low cost [6].With the current trend towards miniaturization, cost-competitiveness and high performance packaging, electro deposition has become the dominant manufacturing technology in many new applications and remains firmly established in others such as micro electro mechanical system (MEMS) devices, magnetic recording head, reading heads and data storage media [1-4]. Moreover, Electrodeposition has been recognized as a preparation method characterized by remarkable degree of reproducibility [7,8]. The electro deposition technique is especially interesting due its cost- effectiveness, easy maintenance and quality deposits. As CoMnP ternary alloy films are having hard magnetic properties various studies have been carried out to develop these magnetic films[9]. Electro-deposition provides an easy way to produce these films with high quality [10]. Up to now, various Co-based permanent- magnet materials have been electrodeposited because of the crystalline structure of cobalt is highly anisotropic [11]. Numerous studies have been carried out to investigate binary and ternary Co based iron group magnetic thin films. They mostly focused on the mechanism of anomalous codeposition, the effect of various additives, effect of plating and the corrosion properties. To our knowledge, there have been a few detailed studies on Co based films prepared using electro deposition [12,13]. The purpose of the present work was to study the effects of bath parameters (current density, pH, and time duration of deposition) mainly on the magnetic properties of electro deposited CoMnP thin films. CoMnP films were characterized using energy dispersive X-Ray Spectroscopy (EDS), X-Ray diffractometer (XRD) and Vibrating sample Magnetometer (VSM) and the influence of the bath parameters on the film composition, structure and magnetic properties were discussed. The influence of the organic additive Saccharin on the magnetic properties was also studied.

Experimental Details

Magnetic CoMnP films were electro deposited from various plating solutions.
Composition of bath A: $CoCl_2$: 0.42M; $CoSo_4$: 0.053M; NaH_2PO_2: 0.2M; $MnCl_2$: 0.4M; NH_4Cl: 1.8 M. **Composition of bath B:** $CoCl_2$: 0.42M; $CoSo_4$: 0.053M; NaH_2PO_2: 0.2M; $MnCl_2$: 0.4M; NH_4Cl: 1.8 M and Saccharin 2 gL^{-1} . **Composition of bath C:** $CoCl_2$: 0.42M; $CoSo_4$: 0.053M; NaH_2PO_2: 0.2M; $MnCl_2$: 0.4M; NH_4Cl: 1.8 M and Saccharin 4 gL^{-1}. The CoMnP films were electro deposited on Copper substrates of size 20 mm (breath) X 120 mm (length) X 0.1 mm (Thickness). Pure Co of the same size was used as anode. For all the bath compositions A,B and C, CoMnP films were electrodeposited at constant pH value 3.00 by varying the current densities (3, 5 and 7$mAcm^{-2}$) at room temperature and for various time duration (15, 30 and 60 Minutes). The thickness of the deposition was measured using digital micrometer. Magnetic properties of the deposited films were studied using Vibrating sample magnetometer (VSM). X- Ray diffrectometer (XRD) was used to study the presence

of various phases in the deposited films. Scanning Electron Microscopy (SEM) was used to study the morphology of these magnetic films. From XRD data, the crystalline size of the deposited CoMnP was studied. Hardness of the coating was calculated using a Vicker's hardness tester by diamond intender method. Adheson of the film was tested by bent test and by scratch test. For each bath composition, magnetic films were deposited to study the effect of organic additive Saccharin on the mechanical and magnetic properties of CoMnP films.

Results and Discussions

Elements present in the film were analyzed by energy dispersive X-ray spectroscopy (EDS) as shown in Figure 1. Elements present in the film were analyzed by the EDS and it confirms the presence of Cobalt, Manganese and Phosphorous in the alloy film. All deposits, which were subjected to EDS analyze, have less than 2 % Phosphorus content.

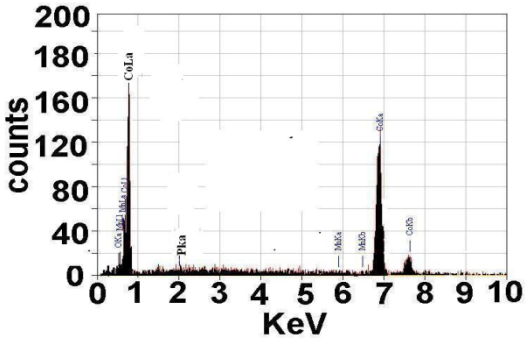

Figure 1: EDS Spectrum of electrodeposited CoMnP: Time of deposition : 60 min; Current Density ; 5 $mAcm^{-2}$; pH: 3; for composition of the bath B.

XRD pattern of Electrodeposited CoMnP thin film for various bath compositions (a) solution A, (b) solution B; Solution A plus Saccharin: 2.0 g/L, (c) solution C; Solution A plus Saccharin: 4.0g/L were presented in Figure 2 (a), (b), and (c).The data obtained from the XRD pattern were compared with the standard data and were found to have hexagonal close packing (hcp) structure and exhibited (201) plane predominately. The (201) plane peak is shifted in all XRD patterns due to film residual stress.from the previous studies [14] it is learnt that the film stress will shift XRD peaks. In the presence of additives few low intensity peaks were also observed for (002), (301), (110) and (200) planes and this is because of the formation of intermetallic CoMnP compound during electro-deposition. Shifting of peaks to the lower angles indicates the increase in lattice constant with the additive concentration.

From the XRD pattern peak, stress in the film was calculated using the formula: Young's modulus = stress/strain. The results are shown in Table 3. CoMnP film produced from a bath with low concentration of Saccharin has low stress and this is due to uniform crystal orientation during electro-deposition. Hence it may be noted

that low concentration of Saccharin acts as a grain refiner and stress reliever. But on increasing the concentration of Saccharin film stress also gets increased. This is due to inclusion of decomposed product in the film from the additive when its concentration is higher.

Crystallite size of the deposits was calculated from the XRD pattern using the formula: crystallite size = $0.9\lambda / \beta \cos \theta$. These values clearly show that the crystallite size of the deposite obtained by electro-deposition process is found to be in nano-scale.

Electro-deposited CoMnP films from all three baths (A, B, and C) conditions as mentioned in XRD studies were subjected to SEM studies. The micrographs are presented in Figure 3 (a),(b), and (c). In general, micro structure of the CoMnP is greatly influenced by the percentage of Phosphorus content. The film with very low concentration of phosphorous appeared to have a crevice pattern and it also appeared less bright to the naked eye. The film deposited from a bath containing higher concentration of additive Saccharin was cracked through the substrate probably due to the high stress associated with the film because of the additive. Stress measurement from XRD pattern also supports this result. The film deposited with out organic additive was also cracked because of the Phosphorus content.

Electro- deposition studies were carried out using different concentrations of Saccharin. Saccharin have been selected because they have been extensively studied as an electroplating additive in the plating perspective.

Table 2(a) lists the magnetic properties of electrodeposited CoMnP thin films for bath A; with out any organic additive. Thickness of deposit increases with increase in current density and time of deposition. Films are dull in appearance and having pits. Films are having very low coercive and Remanent values.

Table 2(b) shows the effect of current density and time of deposition on the thickness and the magnetic properties of the CoMnP films electro-deposited from baths b and C. Thickness of the deposit increases with increase in current density. The magnetic properties of films revealed that these films are having a high coercive and low remanent value when compared to the deposits obtained from films deposited from a bath with out organic additive. Other values like magnetic saturation decrease with increase in thickness and square ness increases with increase in thickness. On increasing the concentration of Saccharin to 4.0 g/L, thickness of the deposit increased with respect to current density. Coercivity values decreased when compared to films obtained from 2.0 g/L Saccharin containing solution. Remanent value increased at high current densities. The change in magnetic properties was because of the stress present in the magnetic film at higher concentration of Saccharin.

Effect of addditives on the thickness and magnetic properties of CoMnP films electro-deposited for the bath B and C are presented in Table 2(b). Thickness of the deposit increases with increase in current density. The magnetic properties of the films revealed that these are having a high coercive and low remanent value when compared to films produced from a bath with out organic additive on increasing the concentration of Saccharin to 4.0 g/L, Thickness of the deposit increased with respect to current density. Coercivity value decreased.

Figure 4 (a), shows the effect of current density on coercivity for the baths B and

C under study with additive Saccharin. This figure clearly shows that the coercivity values increase with increase in current density for the baths under study. It also clearly reveals that increase in the concentration of Saccharin decreases coercivity. The same type of results was noted from figure 4 (b), which is a plot between the time of deposition and coercivity.

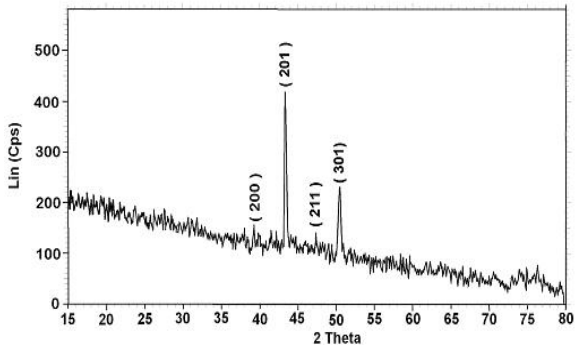

Figure 2(a): XRD pattern of Electrodeposited CoMnP thin film; Time of deposition 60 min; Current Density 5 mA/cm^2; pH:3 ; for composition of the bath A.

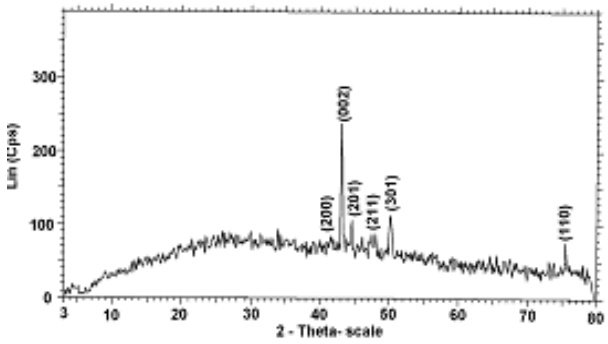

Figure 2(b): XRD pattern of Electrodeposited CoMnP thin film; Time of deposition 60 min; Current Density 5 mA/cm^2; pH:3 ; for composition of the bath B.

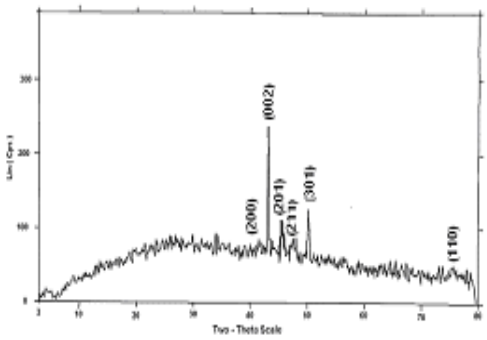

Figure 2(c): XRD pattern of Electrodeposited CoMnP thin film; Time of deposition 60 min; Current Density 5 mA/cm^2; pH:3 ; for composition of the bath C.

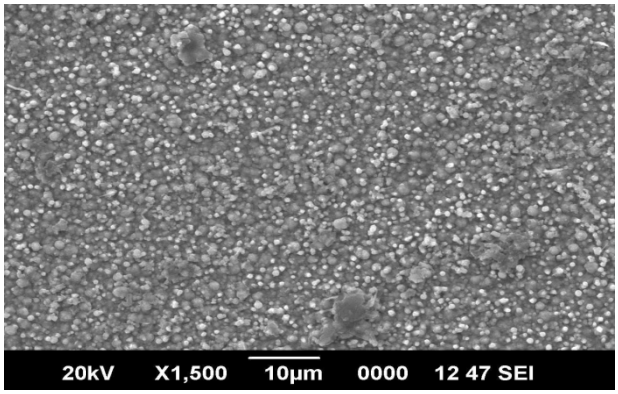

Figure 3(a): SEM image of electrodeposited CoMnP film; composition: Bath A; time of deposition: 60 min; current density: 5 mAcm^{-2}; pH: 3.

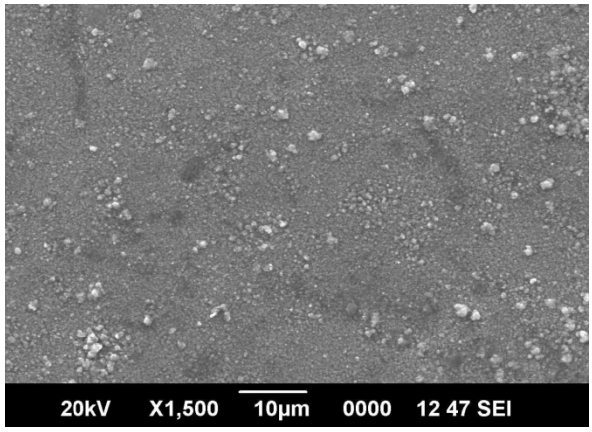

Figure 3(b): SEM image of electrodeposited CoMnP film; composition: Bath B; time of deposition: 30 min; current density: 5 mAcm^{-2}; pH: 3.

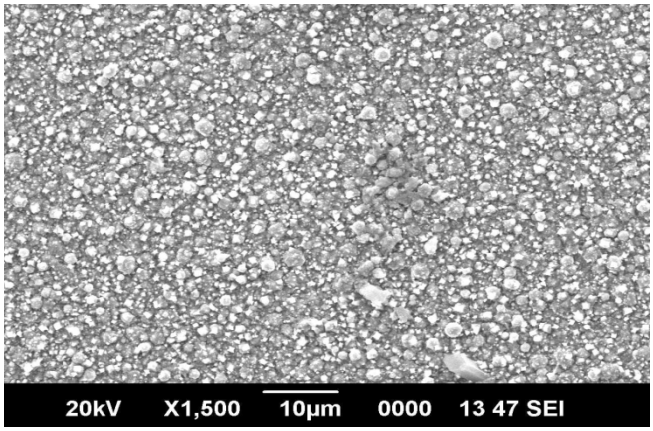

Figure 3(c): SEM image of electrodeposited CoMnP film; composition: Bath C; time of deposition: 60 min; current density: 5 mAcm^{-2}; pH: 3.

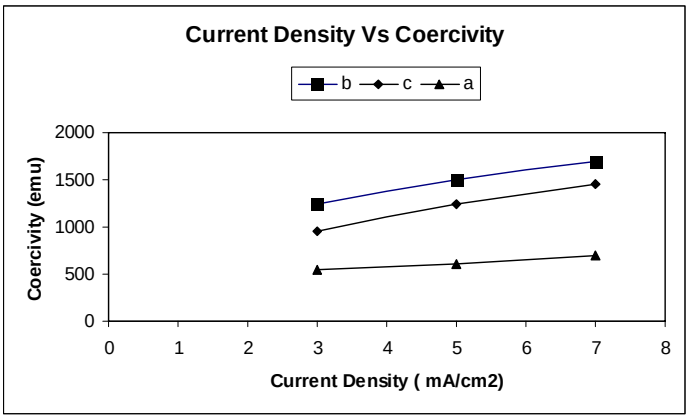

Figure 4(a): Current Density Verses Coercivity: Time of deposition 60 min; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

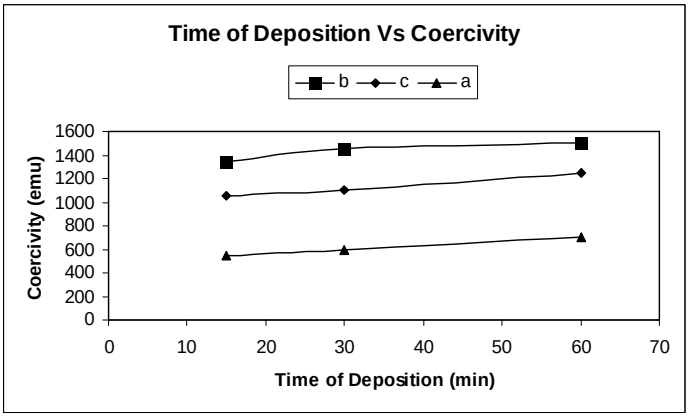

Figure 4(b): Time of Deposition Verses Coercivity: Current Density 5 mA/Cm^2; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

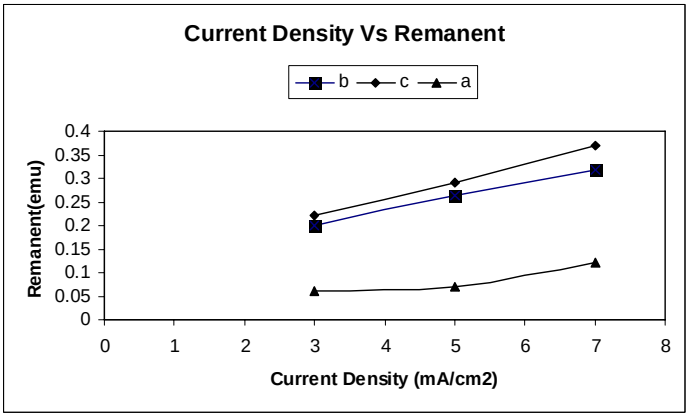

Figure 4(c): Current Density Verses Remanent: Time of deposition 60 min; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

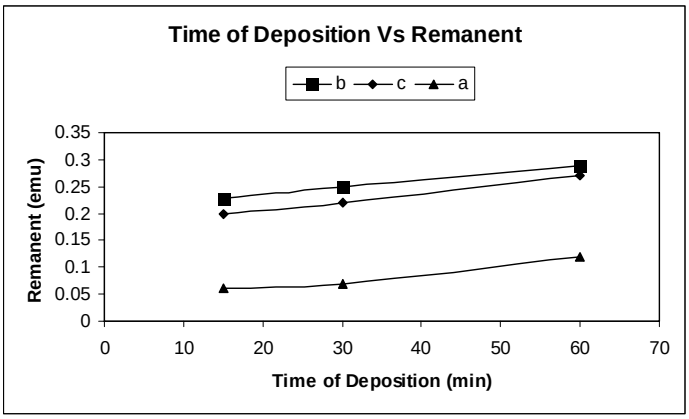

Figure 4(d): Time of Deposition Verses remanent: Current Density 5 mA/Cm^2; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

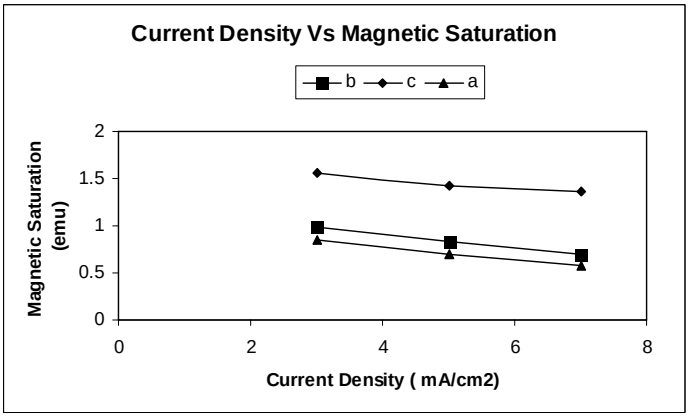

Figure 4(e): Current Density Verses Magnetic Saturation: Time of deposition 60 min; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

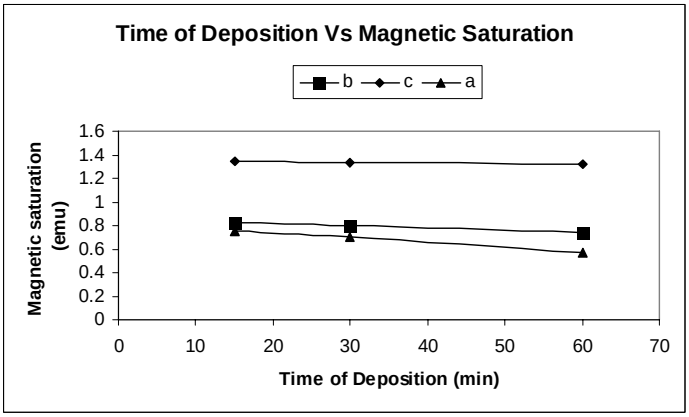

Figure 4(f): Time of Deposition Verses Magnetic Saturation: Current Density 5 mA/Cm^2; pH:3 ; for bath composition A (a),B (b) and for composition bath C (c).

Table 2(a): Magnetic properties of electrodeposited CoMnP thin films for Solution A.

Current density ($mA\text{-}cm^{-2}$)	Time of deposition (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)	Squareness
3	15	0.3	0.97	0.03	300	0.0309
3	30	0.8	0.90	0.04	350	0.0444
3	60	1.2	0.80	0.05	400	0.0625
5	15	0.4	0.65	0.06	550	0.0923
5	30	0.7	0.70	0.07	600	0.1000
5	60	1.8	0.67	0.12	700	0.1791
7	15	1.5	0.65	0.14	800	0.2153
7	30	2.3	0.60	0.17	850	0.2833
7	60	2.7	0.50	0.23	900	0.4600

Table 2(b): Magnetic properties of electrodeposited CoMnP thin films for Bath compositions B and C at a constant Current density 5 mA/cm^2.

Experime-ntal Bath	Time of Deposition (min)	Thick-ness of deposit (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)	Squareness
Bath B	15	2.0	0.83	0.22	1350	0.2746
Bath B	30	3.4	0.80	0.24	1450	0.3112
Bath B	60	4.6	0.74	0.27	1500	0.3648
Bath C	15	2.7	1.35	0.20	1050	0.1481
Bath C	30	4.1	1.33	0.22	1100	0.1654
Bath C	60	5.2	1.32	0.27	1250	0.2045

Figures 4 (c) and (d) shows the effect of current density and time of deposition on the remanent values of the deposits. Like coercive values these values are not in an order i.e., it also increases with increase in current density and time of deposition, but on increasing the concentration of urea, Remanent values increases. Magnetic saturation of these films decrease with increase in current density and time of deposition which is shown in figure 4 (e) and 4 (f).

As the average crystallite size of these films is in the nano scale, considerable changes in the magnetic behaviour can occur. When the crystallize size is reduced to the extend that the domine wall thickness is comparable to the crystallite size the coercivity is found to decrease. But the present work the coercivity increases when crystallite approaches high nano level. This is mainly due to the phosphorous content in the deposit, which was produced from a bath having saccharin 4.0 g/L concentrations. Analysis of crystallite size, microstructure and magnetic properties

confirms that the origins of magnetic properties are because of the strongly interacting array of single domain crystals. This is mainly due to the presence of phosphorous which was incorporated in to the CoMnP films at the required level of the additive. It was absorbed by Miksic etal., [15] that the coercivity of CoMnP deposits increased with increasing film thickness when P is less than 2 Wt %. Phosphorous and the coercivity values increased with increase in film thickness.

Adheson of the film was tested by bent test (bending the film with the substrate is 180^0) and by scratch test (draw equal lines by pin and paste an adhesive tape over the scratches and pull it. If the film comes with the tape then the adhesion is poor). It is showed that the film is having a good adhesion with the substrate.

Table 3: Effect of additive on the mechanical properties of CoMnP film electrodeposited at 5.0 mA/cm^2 for 60 minutes.

Bath composition	Vickers Hardness Number (VHN)	Internal Stress (MPa)
With out additive: Bath A	422	164
With additive Saccharin 2g/L: Bath B	446	144
With additive Saccharin 4g/L: Bath C	396	178

Hardness of these films was examined using a Vicker's hardness tester by the diamond intender method. Table 1 gives the hardness values. Hardness of the film decreases when concentration of urea increases. This may also be due to the higher stress associated with CoMnP film, when it is electro-deposited from a bath containing higher concentration of organic additive. Relative high hardness values for these CoMnP thin film alloys deposited is due to the fact that nano-crystalline alloys offer significantly increased strength.

Conclusions

CoMnP film having good hard magnetic properties can be prepared. Under best condition involving addition of 0.2M of NaH_2PO_2 and 2 g/L of Thiourea at current density 5 mA/cm^2 and time of deposition 60 Minutes, the thickness of the film was found to be 4.6 micrometer with coercivity 1500 Oe. It is found that further increase in the concentration of Saccharin will decrease the hard magnetic properties. 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. Hardness of the films is decreased because of the additive concentration. But organic additive like Saccharin in low concentration will produce a good CoMnP film, which can be used in MEMS devices, because these film have high coercive and low remanent values. Also these films have low stress, good adhesion with the substrate and their crystallite sizes are in nano-scale.

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