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EFFECT OF TEMPERATURE AND ADDITIVES ON ELECTRODEPOSITED CoWP MAGNETIC THIN FILM

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CoWP thin films were electrodeposited in the presence of urea as additive and sodium hypo phosphate as a precursor with a fixed concentration were studied with respect to thickness of the films. It was electrodeposited in various temperature and current densities and for different time in order to get uniform deposits. Vibrating sample magnetometer studies indicate the magnetic saturation(M_s), retentivity (M_r) and coercivity(H_c) of these films. If the temperature was increased remnant polarization (retentivity M_r) of the film also increased. Additive has made a favorable change in the magnetic properties of the film. From XRD data crystallite size of the deposited CoWP and film stress was calculated. Percentage of elemental analysis of CoWP film was obtained by EDAX. Hardness and adhesion of the deposit was obtained by Vicker hardness tester method. Surface morphology analysis was carried out using SEM. Addition of additive should change the morphological structure of the film and produce nano range of average particles. Difference in magnetic properties and structural characteristics are discussed.

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1. Introduction

The method of electrodeposition is large and growing in the electronics industry. The current trends towards miniaturization, cost competitiveness and high performance packaging, electrodeposition has become the dominant manufacturing technology in many new applications and remains firmly established in others such as micro electromechanical system (MEMS) devices, nano electromechanical system(NEMS) devices, magnetic recording head and data storage media [1-4] . The electrodeposition technique is quite advantageous due to its cost effectiveness, easy maintenance and quality deposits.

CoWP films have promising applications as a thin layer above the copper substrate in microelectronic devices and micro electro mechanical systems (MEMS) to prevent copper from oxidation and diffusion [5-11]. CoWP films can also be useful for other applications. CoP is known to have good magnetic properties and has been used recently in integrated sensors and inductors [12-13]. CoW films show some promising physical and mechanical properties such as exceptional hardness, wear and corrosion resistances [14-15]. Therefore, it is envisaged that, with appropriate composition CoWP films may exhibit superior and unique properties and can be utilized as coatings in sophisticated electronic and automobile industries, rocketry and space technology.

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There are some reports in the literature on the fabrication of CoWP films on a copper substrate by electroless deposition from aqueous solution [5-11. It has been claimed that tungsten and phosphorus cannot be electrodeposited individually from aqueous electrolyte [14]. However, tungsten and phosphorus can be codeposited from aqueous electrolyte containing iron group metals (Fe, Co, Ni), which is termed 'induced co-deposition' [14] There are also some reports in the literature on the electrodeposition of CoP [16-18], NiCoP [19,20] and CoW [21,22] films

In the present study we investigated in detail the effects of electrodeposition conditions on the magnetic properties of CoWP. The effects of temperature and current density with constant urea and phosphorous source material in the bath were also investigated.

2. Experimental details

A copper substrate of size 1.5 x 5c.m as cathode and platinum plate is used as anode for galvanostatic electrodeposition method. A d.c current for electrodepostion was passed from a regulated power supply. Analytical grade chemicals were used to prepare bath solution. An adhesive tape was used as mask for all the substrate expect the area on which depositon of film was desired. The copper electrode was buffed for removing scratches in a mechanical polishing wheel using a buffing cloth with aluminum oxide abrasive. After buffed the substrates were cleaned by con H_2So_4 or acetone. Before electrodeposition, these substrates were electro cleaning in an alkaline electro cleaning bath after that the substrates were rinsed in distilled water. Electrodeposion was done by different current density and deposition time.

Electrodeposition of cobalt-tungsten-phosphorus magnetic thin film was plated from a bath contained cobalt sulphate ($CoSO_4.7H_2O$) 0.1 M, sodium tungstate ($Na_2WO_4.2H_2O$) 0.05 M, and tri sodium citrate ($Na_3C_6H_5O_7.2H_2O$) 0.3M, with this composition 0.1 M of sodium hypo phosphate (NaH_2PO_2) and 5.0 g l^{-1} of urea were added to this bath and their effect on the properties of CoWP films was investigated with different temperature as 30ºC, 50ºC and 70ºC. The pH of all electrodeposition baths used in this work was found to be 8.0.The thickness of the deposits was tested using digital micrometer (Mitutoyo , Japan). Magnetic properties of deposited films were studied using vibrating sample magnetometry. X-ray diffractometry (XRD) Rich Seifert, Germany of model 3000 and scanning electron microscopy (SEM) Mosumy Electronics Japan make JEOL were used to study the structure and morphology of these magnetic films respectively. From XRD data crystallite size of the deposited CoWP and film stress was calculated. Percentage of elemental analysis of CoWP film was used by EDAX. Hardness of the deposit was obtained by Vicker hardness tester using diamond intender method. Adhesion of the film was tested by bend and by scratch or chisel test. These tests are widely used in the field of electroplating.

3. Result and Discussion

3.1. Magnetic studies

In general increasing temperature and current density with the time of deposition was found to have little effect on the thickness of the film. However the magnetic properties of the film were found to decrease significantly. On increasing the temp and time the coercivity was found to decrease from 393.9Oe (serial number:14) to 207Oe (serialnumber:26). The morphology of the film however was found to be poor when the electrodeposition bath has room temperature. The effect of temperature was also investigated. Under the best conditions involving addition of 0.1 M of NaH_2PO_2 and 5 g l^{-1} of urea at a current density of 5mA cm^{-2} and time of deposition 30 min with 50ºC temperature, the thickness of the film was found to be 3.0 μm with coercive and remanent values of 393.9 and 0.286 emu (serial number: 14) respectively.

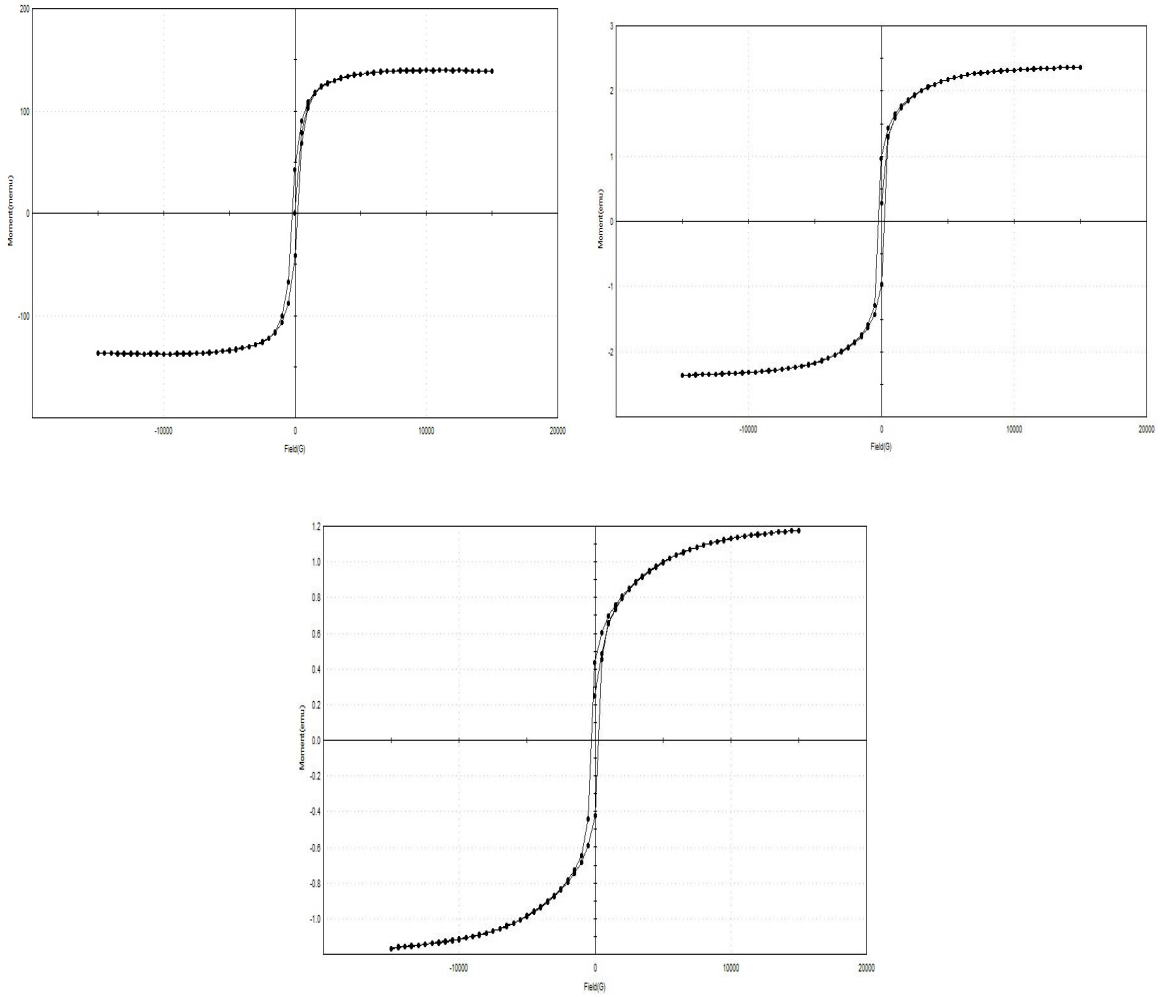

Fig. 1. VSM images of CoWP films electrodeposited for 45 min at 5.0 mA cm^{-2} with 0.1 M NaH_2PO_2 and 5.0 g l^{-1} urea (a) 30 ºC (b) 50 ºC (c) 70 ºC

Table 1: Effect of Temperature and current density on the thickness and magnetic properties of CoWP film electrodeposited for 0.1M of NaH_2PO_2 and 5g/l of urea

S.No	Temp (ºC)	Current density (mA cm^{-2})	Deposition Time (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent polarization (emu)	Coercivity (Oe)	Squareness
1		2.5	15	0.5	0.026	0.011	110.4	0.42
2			30	1.0	0.071	0.020	164.8	0.28
3			45	1.8	0.112	0.024	206.7	0.21
4	30	5.0	15	0.6	0.106	0.035	134.9	0.33
5			30	1.5	0.132	0.041	190.6	0.31
6			45	2.1	0.205	0.042	324.2	0.21
7		7.5	15	1.2	0.087	0.021	148.7	0.24
8			30	2.5	0.106	0.029	170.5	0.27
9			45	3.8	0.299	0.087	361.0	0.29
10		2.5	15	0.6	0.514	0.094	160.4	0.18
11			30	1.5	0.721	0.242	217.1	0.34
12			45	2.5	1.197	0.523	233.2	0.44
13	50	5.0	15	1.0	0.658	0.126	185.5	0.19
14			30	3.0	0.911	0.286	393.9	0.31
15			45	4.5	1.171	0.430	245.5	0.37
16		7.5	15	1.5	0.735	0.261	201.8	0.36
17			30	4.0	1.159	0.534	224.5	0.46
18			45	6.0	1.089	0.342	332.4	0.31
19		2.5	15	0.8	0.862	0.168	170.2	0.19
20			30	2.0	1.001	0.250	217.1	0.25
21			45	3.5	1.530	0.356	293.8	0.23
22	70	5.0	15	1.5	0.971	0.198	184.2	0.20
23			30	5.0	1.078	0.352	233.5	0.33
24			45	8.0	2.362	0.961	214.0	0.41
25		7.5	15	2.0	1.015	0.248	197.2	0.24
26			30	4.5	1.182	0.298	207.0	0.25
27			45	7.5	2.193	0.542	235.7	0.25

Increase in magnetic properties of the films is mainly due to temperature and current density. The electrodeposited films were uniform and bright. The urea molecules thus are found to have leveling effect, which ensures uniform orientation of crystals during electrodeposition. Magnetic properties of the films are increased by increasing the temperature. It was because of the stress present in the films, which was caused by the inclusion of decomposed products of additives

3.2. Structural analysis

Electrodeposited CoWP films were subjected to XRD studies. The X-ray wavelength used was 1.5405 A° of Cu Kα radiation. The XRD data is obtained from the serial numbers 6, 15 and 24 of Table 1 were studied for their structural characteristics. These data were compared with Joint committee for powder diffraction studies data. CoWP films had indicated multilayer hcp of Co_3W (220) and CoP_3(411) plane peaks in the data for films obtained from serial numbers 6 and 24 were shifted because of the film stress is shown in the fig 2. It was known that film stress will shift XRD peaks [24]. Stress of the films were calculated from XRD data using the formula i.e., Youngs modulus=stress / strain. The results are shown in table 2; Stress was low for film obtained from the room temperature. It increased on increasing the electrolyte temperature. Crystallite sizes were also low for films obtained from the room temperature. These were calculated from XRD data using the formula i.e., crystallite size = $0.9\lambda/B\cos\theta$. Crystallite sizes thus obtained were in the nano scale and it was shown in Table2.

Table.2.Crystalline size, hardness and composition of CoWP films for different Temperature for 0.1M of NaH_2PO_2 and 5g/l of urea with 5mA cm^{-2} current density at 45minutes

Temp (ºC)	Crystalline size (nm)	Stress (Mpa)	Vicker Hardness (VHN)	Film Composition (at %)		
				Co	W	P
30	20.6	83.6	192	82.33	17.65	0.02
50	21.5	87.2	196	89.07	9.37	1.56
70	24.8	94.9	211	83.34	11.68	4.98

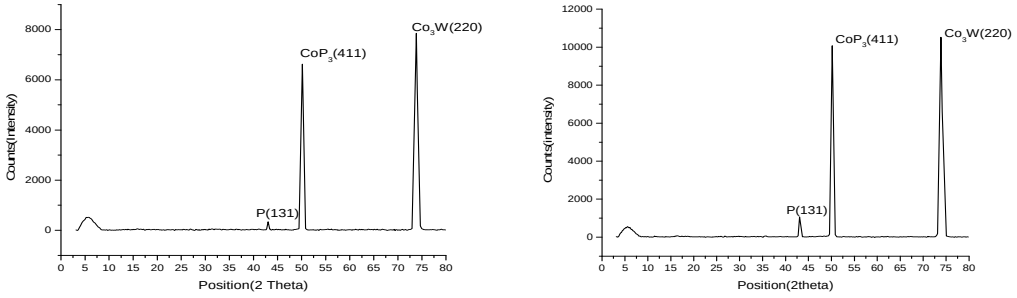

Fig.2. XRD images of CoWP films electrodeposited for 45 min at 5.0 mA cm^{-2} with 0.1M NaH_2PO_2 and 5 g/l Urea a) 30ºC , b) 70 ºC

3.3. Morphological observation

Electrodeposited CoWP films obtained from experiment numbers 6, 15, and 24 of table1 were subjected to SEM. The micrographs are presented in fig3. The crystallinity and roughness of CoWP films are mainly dependent on the amounts of phosphorus and tungsten present in the films which increase with decreasing cobalt and increasing tungsten and phosphorus contents. The film with very low concentration of phosphorus, Fig3.(a) and (b) appeared to have a crevice pattern. The film obtained from 70ºC of temperature was cracked through substrate due to stress of the film as shown in Fig 3(c)

3.4. Mechanical properties

CoWP films, which were selected for XRD and SEM studies, were tested for their Vicker's hardness number. The results are reported in Table 2. In constant bath additives concentrations with increasing temperature are increased the hardness of the film. It was due to the stress present in the film, which caused minute cracks in the structure. Adhesion of the film with the substrate was found to be good.

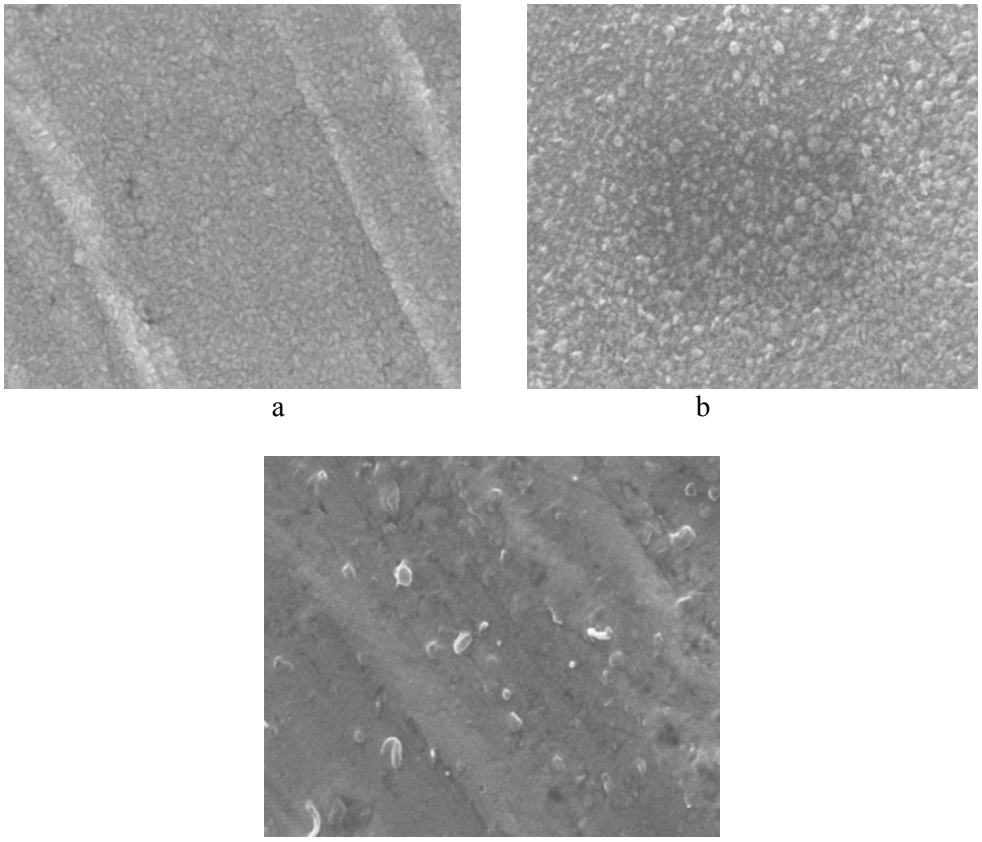

Fig.3. SEM images of CoWP films electrodeposited for 45 min at 5.0 mA cm^{-2} with 0.1 M NaH_2PO_2 and 5.0 g l^{-1} urea (a) 30 ºC (b) 50 ºC (c) 70 ºC

3.5. Elemental analysis

The percentage of film composition from the result of EDAX was reported in Table 2. It was observed that the percentage of phosphorous is increased by increasing the temperature. Similarly the percentage of tungsten is decreased by increasing temperature at constant bath additives. Even with low tungsten content of the films showed high magnetic properties. It was due to the addition of urea in the bath, which improved the crystalline structure of CoWP films.

4. Conclusions

A CoWP film with high hard magnetic properties can be obtained by galvanostatic electrodeposition process. The bath required for electrodeposition contained $CoSO_4.7H_2O$ - 0.1 M, $Na_2WO_4.2H_2O$ - 0.05 M, $Na_3C_6H_5O_7.2H_2O$ - 0.3M, with this composition 0.1 M NaH_2PO_2 and 5.0 g/l of urea. The current density for the deposition was 2.5, 5.0 &7.5 mA cm^{-2}. The temperature of the electrolyte increased the coercive value of the film. The high coercive value obtained in this work was 393.9Oe. This is because of the percentage of the bath additives with moderate temperature, which ensures uniform orientation of crystals during electrodeposition. In 50ºC temperature of electrolyte obtain a CoWP film with improved magnetic, structural and mechanical properties.

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