International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.6, No.1, pp 384-390, Jan-March 2014

Effect of Phosphorous Acid on the Ferrous Tungsten Phosphorous Magnetic Thin Film

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Abstract: The properties of hard magnetic Ferrous Tungsten Phosphorous (Fe-W-P) films electrodeposited in the presence of phosphorous as precursor with varying concentrations were studied for different current densities and deposition time in order to get different thickness and uniform deposits. The magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) of the films were studied using vibrating sample magnetometer. Magnetic properties of the deposited films were increased with the increase of phosphorous. The crystallite size and stress of the deposited thin films were calculated using X-ray diffraction (XRD) studies. Percentages of elemental analysis of Fe-W-P films were obtained using energy dispersive X-ray analysis (EDAX). Surface morphology analysis was carried out using scanning electron microscope (SEM). The magnetic properties and structural characteristics of the thin films deposited under various experimental conditions are discussed. Hardness and adhesion of the deposited thin films were also studied.
Keywords: Electrodeposition, Fe-W-P, EDAX, SEM, XRD, hardness.

1. Introduction

The electrodeposition technique has become the dominant manufacturing technology in all new applications such as micro electromechanical system (MEMS) devices, nano electromechanical system (NEMS) devices, magnetic recording head and data storage media[1]. The advantages of electrodeposition are easy to handle, no need of vacuum and higher deposition rates. Since the world is moving towards miniaturization, cost competitiveness and high performance packaging. Generally ferromagnetic materials like Fe, Co and Ni are played a vital role in the magnetic data storage. The introduction of tungsten into metal deposits allows for a significant improvement of the properties of the obtained coatings, increasing their hardness, corrosion stability, and heat resistance. It is found that tungsten-containing alloys obtained through the galvanic method exceed pure metals of the iron group in corrosion stability due to the tungsten inertia and the lower porosity of the coatings. Ferrous–tungsten coating is considerably cheaper than those of nickel and cobalt and is characterized

by higher physicochemical properties in comparison with pure iron. An iron–tungsten alloy has a higher wear resistance than pure iron. Fe–W alloys are used in both mechanics and micromechanics. The addition of phosphorous maintains high corrosion resistance[2]. There are also some literary reports in the electrodeposition of Ni-Fe-W-P[3], Co-W-P[4] and Co-W[5] films.

In the present study, we investigated in detail the effects of various concentration of phosphorous on the magnetic and structural properties of electrodeposited Fe-W-P thin film.

2. Experimental

2.1 Synthesis and Deposition

A copper substrate of size 1.5 x 5 cm as cathode and stainless steel plate is used as anode for galvanostatic electrodeposition method. Current for electrodepostion was passed from a d.c 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 buffing the substrates were cleaned by con H_2SO_4 or acetone. Before electrodeposition, these substrates were cleaned in an alkaline electro cleaning bath and the substrates were rinsed in distilled water. The electrodeposion was done with different concentration of phosphorous.

Electrodeposition of Fe-W-P magnetic thin film was plated from a bath contained ferrous sulphate ($FeSO_4.7H_2O$) 0.1 M, sodium tungstate ($Na_2WO_4.2H_2O$) 0.05 M, tri sodium citrate ($Na_3C_6H_5O_7.2H_2O$) 0.3 M, boric acid (H_3BO_3) 0.16 M and ammonium sulphate $(NH_4)_2SO_4$ 0.3 M, with this composition 0.1 and 0.2 M of Phosphorous acid (H_3PO_3) were added to this bath and their effect on the properties of Fe-W-P films was investigated with different current density like 20 mA cm^{-2}, 25 mA cm^{-2} and 30 mA cm^{-2} and different deposition time like 15, 30 and 45 minutes.. The pH value was fixed at 8.0 for all the electrodeposition baths.

2.2 Characterization

The thickness of the deposited films was measured using digital micrometer (Mitutoyo, Japan). Magnetic properties of deposited films were studied with vibrating sample magnetometry. The structure and morphology of the magnetic films were studied using X-ray diffractometer (Rich Seifert, model 3000) and scanning electron microscope (JEOL) respectively. The crystallite size and stress of the deposited Fe-W-P film has been calculated from the XRD data. Percentage of elemental analysis of Fe-W-P film was obtained using EDAX. Hardness of the deposited thin film was obtained using Vickers hardness tester through diamond indenter method. Adhesion of the films was tested by bend test and scratch test.

3. Results and Discussion

3.1 Thickness Study

Table 1 summarizes the effect of various concentration of phosphorous acid on the thickness and magnetic properties of Fe-W-P films obtained under different experimental conditions. The thickness of the film was increased with increase in phosphorous as well as increase in current density. The magnetic properties of the thin films were increased with the increase of thickness.

3.2 Surface analysis

3.2.1 Structural analysis

Electrodeposited Fe-W-P films were obtained from the baths maintained at 30 mA cm^{-2} current density for 45 minutes deposition time with different concentration of phosphorous acid were subjected to XRD studies (**Figure 1).** The X-ray wavelength used was 1.5405 Å of Cu-Kα radiation. The data obtained from the XRD pattern were compared with Joint committee for powder diffraction studies data and were found to have Rhombohedral structure with Fe_7W_6 (0210) plane[6] and Hexagonal structure with Fe_2P (312) plane[7]

predominantly. The XRD peaks of thin film and metal were shifted due to the stress of the film[8]. Stress of the films were calculated from XRD data, using the formula,

Young's modulus = Stress / Strain (1)

Stress of the film was low when the bath was in lower concentration of phosphorous (Table 2). The stress of the film increased and crystalline sizes of the film decreased[9] when the concentration of phosphorous was increased. Crystallite size of the deposits were calculated from XRD data using Debye-Scherrer formula

Crystallite size = $0.9\lambda/\beta \cos\theta$ (2)

Crystallite sizes were obtained in the nano scale range.

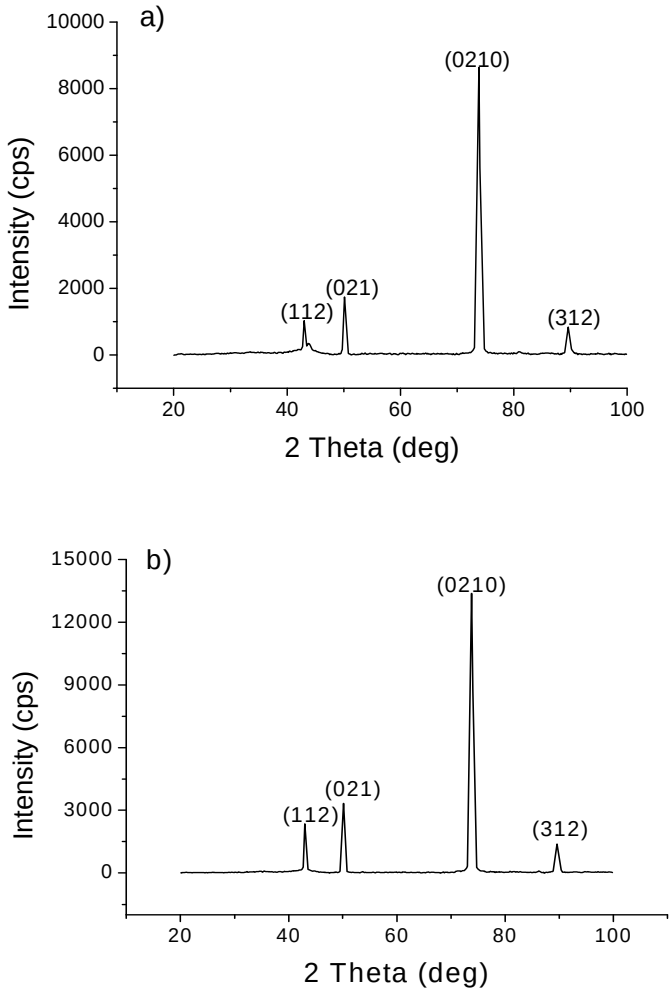
Table 1. Effect of the thickness and magnetic properties of Fe-W-P films electrodeposited for different current densities and different deposition times with 0.1 M and 0.2 M of H_3PO_3.

S. No.	H_3PO_3 (M)	Current density (mA cm^{-2})	Deposition time (minutes)	Thickness of deposit (μm)	Magnetic saturation (A/m)	Remanent polarization (A/m)	Coercivity (Oe)	Squareness
1			15	1.8	4.459	0.341	1261	0.08
2		20	30.	2.5	6.524	0.587	1344	0.09
3			45	3.2	9.269	0.934	1401	0.10
4			15	2.0	5.942	0.524	1315	0.09
5	0.1	25	30	2.8	8.698	0.869	1467	0.10
6			45	3.4	10.656	1.211	1548	0.11
7			15	2.2	7.541	0.650	1398	0.09
8		30	30	3.2	9.948	0.949	1512	0.10
9			45	3.8	12.604	1.578	1754	0.13
10			15	2.5	6.544	0.844	1409	0.13
11		20	30.	3.4	8.658	1.212	1577	0.14
12			45	4.2	11.564	1.865	1648	0.16
13			15	2.7	8.555	1.158	1528	0.14
14	0.2	25	30	3.5	10.451	1.649	1679	0.16
15			45	4.4	13.762	2.754	1720	0.20
16			15	3.4	9.542	1.488	1668	0.16
17		30	30	3.8	12.811	2.577	1725	0.20
18			45	4.8	15.829	3.634	1819	0.23

3.2.2 Morphological observation

Electrodeposited Fe-W-P thin films were obtained from the baths maintained at 30 mA cm^{-2} current density for 45 minutes deposition time with different concentration of phosphorous acid were subjected to SEM (**Figure 2).** The crystallinity of Fe-W-P film mainly depends on the amount of phosphorous which are present in the bath. The surface scans shown the grain sizes are decreased when the phosphorous content in the bath was increased.

Figure 1. XRD images of Fe-W-P films electrodeposited at 30 mA cm^{-2} for 45 minutes deposition time with (a) 0.1 M H_3PO_3 (b) 0.2 M H_3PO_3



3.3 Mechanical Properties

Fe-W-P films, which were selected for XRD and SEM studies, were tested for their Vickers hardness number (**Table 1). Higher** concentration of phosphorous in the bath increased the hardness of the film due to the stress present in the film. Adhesion of the film with the substrate was found to be good.

3.4 Elemental Analysis

Table 2 represents the results of EDAX. It was observed that all the films obtained from various baths had less than 3 % phosphorous. In the higher phosphorous acid content the films showed high magnetic properties with improved crystalline structure.

3.5 Magnetic Studies

The VSM images of Fe-W-P electrodeposited thin films obtained from the baths contained different concentration of phosphorous acid (**Figure 3).** On increasing the phosphorous from 0.1 M to 0.2 M, the coercivity increased from 1754 Oe to 1819 Oe. The magnetic properties of the film are enhanced due to increase in phosphorous. The electrodeposited films were uniform and bright. The morphology of the film was found to be poor when the electrodeposition bath contained lower phosphorous content. With the increase in phosphorous there was significant improvement in the thickness as well as magnetic properties of the film (**Table 1).** Under the best conditions, 30 mA cm^{-2} current density for 45 minutes deposition time with 0.2 M

H_3PO_3, the thickness of the film was found to be 4.8 μm with coercive and remanent values about 1819 Oe and 3.634 A/m respectively.

Figure 2. SEM images of Fe-W-P films electrodeposited at 30 mA cm^{-2} for 45 minutes deposition time with (a) 0.1 M H_3PO_3 (b) 0.2 M H_3PO_3

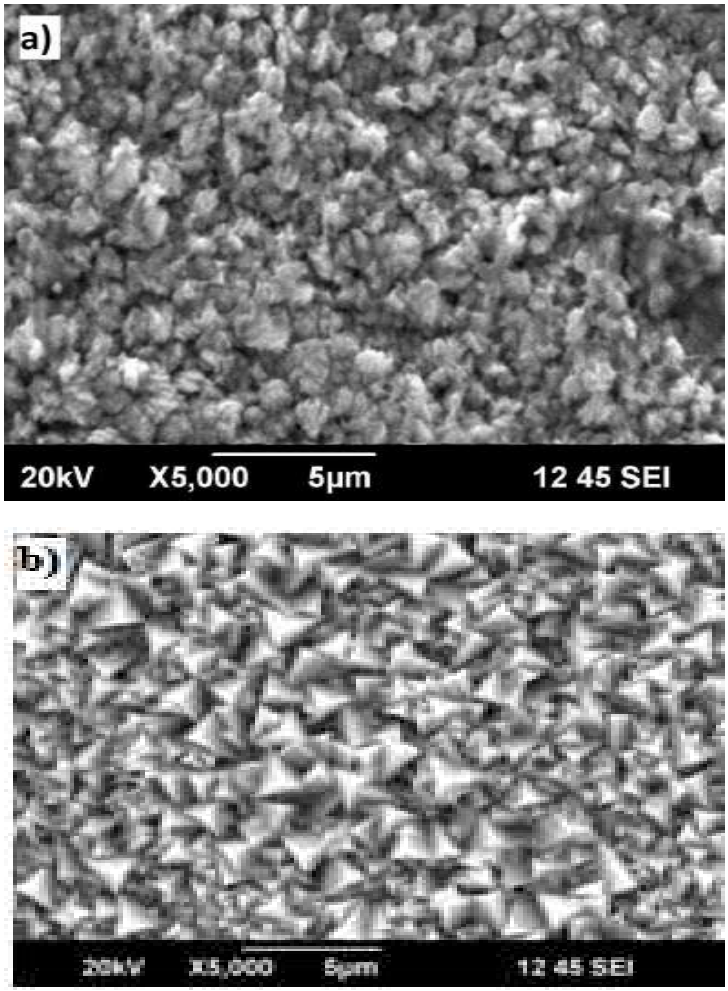
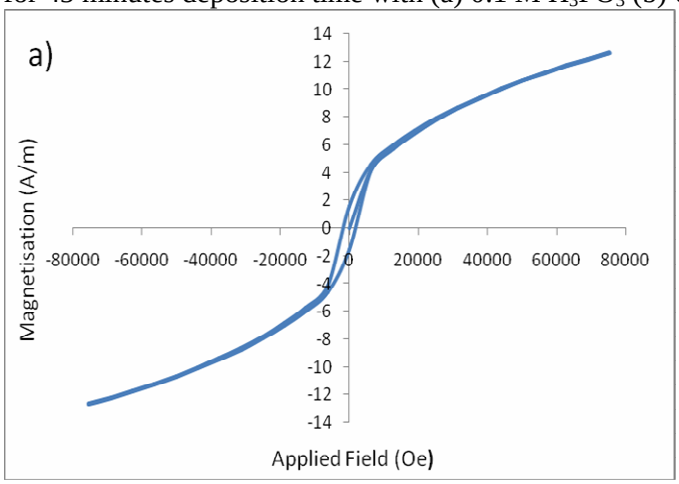
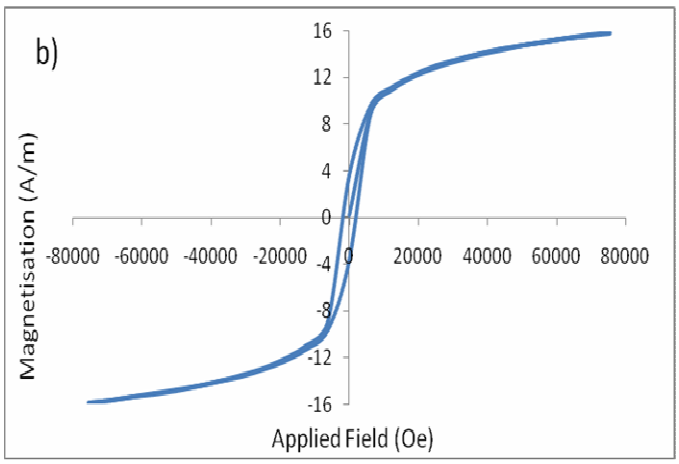


Table 2. Crystalline size, hardness and composition of Fe-W-P films at 45 minutes deposition time.

H_3PO_3 (M)	Current density (mA cm^{-2})	Crystalline size (nm)	Stress (MPa)	Vicker Hardness Number (VHN)	Film Composition		
					Fe	W	P
0.1	20	30.45	582	154	85.22	13.20	1.58
	25	29.96	601	168	86.69	11.59	1.72
	30	28.29	611	189	87.40	10.64	1.96
0.2	20	29.44	599	162	85.89	12.45	1.66
	25	28.81	610	178	86.94	11.12	1.94
	30	27.93	619	192	87.64	10.20	2.16

Figure 3. VSM images of Fe-W-P films electrodeposited at 30 mA cm^{-2} for 45 minutes deposition time with (a) 0.1 M H_3PO_3 (b) 0.2 M H_3PO_3





4. Conclusions

The Fe-W-P thin film having good hard magnetic properties can be electrodeposited from the higher concentration bath of phosphorous. When the phosphorous was increased from 0.1 M to 0.2 M, the stress of the deposited thin film and hardness of the film increased. Also these films have good adhesion with the substrate and their crystalline sizes are in nano scale. High coercivity, remanent and Squareness values were observed as 1819 Oe, 3.634 A/m and 0.23 respectively at 30 mA cm^{-2} current density for 45 minutes deposition time with 0.2 M H_3PO_3. This Fe-W-P thin film has enhanced magnetic, structural and mechanical properties which can be used in MEMS devices and magnetic data storages.

Acknowledgements

The authors would like to express their sincere thanks to STIC, Cochin, India for SEM and XRD studies and IIT, Chennai, India for magnetic studies.

References

1. Myung, N. V., Park, D. Y., Schwartz, M. and Nobe, K., Electrochemical Society Proceedings of Sixth International Symposium on Magnetic Materials, PV 2000-29 (2000).
2. Im, B. M., Akiyama, E., Habazaki, H., Kawashima, A., Asami, K. and Hashimoto, K., The Effect of Phosphorus Addition on the Corrosion Behavior of Amorphous Fe-8cr-P lloys in 9m H_2SO_4, Corrosion Science, 1995, 37, 709.

3. Jamil Ahmad, Katsuhiko Asami, Akira Takeuchi, Dmitri V. Louzguine and Akihisa Inoue, High Strength Ni-Fe-W and Ni-Fe-W-P Alloys Produced by Electrodeposition, Materials Transactions, 2003, 44, 1942.
4. Sasikumar, D., Thangaraj, N., Ganesan, S. and Tamilarasan, K., Effect of Temperature and Additives on Electrodeposited CoWP Magnetic Thin Film, Chalcogenide Letters, 2012, 9,11.
5. Sasikumar, D. and Ganesan, S., Effect of temperature and current density in electrodeposited Co–W magnetic nano thin film, Digest Journal of Nanomaterials and Biostructures, 2010, 5, 477.
6. Arnfelt, H. and Westgren, A., Jernkontorets Ann., 1935, 119, 185.
7. Fujii, H., Komura, S., Takeda, T., Okamoto, T., Ito, Y. and Akimitsu, J., Polarized Neutron Diffraction Study of Fe_2P Single Crystal, J. Phys. Soc. Jpn., 1979, 46, 1616.
8. Noyan, I.C. and Cohen, J.B., Residual stress measurement by Diffraction and Interpretation, Springer-verlag, New York, 1987, 350.
9. Nguyen, V. C., Lee, C. Y., Chang, L., Chen, F. J. and Lin, C. S., The Relationship between Nano Crystallite Structure and Internal Stress in Ni Coatings Electrodeposited by Watts Bath Electrolyte Mixed with Supercritical CO_2, J. Electrochem. Soc., 2012, 159, 393.

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