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Effect of additives on electrodeposited CoWP magnetic nano thin film

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CoWP thin films have electrodeposited in the presence of urea as additive and sodium hypo phosphate as a precursor with a fixed concentration has studied respectively to thickness of the films. It was electrodeposited in various current densities and for different time in order to get uniform deposits. Vibrating sample magnetometer studies indicate that the additive has favorable impact on the magnetic properties of these films. Elemental composition of the films was obtained by using EDAX. Structural and surface morphology analysis was carried out using XRD and SEM respectively. Difference in magnetic properties and structural characteristics are discussed. Hardness and adhesion of the film were also studied.

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1. Introduction

The method of electrodeposition is large and growing in the electronics industry. The current trend towards miniaturization, cost competitiveness and high performance packaging, electrodeposition has become the dominant manufacturing technology in all new applications and remaining 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 which applied above the copper substrate in microelectronic devices and micro electro mechanical systems (MEMS) that 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 film shows that some promising physical and mechanical properties such as exceptional hardness, wear and corrosion resistances [14-15]. Therefore, it is envisaged, with appropriate composition CoWP films may exhibit superior and unique properties that can be utilized as coatings in sophisticated electronic, automobile industries, rocketry and space technology.

A literature has done on the fabrication of CoWP films on a copper substrate which is used by electroless deposition from aqueous solution [5-11]. It has been found that phosphorus in the CoWP layer plays a prominent role against the diffusion of copper by 'stuffing' the grain boundaries of the barrier/capping layers, even though it's containing more than 12 at.% phosphorus cannot be plated by electroless deposition[16]. It has been claimed that tungsten and phosphorus cann't be electrodeposited individually from aqueous electrolyte [14]. However, tungsten and phosphorus can be co-deposited from aqueous electrolyte is containing iron group metals (Fe, Co, Ni), which is entitled 'induced co-deposition' [14] There are also some literary reports in the the electrodeposition of CoP [17-19], NiCoP [20,21] and CoW [22,23] films

The present study has investigated that the effects of electrodeposition conditions on the magnetic properties of CoWP, similarly the effects of concentration of urea and phosphorous source material in the bath

2. Materials and methods

A copper substrate of size 1.5X 5 c.m as cathode and platinum plate is used as anode for galvanostatic electrodeposition method. A d.c current for electrodepostion has 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 except the area on which deposition of film desired. The copper electrode was buffed for removing scratches by using mechanical polishing wheel with a buffing cloth containing aluminum oxide abrasive. After buffed the substrates were cleaned by con H_2So_4 or acetone. Before electrodeposition, these substrates were cleaned in an alkaline electro cleaning bath then the substrates were rinsed in distilled water. The electrodeposion was done by different current density and deposition time.

Electrodeposition of CoWP 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 0.05 and 0.1 M of sodium hypo phosphate (NaH_2PO_2) and 2.5 and 5.0 g l^{-1} of urea were added and the studied effect on the properties of CoWP films. The pH of all electrodeposition baths value to be fixed 8.0.

The thickness of the deposit was measuring by using digital micrometer (Mitutoyo , Japan). Magnetic properties of deposited films were studied with vibrating sample magnetometry. In this technique the material has kept in a sample holder, which was centered in the region between the pole pieces of a laboratory magnet. A slender vertical sample rod connects the sample holder with a transducer assembly. The transducer converts a sinusoidal alternating current drive signal into a sinusoidal vertical vibration of the sample rod. Coils mounted on the pole pieces of the magnet to pick up the signal from the sample motion. 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 the magnetic films. The crystallite size of the deposited CoWP and stress has been calculated from the XRD data. Percentage of elemental analysis of CoWP was explored by EDAX. Hardness of the deposit was obtained using Vicker hardness tester through diamond intender method. Adhesion of the film was tested by chisel test. The above tests are widely used in the field of electroplating

3. Result and discussion

3.1. Thickness Study

It shows the effect of concentration of NaH_2PO_2, urea, current density and deposition time on the thickness obtained under different experimental conditions. In the absence of urea the thickness of the film is increased with increase in current density and also increase in deposition time. However the electrodeposited film had poor magnetic properties. For example the best coercive and remanent obtained in the absence of urea were found to be 17,486A m^{-1} and 0.306 emu (serial number: 8) respectively.

3.2. Surface analysis

3.2.1. Structural analysis

Electrodeposited CoWP films were subjected to XRD studies. The X-ray wavelength was 1.5405 A° of Cu Kα radiation. The XRD data was obtained from the serial numbers 6, 15, 24, 33 and 42 of Table 2 were studied for their structural characteristics. These data has compared with Joint committee for powder diffraction data. CoWP films were indicated multilayer hcp of Co_3W (220) and CoP_3 (411) plane peaks in the data obtained from serial numbers 24 and 42 were shifted because of the film stress is shown in the fig 1. It was known that film stress will migrate to 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 table1; Stress was low obtained from a bath contained 2.5 g l^{-1} of urea. If the urea concentration increases to 5.0 g l^{-1}, the stress also will be increased. It is due to the incorporation of decomposed products of additive in the film. Crystallite sizes were also low obtained from 2.5gl^{-1} urea with 0.1M of NaH_2PO_2. These were calculated from XRD data applying the formula i.e., crystallite size=$0.9\lambda/\beta\cos\theta$. Hence crystallite sizes were obtained in the nano scale and it was shown in Table1.

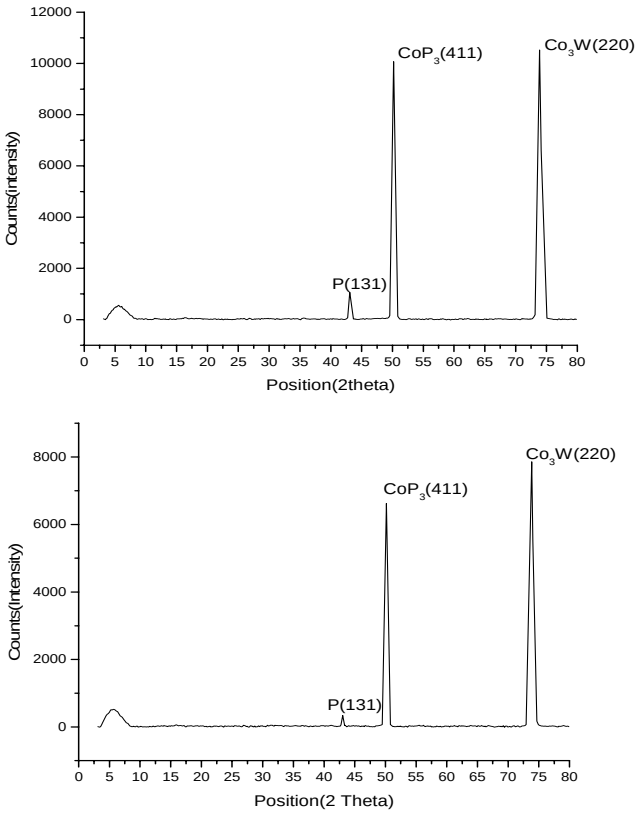

Fig.1. X-rd images of CoWP films electrodeposited for 45 min at 5.0 mA cm^{-2} with 5 g/l Urea a) 0.05 M NaH_2PO_2 , b) 0.1M NaH_2PO_2

Table.1.Crystalline size, hardness and composition of CoWP films for different bath additives for 45minutes at 5mAcm^{-2}

Bath additives		Crystalline size (nm)	Stress (MPa)	Vicker Hardnss (VHS)	Film Composition (at %)		
NaH_2PO_2 (M)	Urea (g/l)				Co	W	P
0.05	0.0	19.8	84.1	192	82.33	17.65	0.02
0.05	2.5	20.7	83.6	180	84.55	15.4	0.05
0.05	5.0	20.84	89.4	185	89.07	9.37	1.56
0.1	2.5	19.41	82.5	189	88.67	9.33	2.00
0.1	5.0	20.65	83.6	192	83.34	11.68	4.98

3.2.2. Morphological observation

Electrodeposited CoWP films obtained from experiment numbers 6, 15, 24, 33 and 42 of table2 were subjected to SEM. The micrographs are presented in fig2. The crystallinity and roughness of CoWP film mainly depends on the amount of phosphorus and tungsten which are present in the film. The crystallinity and roughness may increase when decreasing cobalt (or) increasing tungsten and phosphorus contents. The film has low concentration of phosphorus in Fig2.(a) and (b) appeared to have a crevice pattern. The film was obtained from a bath contained 5.0 g l^{-1} of urea cracked through substrate due to stress of the film as shown in Fig 2(c) and (f)

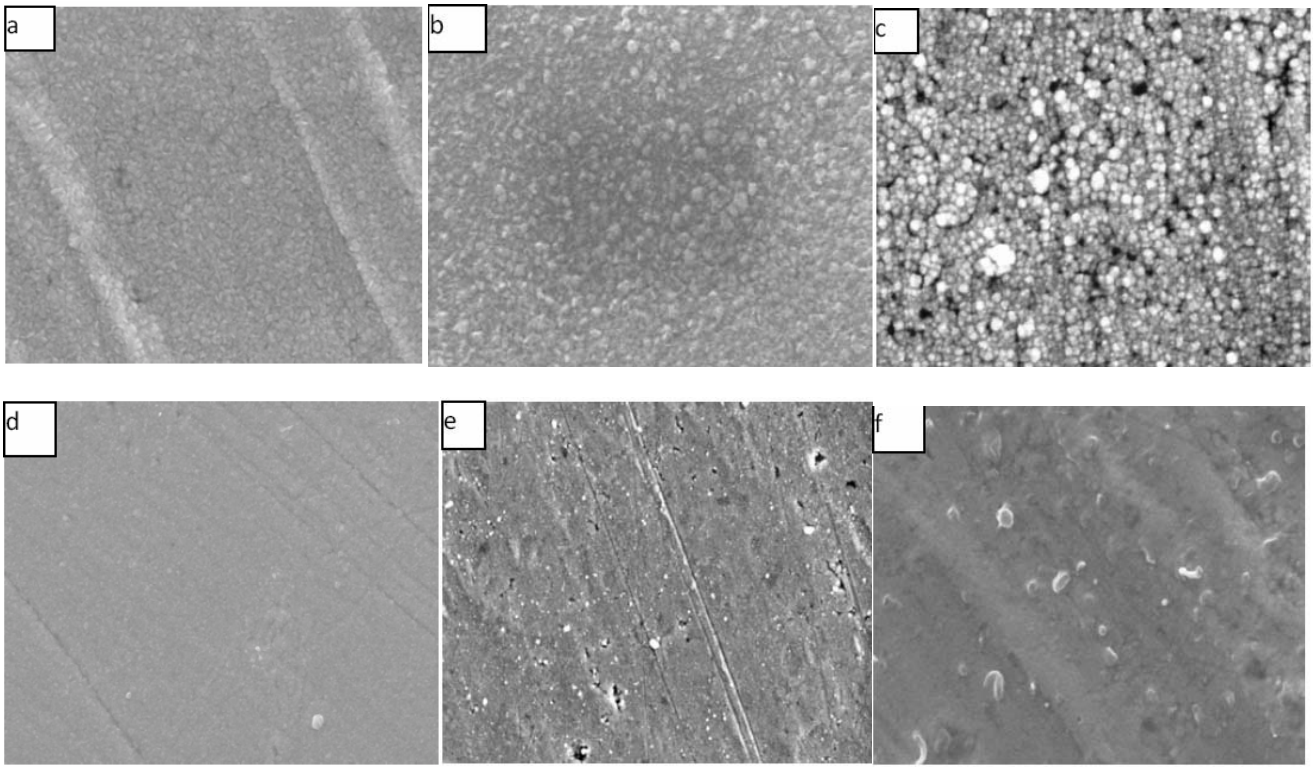

Fig.2 . SEM images of CoWP films electrodeposited for 45 min at 5.0 mA cm^{-2} with 0.05 M NaH_2PO_2 and (a) 0 (b) 2.5 (c) 5.0 g l^{-1} urea and 0.1M NaH_2PO_2 and (d) 0 (e) 2.5 (f) 5.0 g l^{-1} urea.

3.3. Magnetic Studies

In general NaH_2PO_2 addition 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 concentration of NaH_2PO_2 from 0.05 to 0.1 M the coercivity was increased from 14756 A m^{-1} (Serial number: 15) to 19780 A m^{-1} (Serial number: 33). The morphology of the film was found poor when no urea in the electrodeposition bath. The effect of addition of urea was also investigated along with NaH_2PO_2. With the addition of low concentration of urea, and its deposit characteristics as well as magnetic properties improved significantly. Under the best conditions, when involving addition of 0.1 M of NaH_2PO_2 and 5 g l^{-1} of urea at a current density of 7.5 mA cm^{-2} and deposition time about 45 min, then the thickness of the film was found to be 7.9 μm with coercive and remanent values of 44646Am^{-1} and 0.087 emu [serial number: 45] respectively

Table 2: Effect of NaH_2PO_2 and urea on the thickness and magnetic properties of CoWP film electrodeposited for different time and current density

S.No	Bath additives		Current density (mA cm^{-2})	Deposition Time (min)	Thickness of deposit (μm)	Magnetic saturation (emu)	Remanent polarization (emu)	Coercivity (Oe)	Squareness
	NaH_2PO_2 (M)	Urea (g l^{-1})							
1		0.0	2.5	15	0.5	0.516	0.221	16552	0.42
2				30	1.0	0.533	0.251	17624	0.47
3				45	1.8	0.542	0.271	18073	0.50
4			5.0	15	0.6	0.254	0.154	15641	0.60
5				30	1.5	0.314	0.176	16312	0.56
6				45	2.1	0.419	0.195	18092	0.46
7			7.5	15	1.2	0.586	0.273	16580	0.47
8				30	2.5	0.605	0.306	17456	0.51
9				45	3.8	0.669	0.289	18944	0.43
10	0.05	2.5	2.5	15	0.6	0.512	0.232	18124	0.45
11				30	1.5	0.525	0.248	18993	0.47
12				45	2.5	0.532	0.262	19740	0.49
13			5.0	15	1.0	0.051	0.030	14324	0.58
14				30	3.0	0.065	0.032	14712	0.49
15				45	4.5	0.134	0.063	14756	0.47
16			7.5	15	1.5	0.098	0.051	15721	0.52
17				30	4.0	0.166	0.064	16354	0.39
18				45	6.0	0.365	0.170	17394	0.47
19		5.0	2.5	15	0.8	0.186	0.071	17121	0.38
20				30	2.0	0.203	0.086	17850	0.42
21				45	3.5	0.213	0-099	18256	0.46
22			5.0	15	1.5	0.197	0.081	18551	0.41
23				30	5.0	0.216	0.098	19124	0.45
24				45	8.0	0.165	0.078	19650	0.47
25			7.5	15	2.0	0.114	0.042	20145	0.37
26				30	4.5	0.147	0.061	20994	0.41
27				45	7.5	0.297	0.145	21367	0.49
28	0.1	2.5	2.5	15	0.7	0.779	0.289	14235	0.37
29				30	1.8	0.801	0.316	15289	0.39
30				45	3.5	0.818	0.344	16868	0.42
31			5.0	15	1.0	0.187	0.058	17240	0.31
32				30	2.5	0.209	0.071	18250	0.34
33				45	4.1	0.114	0.042	19780	0.37
34			7.5	15	1.2	0.101	0.063	21657	0.62
35				30	3.5	0.151	0.084	23032	0.55
36				45	7.0	0.204	0.070	24184	0.34
37		5.0	2.5	15	1.0	0.026	0.011	17689	0.42
38				30	3.4	0.071	0.020	18872	0.28
39				45	5.5	0.112	0.024	19554	0.21
40			5.0	15	1.5	0.106	0.035	19997	0.33
41				30	3.5	0.132	0.041	20784	0.31
42				45	7.5	0.205	0.042	21881	0.21
43			7.5	15	2.0	0.087	0.021	25802	0.24
44				30	4.3	0.106	0.029	32885	0.27
45				45	7.9	0.399	0.087	44646	0.22

The magnetic properties of the film are increased due to urea. The electrodeposited films were uniform and bright. The urea molecules are having leveling effect, which ensures uniform orientation of crystals during electrodeposition. On increasing the concentration of NaH_2PO_2 and urea, magnetic properties of the films are increased. It was because of the stress present in the films, which was caused by the inclusion of decomposed products of additives.

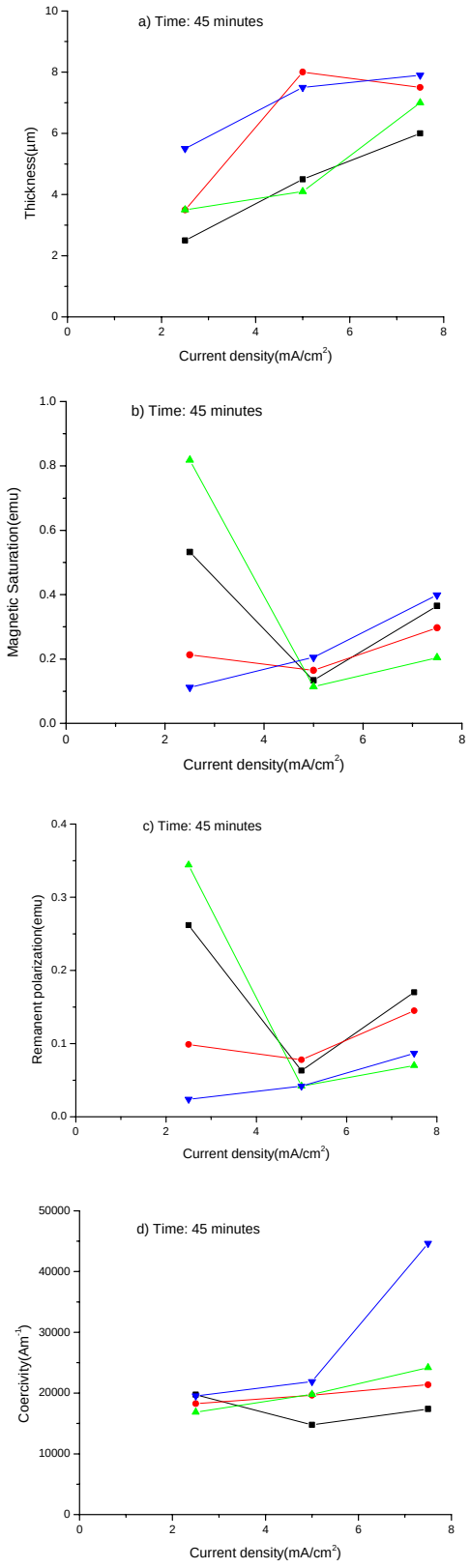

Fig.3 Effect of time of deposition on film thickness, magnetic saturation, remanent polarization and coercivity of CoWP films electrodeposited with (–■–) NaH_2PO_2: 0.05 M; Urea: 2.5 g l^{-1}, (–●–) NaH_2PO_2:0.05 M; Urea: 5.0 g l^{-1}, (–▲–) NaH_2PO_2: 0.1 M; Urea: 2.5 g l^{-1}, (–▼–) NaH_2PO_2: 0.1 M; Urea: 5.0 g l^{-1}.

Fig.3 (a) shows the effect of current density at 45 min of deposition on the thickness of the film. If the current density increases, the thickness of the film will be increased in all concentrations of additives. Fig.3(b) and(c) shows magnetic saturation and remanent polarization of the films are increased after increasing the current density with a bath contained 5 gl^{-1} of urea. Fig 3(d) shows coercivity of the film is increased if increase the current density. The film is deposited from a bath contained 5 g l^{-1} of urea and 0.1 M NaH_2PO_2 with high coercivity. In general magnetic properties of the films were increased when increase current density at 45 min of deposition.

3.4. Mechanical properties

CoWP films, which were selected for XRD and SEM studies, and tested for their Vicker's hardness number. The results are shown in Table 1. Bath additive concentrations will increase the hardness of the film. It was happened due to the stress present in the film, which caused small cracks in the structure. Adhesion of the film with the substrate was found to be good.

3.5. Elemental analysis

The percentage of film composition from the result of EDAX was reported in Table 1. It was observed that the percentage of phosphorous is increased by increasing the bath additives. Similarly the percentage of tungsten is decreased by increasing the bath additives. The phosphorus content of the film is high which stimulated to get high magnetic properties. It was cause due to the addition of urea in the bath to improve the crystalline structure of CoWP films.

4. Conclusions

A CoWP film with soft magnetic properties can be obtained by galvanostatic electrodeposition process. The electrodeposition requires $CoSO_4.7H_2O$ - 0.1 M, $Na_2WO_4.2H_2O$ - 0.05 M, $Na_3C_6H_5O_7.2H_2O$ - 0.3M, with this composition 0.05 and 0.1 M NaH_2PO_2 and 2.5 and 5.0 g l^{-1} of urea. The current density of the deposition was 2.5, 5.0 &7.5 mA cm^{-2}. Addition of urea is increased the coercive value of the film. The high coercive value 44,646 A m^{-1} was obtained in this work. The urea molecules have the leveling effect, which ensures uniform orientation of crystals during electrodeposition. 5 g l^{-1} of urea with 7.5 mA current density was found to be the optimum concentration in the bath in order to obtain a CoWP film with improved magnetic, structural and mechanical properties.

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