Mechanical and magnetic properties of nanostructured CoNiP films

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Abstract. The electroplating 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 electro-mechanical (MEMS) devices. Due to these potential applications, deposition of magnetic film draws special attention and it needs a cost-effective process. Electro-deposition being cost-effective, in the present work cobalt-based magnetic films were deposited electro-chemically and deposition characteristics were studied. Effect of concentration of organic additives such as urea and thiourea in the presence of sodium hypophosphite was studied. Surface characterisation was carried out using X-ray diffractometer (XRD) and scanning electron microscope (SEM). Elemental compositions of the films were studied using atomic absorption spectrometer (AAS) and showed phosphorous content was less than 1%. Samples were subjected to vibrating sample magnetometer (VSM) and studies showed that organic additive has altered magnetic properties of these films. The reason for change in magnetic properties and structural characteristics because of the additives were discussed. Mechanical properties such as residual stress, hardness and adhesion of the films were also examined and reported.

Keywords. Electro-deposition; CoNiP magnetic film; magnetic properties.

PACS No. 75.75.+a

1. Introduction

The importance of electro-deposition as a fabrication technology in the electronic industry is large and growing. With the current trends 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]. The electro-deposition technique is especially interesting due to its cost-effectiveness, easy maintenance and quality deposits.

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As CoNiP ternary alloy films are having hard magnetic properties various studies have been carried out to develop these magnetic films [5]. Electro-deposition provides an easy way to produce these films with high quality [6]. These kinds of films were electro-deposited on silicon by Munford *et al* [7] and they studied the morphology and magnetic properties of these films. They found a convenient method for fabricating thin magnetic films and magnetic sensors with silicon technology. Numerous such applications of CoNiP films were reported by many researchers [8–10].

Electroless deposition process has been studied by a number of investigators to develop CoNiP magnetic thin films for magnetic recording media applications [11,12]. However very few electro-deposition studies have been carried out in order to study the magnetic properties of these films at various electro-deposition conditions and also with additives [5].

In the present study, we investigate in detail the effect of electro-deposition conditions and various concentrations of urea and thiourea used in the bath, on the hard magnetic properties of these films by studying magnetization and demagnetization curves. In addition surface morphology, elemental composition, hardness and adhesion of the coating were also studied.

2. Experimental

A copper substrate of size (1.5×5.0 cm) as cathode and pure nickel of same size as anode were used for galvanostatic electro-deposition experiments. A regulated DC power supply was used to pass the required current. All the chemicals used were of AR grade. An adhesive tape was used to mask off all the substrate except the area on which deposition of thin film was desired. Each substrate was polished in a polishing wheel and de-greased using acetone. Just before electro-deposition these substrates were electrocleaned in an alkaline electrocleaning bath of sodium hydroxide: 7.0 g/L; sodium carbonate: 20.0 g/L; trisodium phosphate: 9.0 g/L and sodium metasilicate: 24.0 g/L. The bath was operated at 70°C and 3.0 A/dm^2 current density and then rinsed in distilled water. Electro-deposition was carried out with varying current densities and time of deposition.

CoNiP magnetic thin films were electro-deposited from the following bath compositions CoCl$_2$: 0.20 M, NiCl$_2$: 0.20 M, NH$_4$Cl: 0.25 M and NaH$_2$PO$_2$: 0.2 M. Hereafter the above bath composition will be referred to as 'solution A'. To this electrolyte organic additives like urea and thiourea were added in varying concentrations. In each concentration magnetic films were deposited to study the effect of organic additives on mechanical and magnetic properties of CoNiP films.

The pH of all the electro-deposited baths used in this work was found to be 3.0. The thickness of the deposits was tested using digital micrometer. Magnetic properties of the deposited films were studied using vibrating sample magnetometer (VSM). X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to study the surface morphology of these magnetic films. From XRD data crystallite size of the deposited CoNiP and film stress were studied. Percentage of elements such as Co, Ni and P present in the deposit were analysed using atomic absorption spectrometer (AAS). Hardness of the coating was calculated using a
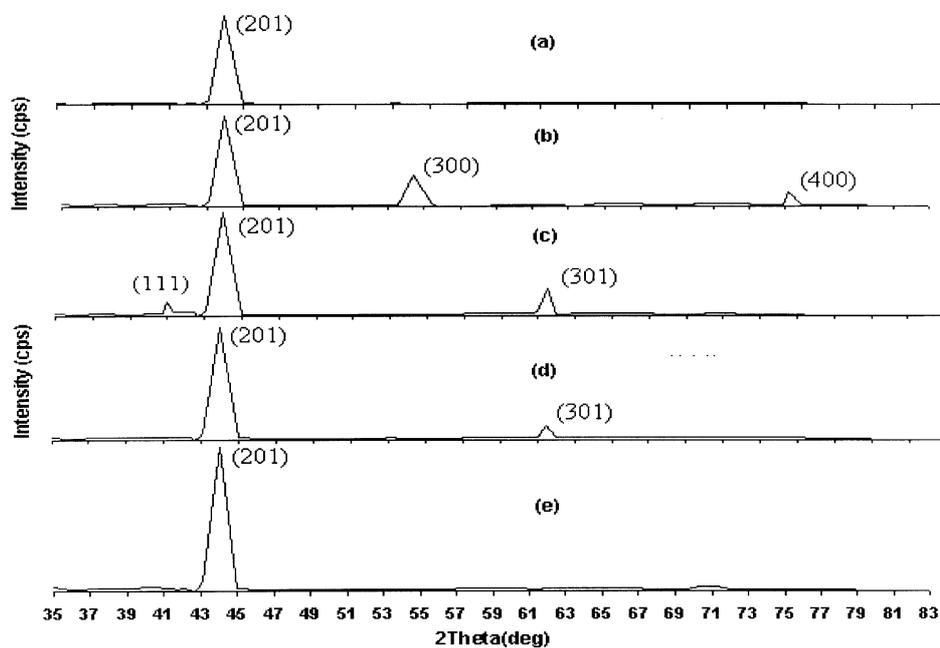
Figure 1. XRD patterns for electro-deposited CoNiP film at current density: 5.0 mA/cm^2 and for 60 min.

Vicker's hardness tester using diamond intender method. Adhesion of the film was tested by bend test (bending the film with substrate to 180°) 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 the tape then adhesion is poor).

3. Results and discussion

3.1 *Surface characterization*

X-ray diffraction patterns of various CoNiP electro-deposits produced from the following baths: (a) solution A, (b) solution A; urea: 2.5 g/L, (c) solution A; urea: 5.0 g/L, (d) solution A; thiourea: 2.5 g/L, (e) solution A; thiourea: 5.0 g/L for 5.0 mA/cm^2 and 60 min were fixed as current density and time of deposition respectively for electro-deposition (figure 1). 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 (2 0 1) plane pridominantly. The (2 0 1) plane peak is shifted in all XRD patterns due to film residual stress. In the case of films and metals XRD peaks will be shifted because of the stress of the material [13]. In the presence of additives few low intensity peaks were also observed for (3 0 0), (3 0 1) and (4 0 0) planes and this is because of the formation of intermetallic CoNiP compound (hcp) during electro-deposition.

Table 1. Effect of additives on the structural and mechanical properties of CoNiP film electrodeposited at 5.0 mA/cm^2 for 60 minutes.

Solution A		Crystalline size (nm)	Vickers hardness (VHN)	Internal stress (Mpa)	Film composition (at.%)		
					Co	Ni	P
Without additive		60	432	120	83.4	16.0	0.6
Additive concentration (g/L)							
Urea	2.5	50	440	110	84.0	15.8	0.2
	5.0	53	366	130	84.2	15.0	0.8
Thiourea	2.5	58	441	130	84.5	15.1	0.4
	5.0	62	396	150	84.0	15.1	0.9

From the XRD pattern peak, stress in the film was calculated using the formula: Youngs modulus = stress/strain. The results are shown in table 1. CoNiP 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 reliver. But on increasing concentration of urea and thiourea film stress is also 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 were calculated from the XRD pattern using the formula: Crystallite size = $0.9\lambda/B\cos\theta$. These values clearly show that the crystallite size of the CoNiP deposit obtained by electro-deposition process are in the nano scale. The crystallite size of the deposits are given in table 1. This analysis reveals the effect of urea on the crystallite size of the deposit.

Electro-deposited CoNiP films from all five conditions as mentioned in XRD studies were subjected to SEM studies. The micrographs are presented in figure 2. In general, microstructure of the CoNiP is greatly influenced by the percentage of phosphorus content. The film with very low concentration of phosphorus 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 (urea) was cracked through the substrate probably due to the high stress associated with the film because of the additive. Stress measurements from XRD pattern also supports this result. The film deposited without organic additive was also cracked because of the phosphorous content.

Elements present in the film were analysed by atomic absorption spectrometer and the results are presented in table 1. All deposits, which were subjected to analysis, have less than 1% phosphorous content. It was observed by Miksic *et al* [14] that the coercivity of CoNiP deposits increased with increasing film thickness when P is less than 2 wt %. CoNiP film produced from solution with 2.5 g/L urea has less than 2 wt %. Phosphorous and the coercivity values increased with increase in film thickness.
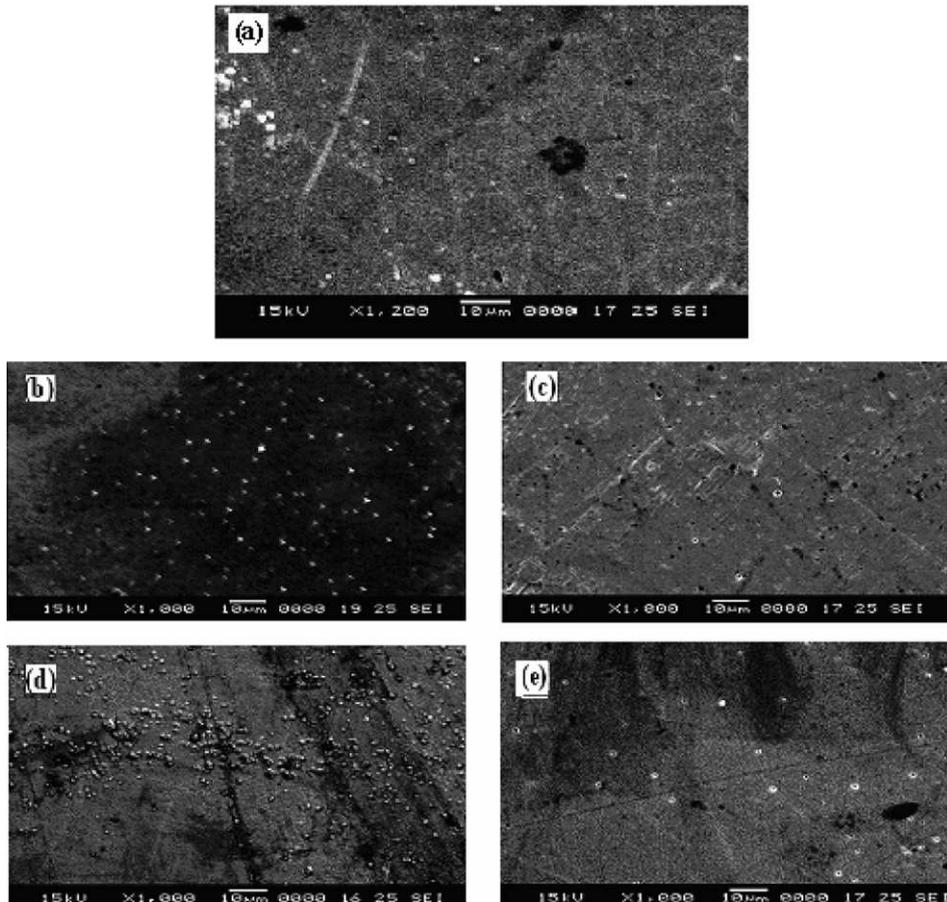
Figure 2. Electron micrographs of CoNiP films electro-deposited at 5.0 mA/cm^2 and for 60 min. (**a**) Solution A, with (**b**) urea: 2.5 g/L, (**c**) urea: 5.0 g/L, (**d**) thiourea: 2.5 g/L (**e**) thiourea: 5.0 g/L.

3.2 *Magnetic properties*

Electro-deposition studies were carried out using different concentrations of urea. Urea has been selected because urea and thiourea have been extensively studied as an electroplating additive in the plating perspective. Table 2 presents the results of electro-deposition of CoNiP and their magnetic properties. The bath used for deposition is solution A; and without 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.

With solution A various concentration of phosphorus source material and urea were added and electro-deposition studies were carried out. In all the

electro-deposition studies films produced were uniform and bright. This is because of additive, which will uniformly orient the crystallization process during deposition by adsorbing itself on the initially-deposited crystals.

Table 3 shows the effect of current density and time of deposition on the thickness and magnetic properties of CoNiP films electro-deposited from a bath having solution A and NaH_2PO_2: 0.2 M and urea: 2.5 g/L. Thickness of the deposit increases with increase in current density. The magnetic properties of films revealed

Table 2. Effect of current density and time of deposition on the thickness and magnetic properties of CoNiP film electro-deposited from solution A.

Current density (mA/cm^2)	Time of deposition (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity	Squareness
2.5	15	0.5	0.90	0.04	300	0.04
	30	1.0	0.85	0.05	400	0.05
	60	1.2	0.82	0.06	500	0.07
5.0	15	0.5	0.80	0.07	600	0.08
	30	1.0	0.77	0.08	750	0.10
	60	2.4	0.75	0.10	800	0.13
7.5	15	0.8	0.74	0.11	850	0.14
	30	1.9	0.72	0.13	930	0.18
	60	3.7	0.70	0.15	1000	0.21

Table 3. Effect of current density on the thickness and magnetic properties of CoNiP film electro-deposited for 60 min from solution A with additives.

Current density mA/cm^2	Additive concentration (g/L)		Thickness (μm)	Magnetic saturation (emu)	Remanent (emu)	Coercivity (Oe)	Squareness
	Urea	Thiourea					
2.5	2.5	0.0	2.5	1.08	0.20	1300	0.18
	0.0	2.5	3.0	0.43	0.10	800	0.23
	5.0	0.0	3.0	1.42	0.25	1100	0.17
	0.0	5.0	2.5	0.25	0.06	500	0.23
5.0	2.5	0.0	4.5	0.93	0.25	1700	0.26
	0.0	2.5	5.0	0.40	0.12	950	0.30
	5.0	0.0	5.0	1.38	0.30	1300	0.20
	0.0	5.0	4.7	0.20	0.08	650	0.40
7.5	2.5	0.0	8.0	0.79	0.30	2100	0.37
	0.0	2.5	8.0	0.39	0.15	1100	0.38
	5.0	0.0	9.0	1.34	0.40	1800	0.29
	0.0	5.0	6.5	0.16	0.10	800	0.60

that these films are having a high coercive and low remanent value when compared to the deposits obtained from films deposited from a bath without organic additive. Other values like magnetic saturation decreases with increase in thickness and squareness increases with increase in thickness. On increasing the concentration of urea to 5.0 g/L, thickness of the deposit increased with respect to current density. Coercivity values decreased when compared to films obtained from 2.5 g/L urea containing solution. Remanent value increased at higher current densities. The change in magnetic properties was because of the stress present in the magnetic film at higher concentration of urea.

Effect of current density on the thickness and magnetic properties of CoNiP films electro-deposited from a bath having solution A and thiourea: 2.5 g/L is given in table 3. 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 without organic additive. On increasing the concentration of thiourea to 5.0 g/L, thickness of the deposit increased with respect to current density. Coercivity values decreased.

Figure 3a shows the effect of current density on coercivity for all baths under study with additive for electro-deposition. This figure clearly shows that coercivity values increase with increase in current density for all four types of baths under study. It also clearly reveals that increase in the concentration of urea decreases coercivity. The same type of results was noted from figure 3b, which is a plot between time of deposition and coercivity.

Figures 3c and 3d show 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 value increases. On increasing the concentration of NaH_2PO_2 it reduced even with an increase in the concentration of urea. From this it may be understood that at lower concentration of NaH_2PO_2 the role of additive is more. Magnetic saturation of these films decreases with increase in current density and time of deposition. This is shown in figures 3e and 3f.

As the average crystallite size of these films are in the nano scale, considerable changes in the magnetic behaviour can occur. When the crystallite size is reduced to the extent that the domain wall thickness is comparable to the crystallite size, the coercivity is found to decrease. But in the present work the coercivity increases when crystallite size approaches high nano level. This is mainly due to the low phosphorous content in the deposit, which was produced from a bath having urea with 2.5 g/L concentrations. Analysis of crystallite size, microstructure and magnetic properties confirm that the origin of magnetic properties is because of the strongly interacting array of single domain crystals. This is mainly due to the presence of phosphorous, which was incorporated into the film at the required level by the additive.

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
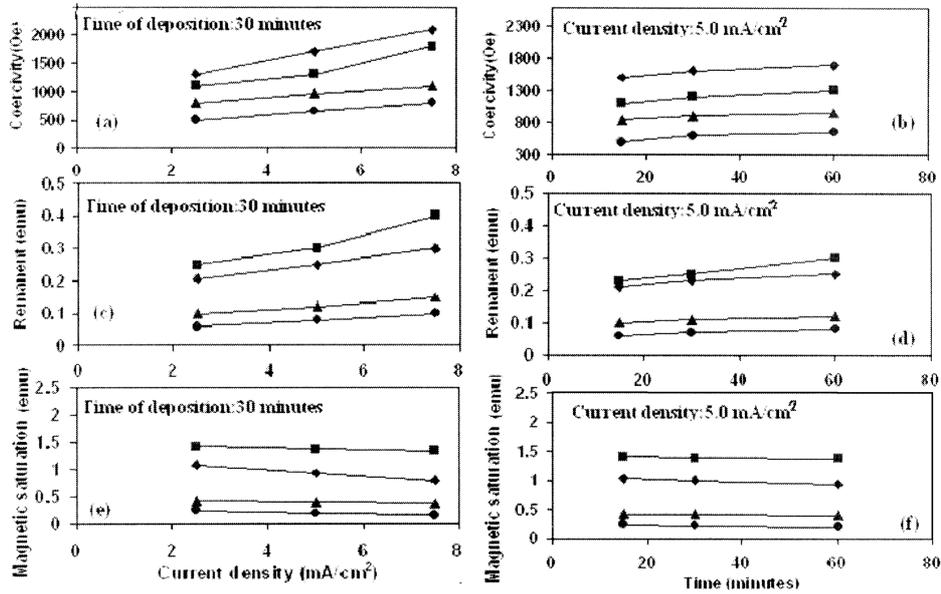
Figure 3. Effect of current density (left) and time of deposition (right) on film thickness, coercivity, remanent magnetic saturation of CoNiP films electro-deposited from solution A and with (—◆—) urea: 2.5 g/L, (—■—) urea: 5.0 g/L, (—▲—) thiourea: 2.5 g/L, (—●—) thiourea: 5.0 g/L.

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 CoNiP film, when it is electro-deposited from a bath containing higher concentration of organic additive. Relatively high hardness values for these alloy deposits and their conventional alloy is due to the fact that nanocrystalline alloys offer significantly increased strength and hardness.

4. Conclusion

A CoNiP film having good hard magnetic properties can be electro-deposited from a bath containing the following composition: $CoCl_2$: 0.2 M, $NiCl_2$: 0.2 M, NH_4Cl: 0.25 M, NaH_2PO_2: 0.2 M and urea: 2.5 g/L at current density of 5.0 mA/cm^2. Increase in the concentration of phosphorous and urea 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 increase in urea concentration. But organic additives like urea in low concentration will produce a good CoNiP film, which can be used in MEMS devices, because these films 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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