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Influence of organic additive Thiourea on the properties of hard magnetic CoMnP thin film alloys electrodeposited from chloride bath

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Thin films of CoMnP alloy have been deposited by electrodeposition technique on copper substrate with different concentration of NaH_2PO_2 and Thiourea in the chemical bath to investigate the structural and magnetic properties of CoMnP compounds. The structural and surface morphology of the film were detected using X-ray diffractogram (XRD) and Scanning electron Microscope (SEM) respectively. The constitutions in the film were determined by Energy Dispersive X-Ray Spectroscopy (EDS) technique. The magnetic properties such as the coercivity and the magnetic saturation of the films were studied with the help of Vibrating Sample Magnetometer (VSM). The deposit were found to be smooth, nanocrystalline and with good adherence to the copper substrate. The increase in the NaH_2PO_2 and Thiourea concentration in the bath causes a decrease in Mn content and increase in the P content of the film. Among the different compositions, CoMnP compound exhibit good hard magnetic properties, under the best condition involving addition of 0.2M of NaH_2PO_2 and 2 g-L^{-1} of Thiourea at a current density of 7 mA-cm^{-2} and time of deposition 60 minutes, the thickness of the film was found to be 3.3 micrometer with coercivity 1550 Oe and remanent 0.68 emu.

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Keywords: Electrodeposition, CoMnP thin films, Organic additive Thiourea, EDS, XRD, SEM

1. Introduction

Development of microelectromechanical systems [MEMS] and magnetic recording devices requires hard magnetic films with both high coercivity and remanence [1]. Electrodeposited magnetic thin films are important in computer read/ write heads and MEMS because of their fiexibility, capability, quality and low cost [2]. Recent investigations have highlighted electrodeposition as an attractive approach for the preparation of nanostructured materials. Electrodeposition provides a cost effective and non-equipment-intensive method for the preparation of nanocrystalline nano phase metallic materials i.e., metals, alloys, compositionally modulated alloys and composites [3]. Moreover, Electrodeposition has been recognized as a preparation method characterized by remarkable degree of reproducibility [4,5]. Up to now, various Co-based permanent- magnet materials have been electrodeposited because of the crystalline structure of cobalt is highly anisotropic[6]. 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 [7,8]. 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 Thiourea on the magnetic properties was also studied.

2. Experimental details

CoMnP thin films were electrodeposited from chloride baths. Table 1 lists the plating solution composition investigated.

All the CoMnP films were electrodeposited at constant pH value 3.00.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.Current for electrodeposition was passed from a regulated direct current unit. Analytical reagent grade chemicals were used to prepare baths. Each substrate was buffed for removing scratches in a mechanical polishing wheel using a buffing cloth coated with aluminium oxide abrasive.

Table 1. Sample composition.

Electrochemical bath	Plating solution composition
Sample one	$CoCl_2$: 0.42M; $CoSo_4$: 0.053M ; $MnCl_2$: 0.4 M ; NH_4Cl : 1.8 M and NaH_2Po_2 :0.2 M
Sample two	Sample one composition plus Thiourea 2 gL^{-1}
Sample three	Sample one composition plus Thiourea 4 gL^{-1}
Sample four	$CoCl_2$: 0.42M; $CoSo_4$: 0.053M ; $MnCl_2$: 0.4 M ; NH_4Cl : 1.8 M and NaH_2Po_2 :0.4 M
Sample five	Sample four composition plus Thiourea 2 gL^{-1}
Sample six	Sample four composition plus Thiourea 4 gL^{-1}

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^{-1}; sodium carbonate: 20.0 g l^{-1}; trisodium phosphate: 9.0 g l^{-1} and sodium metasilicate: 24.0 g l^{-1}. The bath was operated at 70° 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 current density and time of deposition.

The thickness of the deposits was tested using digital micrometer. Magnetic properties of deposited films were studied using vibrating sample magnetometer. 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 CoMnP and film stress were calculated. Percentage of elements such as Co, Mn and phosphorous present in the deposits were obtained.

3. Results and discussions

Elements present in the film were analyzed by energy dispersive X-ray spectroscopy (EDS) and the results are shown in Table II.

Table 2. Film Composition.

Bath	Film composition (at %)		
	Co	Mn	P
Sample one	97.68%	1.47%	0.85%
Sample two	97.23%	1.35%	1.42%
Sample three	96.90%	1.17%	1.93%
Sample four	98.38%	1.27%	0.45%
Sample five	97.93%	1.15%	0.92%
Sample six	97.45 %	0.97%	1.58%

Fig. 1 shows the EDS image of electrodeposited CoMnP film; Composition: Sample six; Time of deposition: 30 Min; Current Density: 5 $mAcm^{-2}$; pH: 3.

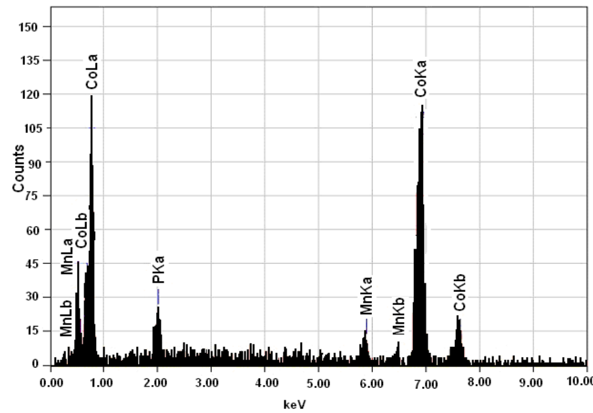

Fig. 1. EDS Spectrum of electrodeposited CoMnP: Time of deposition : 30 min; Current Density ; 5 $mAcm^{-2}$; pH: 3; for sample six.

It was observed that all the films obtained from various baths had less than 2.0% phosphorous. Even with low phosphorous content the films showed high magnetic properties. The improved crystalline structure of CoMnP films was due to the addition of Thiourea in the various baths. Electro deposited CoMnP films were subjected to XRD studies. X-ray Diffraction patterns of various CoMnP electrodeposits produced from various current densities 3, 5 and 7 mA cm^{-1} and various time of depositions 15, 30 and 60 minutes were obtained. The XRD pattern is presented in the Fig. 2 and Fig. 3.

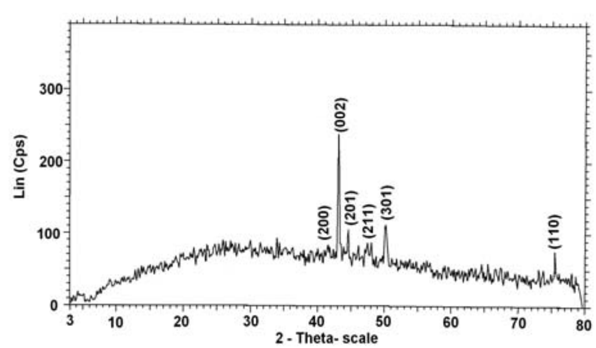

Fig. 2. XRD pattern of Electrodeposited CoMnP thin film; Time of deposition 30 min; Current Density 3 mA/cm^2; pH:3 ; for sample one.

The intensity data obtained was from 20 º to 80 º. The XRD datas obtained are compared with Joint Committee for Powder Diffraction Data.

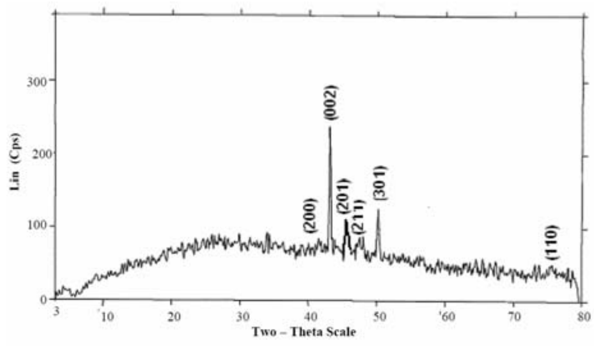

Fig. 3. XRD pattern of Electrodeposited CoMnP thin film; Time of deposition 60 min; Current Density 7 mA/cm^2; pH:3 ; for sample two.

CoMnP films has Hexagonal Close Packed (hcp) structure and exhibited (002),(201)and (110) plane primarily. (201) plane peaks in the data for films obtained for sample one and sample two has shifted because of the film stress. From the previous studies [9], it is learnt that the film stress will shift XRD peaks. The crystalline sizes of the deposits were calculated from Debye – Scherrer formula d = 0.9 λ / β Cos θ in meters.Where, λ is the wavelength of radiation. $\lambda_{Cu} =$ 1.54056 Aº. β is full width at half maximum (FWHM in radians). θ is the position of the maximum diffraction. The values obtained clearly shows that the crystalline sizes are in nanoscale. (002) and (201) Plane peak in the data for films obtained from sample one and sample two were shifted because of film stress. Stress was low for both sample two and sample three which contains 2 gL^{-1} of thiourea. It increased on increasing the concentration of thiourea to 4 gL^{-1} in the baths sample five and sample six. It is because of incorporation of decomposed products of additive in to the film.

Electrodeposited CoMnP films for all the bath compositions were subjected to SEM studies. The monographs are shown in Fig. 4 to Fig. 6. Fig. 4 shows the SEM image of electrodeposited CoMnP film; Composition : Sample three; Time of deposition: 60 Min; Current Density: 5 mAcm^{-2}; pH: 3. Figure V shows the SEM image of electrodeposited CoMnP film; Composition : sample four; Time of deposition: 30 Min; Current Density: 3 mAcm^{-2}; pH: 3. Figure VI shows the SEM image of electrodeposited CoMnP film; Composition : sample five; Time of deposition: 60 Min; Current Density: 7 mAcm^{-2}; pH: 3. The film with very low concentration of Thiourea appeared to have a crevice pattern as shown in the Figure IV. The film obtained from a bath contained 4 gL^{-1} of Thiourea was cracked through substrate due to the stress of the film as shown in the Figure V. In general, micrograph of the CoMnP film is greatly influenced by the additive Thiourea and current density. Adhesion of the film with the substrate is tested by bend test and scratch test. It is found that film is having good adhesion with the substrate.

Electrodeposition studies are carried out for different bath compositions and for different bath conditions. Table 3 to 8 shows the results of electrodeposition of CoMnP and their magnetic properties. The thickness of the film for various current densities and time of deposition are also shown in Table 3 to 8. The magnetic properties of the film were found to increase with current density and duration of deposition. The effect of addition of Thiourea in to the baths (i.e., sample two,three,five and six) along with NaH_2PO_2 was investigated. The magnetic properties of the thin film improve significantly upon adding low concentration the additive Thiourea. Under the best condition involving addition of 0.2M of NaH_2PO_2 and 2 gL^{-1} of Thiourea at a current density of 7 mA-cm^{-2} and time of deposition 60 minutes, the thickness of the film was found to be 3.3 micrometer with coercivity 1550 Oe and remanent 0.68 emu. With further increase in NaH_2PO_2 concentration, the thickness of the film found to be 3.7 micrometer with coercivity value of 1350 Oe and remanent value of 0.44 emu. Increase in magnetic properties of the films is mainly due to Thiourea.

Table 3. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample one.

Current density (mA-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	0.78	0.06	550	0.0923
5	30	0.7	0.72	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	1.3	0.60	0.17	850	0.2833
7	60	2.7	0.50	0.23	900	0.4600

Table 4. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample two.

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	0.47	0.11	550	0.2340
3	30	0.8	0.45	0.12	600	0.2666
3	60	1.4	0.42	0.14	650	0.3333
5	15	0.7	0.40	0.17	750	0.4250
5	30	1.1	0.37	0.18	800	0.4864
5	60	1.4	0.35	0.20	900	0.5714
7	15	0.9	0.32	0.26	1000	0.8125
7	30	1.3	0.30	0.28	1100	0.9333
7	60	2.2	0.29	0.31	1200	1.0689

Table 5. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample three.

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	1.00	0.37	950	0.3700
3	30	0.7	0.80	0.41	1000	0.5125
3	60	1.2	0.78	0.44	1050	0.5641
5	15	0.9	0.75	0.49	1100	0.6533
5	30	1.1	0.72	0.55	1150	0.7638
5	60	2.8	0.69	0.57	1250	0.8260
7	15	0.8	0.65	0.61	1350	0.9384
7	30	1.5	0.62	0.63	1500	1.0161
7	60	3.3	0.60	0.68	1550	1.1333

Table 6. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample four.

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	0.80	0.03	300	0.0375
3	30	0.7	0.75	0.04	350	0.0533
3	60	1.2	0.80	0.05	400	0.0625
5	15	0.5	0.77	0.06	550	0.0779
5	30	1.4	0.71	0.07	600	0.0985
5	60	2.1	0.70	0.12	700	0.1714
7	15	0.7	0.68	0.14	800	0.2058
7	30	1.6	0.65	0.17	850	0.2615
7	60	2.9	0.61	0.23	900	0.3770

Table 7. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample five.

Current density (mA-cm^{-2})	Time of deposition (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)	Squareness
3	15	0.3	1.14	0.08	600	0.0701
3	30	1.1	1.38	0.12	650	0.0869
3	60	1.2	1.35	0.18	675	0.1333
5	15	0.8	1.30	0.21	750	0.1615
5	30	1.2	1.28	0.24	850	0.1875
5	60	2.1	1.15	0.29	950	0.2521
7	15	0.6	0.90	0.33	1150	0.3666
7	30	1.8	0.80	0.39	1200	0.4875
7	60	2.2	0.75	0.44	1350	0.5866

Table 8. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for Sample six.

Current density (mA-cm^{-2})	Time of deposition (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)	Squareness
3	15	0.7	0.33	0.06	250	0.1818
3	30	1.2	0.31	0.09	300	0.2903
3	60	2.2	0.30	0.11	350	0.3666
5	15	1.1	0.28	0.13	450	0.4642
5	30	2.2	0.29	0.14	600	0.4827
5	60	2.7	0.25	0.16	675	0.6400
7	15	0.9	0.22	0.18	800	0.8181
7	30	2.7	0.21	0.19	1000	0.9047
7	60	3.7	0.20	0.19	1100	0.9500

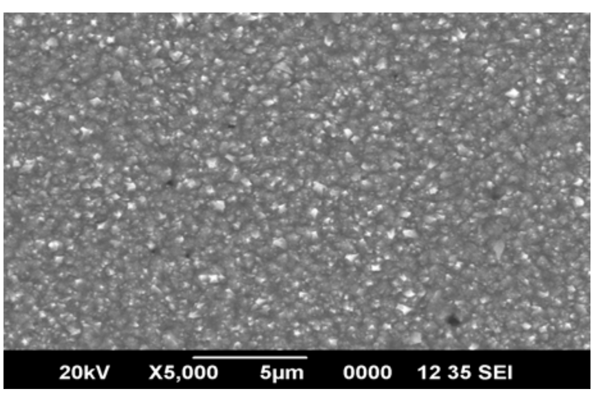

Fig. 4. SEM image of electrodeposited CoMnP film;Composition : sample three;Time of deposition: 60 Min; Current Density: 5 mAcm^{-2}; pH: 3

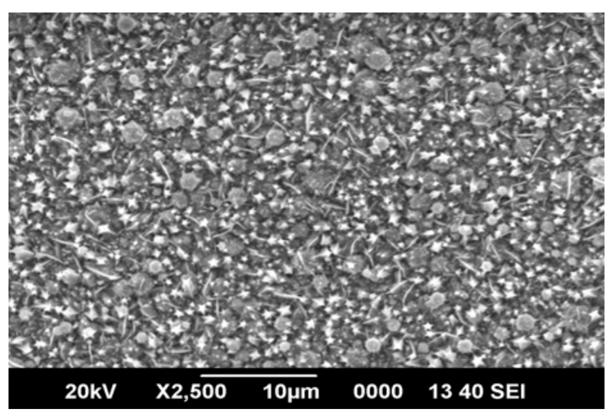

Fig. 5. SEM image of electrodeposited CoMnP film;Composition : sample four;Time of deposition: 30 Min; Current Density: 3 mAcm^{-2}; pH: 3

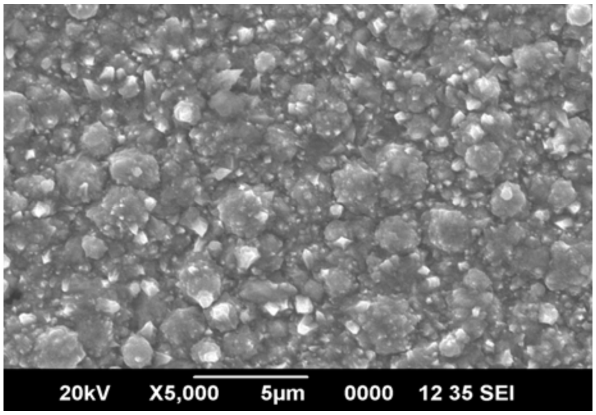

Fig. 6. SEM image of electrodeposited CoMnP film;Composition : sample five; Time of deposition: 60 Min; Current Density: 7 mAcm^{-2}; pH: 3

The electrodeposited films were uniform and bright. The Thiourea molecules are found to have leveling effect, which ensures uniform orientation of crystals during electrodeposition. On increasing the concentrartion of NaH_2PO_2 and Thiourea, the magnetic properties of the film decreased because of the stress present in the films. Stress is caused by the inclusion of decomposed products of additives.

4. Conclusions

CoMnP thin films could be successfully deposited by electrochemical deposition technique. Effect of deposition condition and Thiourea concentrations in the starting solution (Sample one and sample four)on the formation of CoMnP thin films was investigated. The concentrations of the constituents in the starting solution were optimized using a Hull cell. CoMnP films had Hexagonal Close Packed (hcp) structure and exhibited (002),(201) and (110) plane. Under the best condition involving addition of 0.2M of NaH_2PO_2 and 2 g-l^{-1} of Thiourea at a current density of 7 mA-cm^{-2} and time of deposition 60 minutes, the thickness of the film was found to be 3.3 micrometer with coercivity 1550 Oe and remanent 0.68 emu. (201) Plane peak in the data for films obtained from sample one and sample four were shifted because of film stress.

From literatures, It is known that film stress will shift XRD peaks[9]. Stress was low for bath sample two and sample three which contains 2 gL^{-1} of Thiourea. It increased on increasing the concentration of Thiourea to 4 gL^{-1} in the baths sample five and sample six. It is because of incorporation of decomposed products of additive in to the film. The CoMnP alloy deposited from the chloride bath can further be studied for its corrosion properties. CoMnP thin films can be synthesized from various additives such as urea and saccharin using electrochemical deposition technique and its magnetic properties can be examined for better magnetic properties.

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