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EFFECTS OF CURRENT DENSITY ON ELECTRODEPOSITED CoMnP THIN FILMS

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ABSTRACT

CoMnP thin films alloys were fabricated by electro deposition and the dependence of their magnetic properties on the current density were investigated using Vibrating Sample Magnetometer (VSM). Structure and the morphology of the film were studied using X-Ray diffractometer (XRD) and the Scanning Electron Microscopy (SEM). Elemental compositions of the film were studied using Energy Dispersive X-Ray Spectroscopy (EDS). Films are shiny and smooth. The deposited Cobalt (Co) increased from about 77 to 97 Mass % with increasing current density until 7 $mAcm^{-2}$ whereas the deposited Manganese (Mn) decreased from about 0.67 to 0.17 Mass % with increasing current density till 7 $mAcm^{-2}$. The deposited Phosphorous (P) of about 0.5 Mass% was independent of the current density. The X-Ray diffraction measurement showed that all peaks of CoMnP films were consistent with those of a typical Co hcp phase. An increase in the current density yielded a decreased sharpness of the major peaks. Also the peak position shift to lower angle which means the lattice constant increased with increasing current density. The magnetic saturation value decreased from about 0.97 to 0.5 emu with increasing current density. The coercivity measured in the perpendicular direction increased from about 300 to 900 Oe with increasing current density. Reasons for variation in magnetic properties and structural characteristics are discussed.

Keywords: CoMnP thin films, current density, magnetic saturation, coercivity.

INTRODUCTION

Magnetic films are interesting due to their many applications in the magnetic industry and they show various crystallographic and magnetic properties. Considerable interest has recently been aroused in the fabrication and the properties of nano-sized particles of magnetic materials [1-3]. Electro chemical Deposition technique has been shown to be very convenient for thin films because of its simplicity of use and low cost [4-5]. Recently, electro chemical processes have been widely used in electronic industries [6-13]. Computer read / writes heads [7-8], Micro Electro Mechanical Systems (MEMS) [9-11], Ultra Large Scale Integration devices (ULSI) [12-13] and electric circuit packaging [14]. The electro chemical process has many advantages over Vacuum process because of near operation, easy scale up and maintenance, low cost, relatively rapid deposition rate and the ability to "Tailor" deposit structure and properties [15]. One of the principle merits of electro deposition is that by varying the exact conditions of deposition, it is possible to fine tune the properties of the layer to suit specific requirements and to prepare Magnetic thin films, multilayer and nano wires. [16-18] i.e., the electrode position technique can provide multi component compounds with homogeneous compositions, so it has been employed to prepare various Magnetic materials. 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 co deposition, 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 [19-21]. 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 Digital Micrometer, 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 inorganic additive (NaH_2PO_2) on the magnetic properties was also studied.

MATERIALS AND METHODS

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: 0.4M; $MnCl_2$: 0.4M; NH_4Cl:1.8 M. 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 both the bath compositions A and B, CoMnP films were electrodeposited at constant pH value 3.00 by varying the current densities (3, 5 and 7$mAcm^{-2)}$ at room temperature. For various time durations (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.

RESULTS AND DISCUSSIONS

Elemental composition of the film was studied using energy dispersive spectroscopy (EDS). The EDS pattern of the sample is shown in Figure-1, which confirms the presence of Co, Mn and P. The Co content increases from about 77 to 97 Mass% at room temperature, with increasing current density until 7 $mAcm^{-2}$ whereas the Mn content decreased from about 0.67 to 0.17 Mass% with increasing current density until 7 $mAcm^{-2}$. The P content at about 0.5 Mass% was independent of current density.

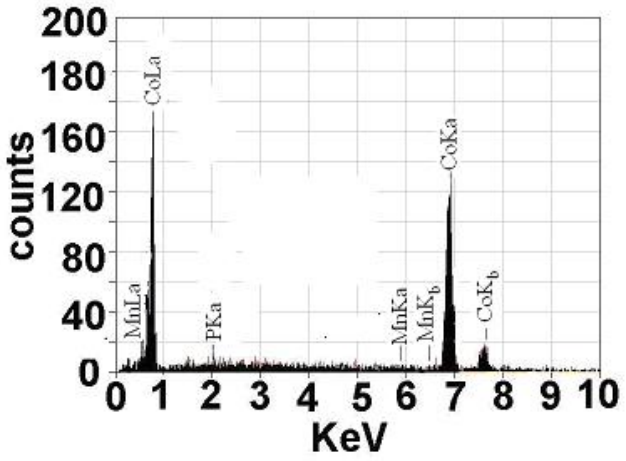

Figure-1. EDS Spectrum of electrodeposited CoMnP: time of deposition: 60 min; current density: 5 $mAcm^{-2}$; pH: 3 for bath A composition.

It was observed that the P concentration in both the Chloride Baths A and B was independent of current density measured at room temperature.

To study the influence of the current density on the structure of the electrodeposited CoMnP, XRD measurements were carried out. Figure-2(a), (b) and (c) shows the X-Ray Diffraction pattern of CoMnP film at current densities at 3, 5 and 7 $mAcm^{-2}$ and time duration of deposition (15, 30 and 60 Min) respectively. All XRD patterns have sharp peaks. The presence of sharp peaks indicates the crystalline of the sample. The electro deposits obtained from solutions containing lower concentrations of NaH_2PO_2 exhibited hcp structures with (201) and (301) planes with nanocrystalline size of 20 - 80 nm. Higher concentration of NaH_2PO_2 additive resulted with deposit nanocrystalline grains in the nano scale range. The apparent grain size is calculated using Debye-scherrer formula $d_{hkl} = K\lambda / \beta\cos\theta$, where K is the Scherrer constant with the value of 0.94, λ is the wavelength of the rays which is equal to 1.5406 A^0 for Cu target, θ is the Bragg's angle and β is the peak half width in radian unit. The sharp peak at 2θ and corresponding β was used to calculate the grain size of the alloy deposited and the grain size was found to be in nanoscale. These conditions appear to be closely related to increased deposit coercivity. The presence of bcc (200) and bcc (211) peaks confirmed the formation of alloys. From the XRD patterns, we know that all the peaks of the CoMnP films are consistent with the typical Co hcp and Mn bcc mixed phase. An increase in the current density yielded a decrease in the sharpness of the major peaks, as shown in Figure-2(a), (b) and (c). That is a decrease in the grain size of our samples. Also the peak position shifts to lower angle. Shifting of peak to lower angles indicate the increase in lattice constant with current density.

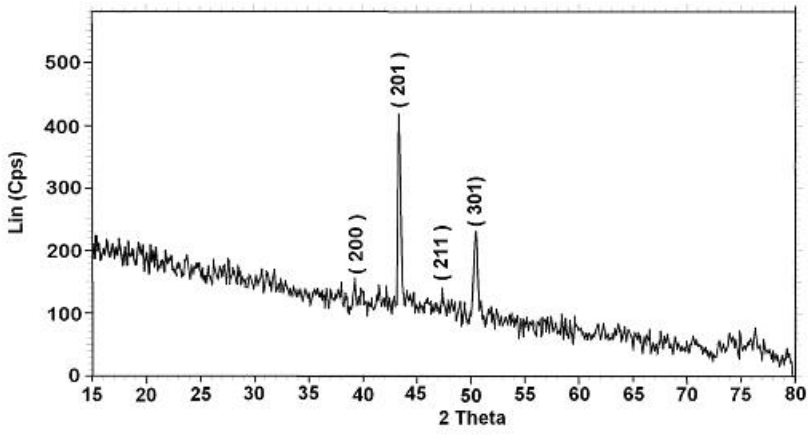

Figure-2(a). XRD pattern of electrodeposited CoMnP film; time of deposition: 30 min; current density: 3 $mAcm^{-2}$; pH: 3 for bath A composition.

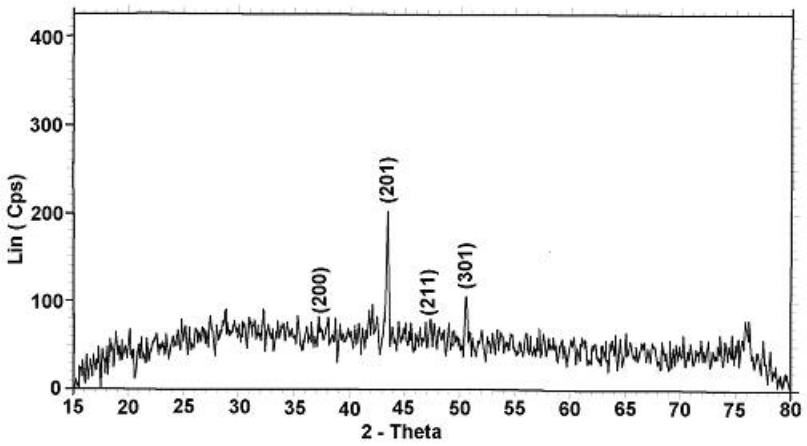

Figure-2(b). XRD pattern of electrodeposited CoMnP film; time of deposition: 60 Min; current density: 5 $mAcm^{-2}$; pH: 3 for bath B composition.

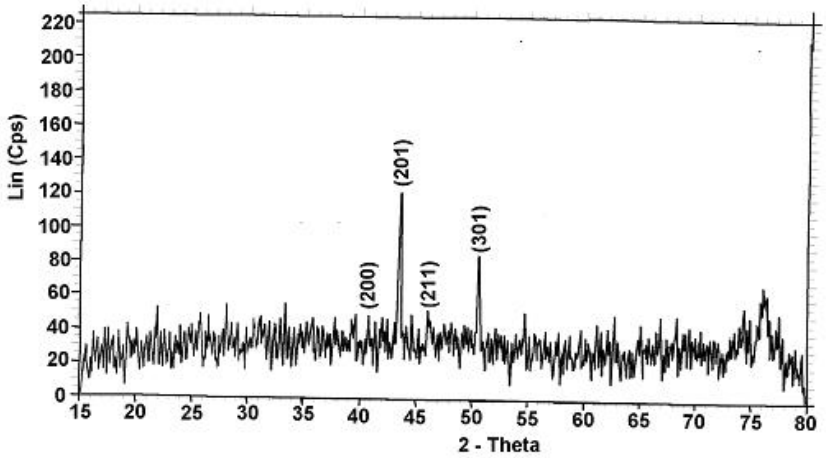

Figure-2(c). XRD pattern of electrodeposited CoMnP film; time of deposition: 30 min; current density: 7 $mAcm^{-2}$; pH: 3 for bath B composition.

Electrodeposited CoMnP thin films at various time of deposition (15, 30 and 60 min) at current densities 3, 5 and 7 $mAcm^{-2}$ were subjected to Scanning Electron Microscope (SEM) studies. SEM images for different combinations of current density and Time duration of deposition at constant pH = 3 are shown in Figure-3 (a), (b) and (c).

At low current density and time duration of deposition as in Figure-3(a), the surface is bright and rough with some cracks due to internal stress. At medium current density and at medium time duration of deposition as in Figure-3(b), the surface is uniform and bright with cracks due to internal stress. As in Figure-3(c), Alloys deposited at high current density and at high time duration of deposition have uniform granular structure on the smooth surface.

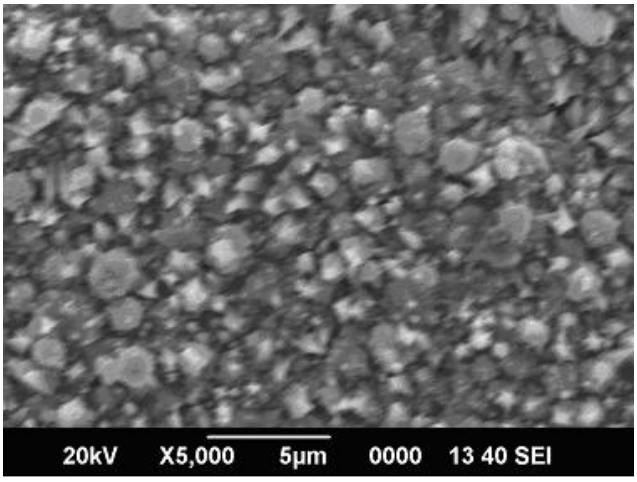

Figure-3(a). SEM image of electrodeposited CoMnP film; composition: bath A; time of deposition: 15 min; current density: 3 $mAcm^{-2}$; pH: 3.

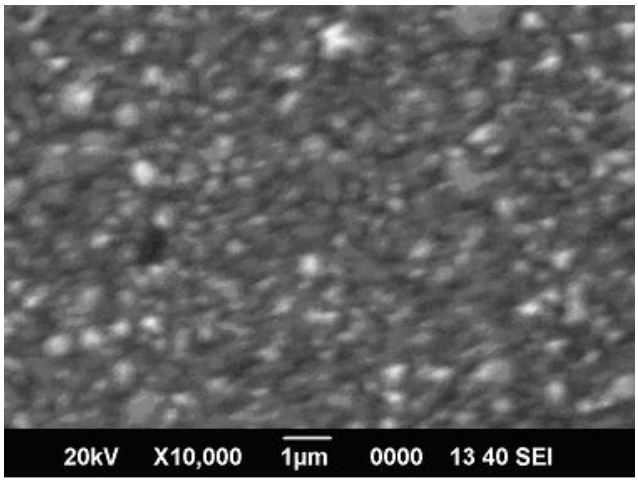

Figure-3(b). SEM image of electrodeposited CoMnP film; composition: bath B; time of deposition: 30 min; current density: 5 $mAcm^{-2}$; pH: 3.

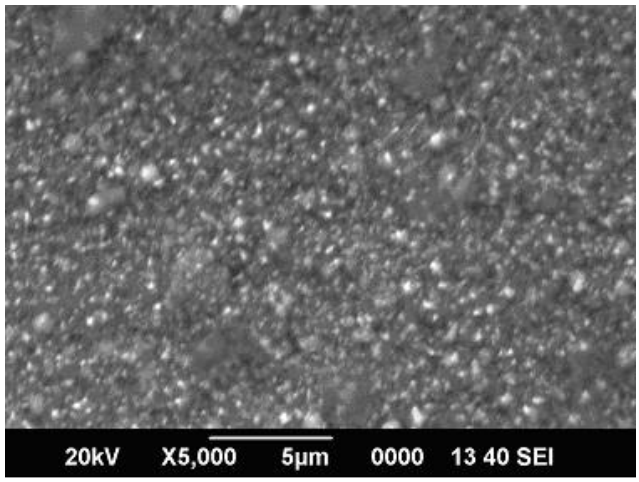

Figure-3(c). SEM image of electrodeposited CoMnP film; composition: bath B; time of deposition: 60 min; current density: 7 $mAcm^{-2}$; pH: 3.

Table-1. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for bath A.

Current density	Time of deposition	Thickness of deposit	Magnetic saturation	Remanent	Coercivity	Squareness
$mAcm^{-2}$	Min	micrometer	emu	emu	Oe	
3	15	0.3	0.97	0.03	300	0.030
3	30	0.8	0.90	0.04	350	0.044
3	60	1.2	0.80	0.05	400	0.062
5	15	0.4	0.65	0.06	550	0.077
5	30	0.7	0.78	0.07	600	0.097
5	60	1.8	0.72	0.12	700	0.179
7	15	0.5	0.65	0.14	800	0.215
7	30	1.3	0.60	0.17	850	0.283
7	60	2.7	0.50	0.23	900	0.460

Table-2. Effect of current density at room temperature on the thickness and magnetic properties of electrodeposited CoMnP thin films for bath B.

Current density	Time of deposition	Thickness of deposit	Magnetic saturation	Remanent	Coercivity	Squareness
$mAcm^{-2}$	Min	micrometer	emu	emu	Oe	
3	15	0.3	0.80	0.03	250	0.037
3	30	0.7	0.75	0.04	300	0.053
3	60	1.2	0.70	0.05	350	0.071
5	15	0.5	0.77	0.07	500	0.090
5	30	1.4	0.71	0.08	550	0.112
5	60	2.1	0.70	0.12	700	0.171
7	15	0.7	0.68	0.14	750	0.205
7	30	1.6	0.65	0.18	800	0.276
7	60	2.9	0.61	0.23	850	0.377

Tables 1 and 2 show the variation of the saturation magnetization (M_s) of electrodeposited CoMnP for bath A and B, respectively. The saturation Magnetisation varies from about 0.97 emu to 0.50 emu with increasing current density for bath A and varies from about 0.80 emu to 0.61 emu with increasing current density for bath B. The observed that the saturation magnetization variation is reasonable from the fact that the saturation magnetization is an intrinsic magnetic property which depends only on the film composition. It is observed that the saturation magnetization of electrodeposited CoMnP was independent of anion type and it varies with increasing P content.

Tables 1 and 2 show the variation of the coercivity (H_c) of electrodeposited CoMnP for bath A and B, respectively. The coercivity measured in perpendicular direction increased from about 300 Oe to 900 Oe with increasing current density for bath A and increased from about 250 Oe to 850 Oe with increasing current density for bath B. These magnetic properties could be related to the composition of the films. The compositions of Co content increased with increasing current density, so the film becomes more strongly ferromagnetic.

CONCLUSIONS

CoMnP films were electrodeposited from chloride bath. The effects of current density and duration of deposit on the CoMnP thin film properties were studied. As the current density and time of deposition of the bath increases the thickness of the film increases. XRD pattern revealed the presence of hcp and bcc phases in the deposit. The deposit are uniform, nanocrystalline in nature and granular in structure. Hard magnetic materials have been alloys based on cobalt because its hcp crystalline structure is highly anisotropic. Alloying element tend to concentrate at grain boundries. Thus, the resulting structure consists of isolated magnetic Co grains surrounded by weak magnetic boundries. Such micro structural formations increase the energy barrier for magnetic realignment of the domains and thereby increase the overall coercivity of the film, making them magnetically hard. In this study, it is observed that the deposit obtained at current density $7mAcm^{-2}$ and time duration of deposition 60 minutes was found to be so smooth and have no cracks with high corecivity value of 900 Oe. This CoMnP alloy deposited from the chloride bath can further be studied for its electrical and corrosion properties.

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