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Effect of current density on electrodeposited ferrous tungsten thin films

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Ferrous tungsten (Fe-W) electrodeposited thin film properties have been studied for different current densities and different deposition times. The magnetic saturation (M_s), retentivity (M_r) and coercivity (H_c) of the films have been studied using vibrating sample magnetometer. The retentivity (M_r) and the magnetic saturation (M_s) of the deposited films increased with the increase of current density. The crystallite size and stress of the deposited thin films were calculated using X-ray diffraction (XRD) studies. Percentage of elemental analysis of Fe-W films has been obtained using energy dispersive X-ray analysis (EDAX). Surface morphology analysis has been carried out using scanning electron microscope (SEM). The magnetic properties and structural characteristics of the thin films deposited under various experimental conditions are discussed. The hardness and adhesion of the deposited thin films were also studied.

Keywords: Electrodeposition, Fe-W, EDAX, Scanning electron microscope, XRD, Hardness, Thin films

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]. Electrodepositions of hard magnetic films are growing vigorously in the electronics industry. The world is moving towards miniaturization, cost competitiveness and high performance packaging. The advantages of electrodeposition are easy to handle, no need of vacuum and higher deposition rates. Ferromagnetic materials like Fe, Co and Ni play a vital role in the magnetic data storage. Among other methods of plating, iron plating displays specific features of interest such as (i) abundant availability of iron; (ii) welding of electrodeposited iron and plating of other metals on it with ease and (iii) superior drawing properties of iron in the soft state. The ferrous sulphate bath produces deposits that are smooth and normally light gray in colour. There is little tendency towards pitting and thick deposits can be produced at room temperature. The introduction of tungsten into metal deposits allows for a significant improvement of the properties of the obtained coatings, 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. The tungsten cannot be electrodeposited individually from aqueous electrolyte. However, tungsten can be co-deposited from aqueous electrolyte containing iron group metals (Fe, Co, Ni), which is entitled Induced Co-deposition[2]. An iron–tungsten alloy has a higher wear resistance than pure iron. Fe-W alloys are used in both mechanics and micromechanics. They can be used as barrier layers for ultra-large-scale and micro-electromechanical systems applications[3,4]. Ferrous-tungsten coating is considerably cheaper than those of nickel and cobalt and is characterized by higher physic-chemical properties in comparison with pure iron. There are also some literary reports regarding the electrodeposition[5-9] of Fe-W, Ni-W and Co-W. The effects of current density on the magnetic properties of ferrous tungsten films have been studied. The structure, morphology and EDAX analysis of Fe-W film have also been investigated.

2 Experimental Details

2.1 Synthesis and deposition

A copper substrate of size 1.5×5 cm is used as cathode and stainless steel plate acts as anode for galvanostatic electrodeposition method. Films were deposited using *dc* regulated power supply. Analytical grade chemicals were used to prepare bath solution. The substrate is masked using the adhesive tape leaving the area on which the film is to be deposited. The copper electrode was buffed for removing scratches using mechanical polishing wheel with a buffing cloth containing aluminium oxide abrasive. After buffing, the substrates were cleaned using concentrated sulphuric acid (H_2SO_4) or acetone. Before electrodeposition, these substrates were again cleaned in an alkaline electro cleaning bath and finally rinsed in distilled water. The electrodeposition was done for different current densities and deposition times.

Electrodeposition of Fe-W 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 and their effect on the properties of Fe-W films has been investigated with different current densities at 20, 25 and 30 mA cm^{-2}. The *p*H value was fixed at 8.0 for all the electrodeposition baths.

2.2 Characterization

The thickness of the deposited films has been measured using digital micrometer (Mitutoyo, Japan). Magnetic properties of deposited films have been studied with vibrating sample magnetometry. The structure and morphology of the magnetic films have been 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 film have been calculated from the XRD data. Percentage of elemental analysis of Fe-W film was obtained using EDAX. Hardness of the deposited thin film was obtained using Vickers hardness tester through diamond intender method. Adhesion of the films was tested by bend test and scratch test. These tests are widely used in the field of electroplating.

3 Results and Discussion

Table 1 summarizes the effect of current density and deposition time on the thickness obtained under different experimental conditions. The thickness of the deposited films was increased with increase in current density and deposition time. The magnetic properties of the thin film have been found to increase with the increase of thickness.

Electrodeposited Fe-W films were subjected to XRD studies. The X-ray wavelength was used 1.5405 Å of Cu Kα radiation. Films obtained from various current density baths like 20, 25 and 30 mA cm^{-2} for 45 min deposition time were studied for their structural characteristics and are shown in Fig. 1. The data obtained from the XRD pattern were compared with Joint committee for powder diffraction studies data and found to have rhombohedral structure and exhibited Fe_7W_6 (116) plane [10] predominantly. The XRD peaks of thin film were shifted due to the stress of the film [11]. Stress of the films has been calculated from XRD data, using the formula,

$$\text{Young's modulus} = \text{stress/strain} \quad \ldots(1)$$

The results are presented in Table 2. Stress of the film was low when the bath was in lower current density. The stress of the film increased and crystalline sizes of the film decreased[12] with the increase in the current density. Crystallite size of the deposits has been calculated from XRD data using Debye-Scherrer formula[13]:

$$\text{Crystallite size} = 0.9\lambda/\beta\cos\theta \quad \ldots(2)$$

Crystallite sizes were obtained in the nano scale range and the results are presented in Table 2.

Electrodeposited Fe-W thin films obtained from the baths maintained at current densities 20, 25 and 30

Table 1 — Effect of the thickness and magnetic properties of Fe-W thin films electrodeposited for different deposition time and current densities

S. No.	Current density (mA cm^{-2})	Deposition Time (mins)	Thickness of deposit (μm)	Magnetic saturation (A/m)	Remanent polarization (A/m)	Coercivity (Oe)	Square ness
1		15	1.2	3.794	0.189	1278	0.05
2	20	30	2.0	4.867	0.352	1396	0.07
3		45	2.8	5.322	0.510	1551	0.10
4		15	1.4	6.792	0.408	1421	0.06
5	25	30	2.2	10.441	0.835	1590	0.08
6		45	3.1	13.396	1.514	1609	0.11
7		15	1.9	9.545	0.668	1508	0.07
8	30	30	2.5	15.358	1.526	1683	0.10
9		45	3.8	20.493	2.842	1895	0.14

mA cm^{-2} are shown in Fig. 2(a, b and c), respectively. The crystallinity of Fe-W film mainly depends on the amount of ferrous and tungsten which is present in the film. The film with low concentration of ferrous obtained from a bath which is maintained at a current density of 20 mA cm^{-2} as shown in Fig. 2(a). The tungsten content in the deposited alloys affects strongly the surface topography. The film fabricated at current density of 20 mA/cm^2 has maximal tungsten content and very fine homogeneous surface with spherical, compact and smooth grains. The films obtained from a bath maintained at 25 mA cm^{-2} and 30 mA cm^{-2} current densities show crack due to stress of the film, as shown in Fig. 2(b and c). The surface scans shown that the grain sizes are decreased when the current density is increased. The VSM images of

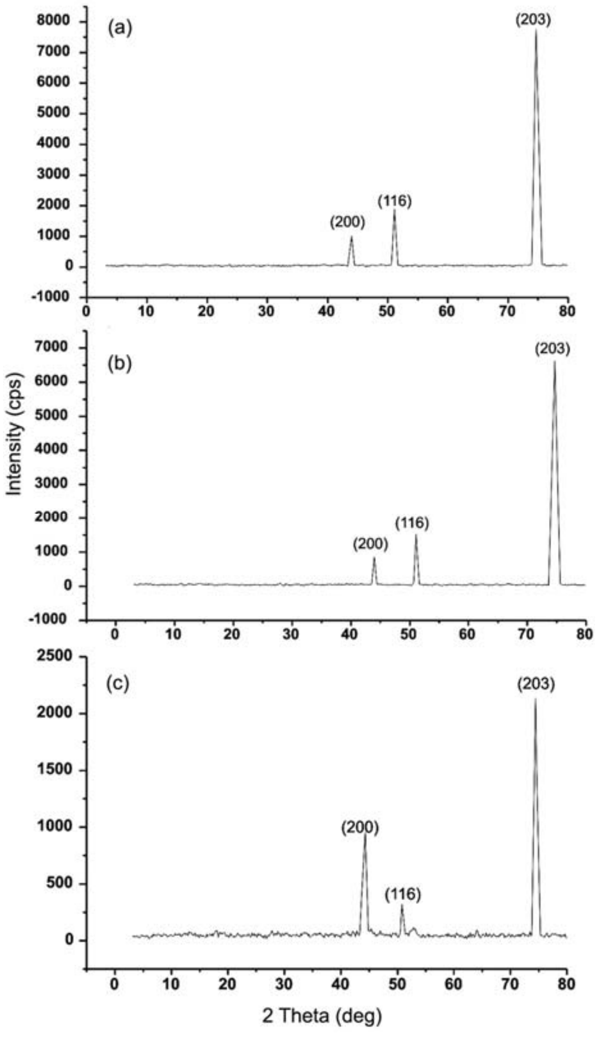

Fig. 1 — XRD images of Fe-W electrodeposited thin films for 45 min at (a) 20 mA cm^{-2} (b) 25 mA cm^{-2} (c) 30 mA cm^{-2}

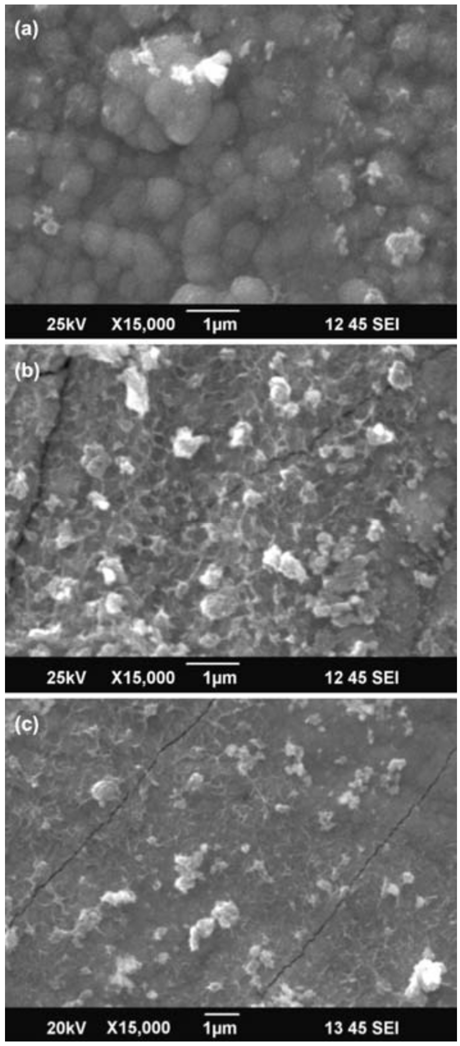

Fig. 2 — SEM images of Fe-W electrodeposited thin films for 45 min at (a) 20 mA cm^{-2} (b) 25 mA cm^{-2} (c) 30 mA cm^{-2}

Table 2 — Crystalline size, hardness and composition of Fe-W films for different current densities at the deposition time of 45 minutes

Current Density (mA/ cm^2)	Obtained data (2θ)	Standard data (2θ)	Crystalline size (nm)	Stress (MPa)	Vickers Hardness (VHN)	Film Composition (at %)	
						Fe	W
20	51.104	50.855	27.65	617	160	74.6	25.4
25	51.089	50.855	27.34	621	164	78.2	21.8
30	50.810	50.855	26.68	636	167	79.4	20.6

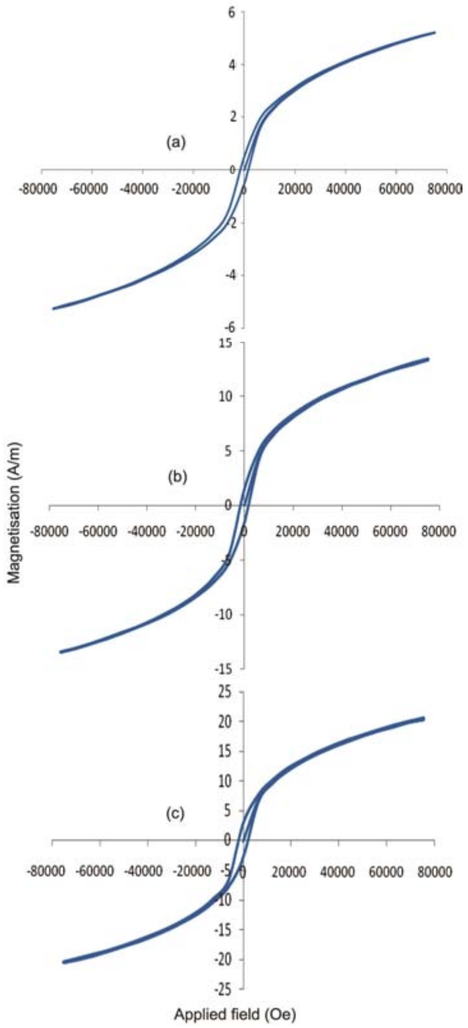

Fig. 3 — VSM images of Fe-W electrodeposited thin films for 45 min at (a) 20 mA cm^{-2} (b) 25 mA cm^{-2} (c) 30 mA cm^{-2}

Fe-W electrodeposited thin films are shown in Fig. 3(a,b and c). On increasing the current density from 20 to 30 mA cm^{-2} the coercivity increased from 1551 to 1895 Oe.

The Fe-W films were subjected to XRD studies and Vickers hardness test and the results are presented in Table 2. Usually, the increase in the hardness is accompanied by a decrease in the grains size and the crystal dislocations in the electroplated alloy[14,15]. The hardness of the film increases when the current density of the bath increases. The reason can be attributed to the presence of cracks which occurred due to the increase in the stress of the film. Bend and scratch test were done to test the adhesion of the film and it was found to be good.

Elemental analysis done by EDAX is reported in Table 2. The films which have above 74% Fe content have high magnetic properties. It was observed that the percentage of ferrous increased with increase of current densities. The increase in current density reduced the tungsten content in the film.

4 Conclusions

The Fe-W thin film having good hard magnetic properties can be electrodeposited from the higher current density bath. When the current density was increased, the stress of the deposited thin film also increased which is a cause for cracks in the thin film and the hardness of the film also increased at 30 mA cm^{-2} current density. Also these films have good adhesion with the substrate and their crystalline sizes are in nano scale. The high coercivity, remanent polarisation and squareness values achieved about 1895 Oe, 2.842 A/m and 0.14, respectively at 30 mA cm^{-2} current density with 45 min deposition time. This thin film has enhanced magnetic, structural and mechanical properties which can be used in MEMS devices and magnetic data storages.

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