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Effect of current density on electrodeposited cobalt ferrous tungsten magnetic thin films

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Co-Fe-W electrodeposited magnetic thin film properties were studied to identify the possible applications in different area. The film was prepared using the electrodeposition method with different current densities, in order to get the uniform deposition with different thickness. A vibrating sample magnetometer studies provide the value of magnetic saturation (Ms=0.112emu), retentivity (Mr=0.020emu) and coercivity (Hc=88.95Oe). The prepared film is (45min, thickness is 3.10μm) more suitable to develop tiny integrated memory devices. X-ray diffraction studies (XRD) confirm the cubic crystalline nature of the prepared thin films. Surface morphology analysis clearly shows the uniform thickness (0.2 μm) of the thin film [scanning electron microscope (SEM)]. The highest percentage of Co, Fe and W composition in the thin films were obtained by using energy dispersive X-ray analysis. The maximum hardness value is 212/7.5 $mAcm^{-2}$ for 45min and best adhesion with desirable magnetic properties have been reported in the present communication.

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1. Introduction

Magnetic and non-magnetic metals attracted various researchers, which brings more interest to fabricate the electrodeposition of multilayer's thin film for technological applications [1]. Capel et al. reported that the improved wear resistance and its coefficient of friction on Co-W-Fe thin films [2]. There are numerous techniques such as electrodeposition, direct current sputtering, radio frequency sputtering, chemical vapor deposition and physical vapor deposition for preparing the magnetic thin films had been reported [3-7]. Among these techniques, electro deposition seems to be an interesting technique to prepare magnetic alloys because of its high coating rate, convenient to control composition, good adhesion and lower cost [8].

Electrodeposition technique has wide range of applications in electronics, magneto electronics, magnetic recording and microsystems industries due to its unique features [9-13]. The accumulative of pH value in the chemical bath, increases the deposition of tungsten in the thin films which in turn increases the micro hardness of the film [14]. The electrodeposition coating at different compositions brings change in the morphology/phase structure. The properties of the deposited alloys are strongly depends on the parameters such as bath composition, deposition potential, pH, substrate, reference electrode and applied current [15,16]. At lower concentration region, the magnetic moment increases due to the isolation of magnetic grains. It was also observed that the decrease of coercive field which increases cobalt-ferrite concentration due to higher inter particle magnetic interaction of the agglomerated grains [17]. The interaction between grain size and dislocation density clearly shows the variation of hardness in the thin films [18]. When the current densities increase, the cobalt content rises whereas the iron decreases in the prepared thin film [19]. Cobalt is the substantial element in the magnetic industry and the iron

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content increase the magnetic saturation in the thin film [20]. The structure and composition of electrodeposited amorphous and crystalline thin films were analysed by different research groups [21–25]. In the present work, the effects of current density on the magnetic properties of cobalt ferrous tungsten films have been studied. The structure, morphology, and EDAX analysis of Co-Fe-W film have been investigated and reported.

2. Materials and methods

The copper substrate (1.5 x 5 cm) acts as a cathode while the stainless steel plate as an anode in the galvanostatic electrodeposition method. DC regulated power supply was used to draw current for electrodeposition. Analytical-grade chemicals were used to prepare the bath solution. The substrates were cleaned by concentrated H_2SO_4 and acetone. Before electrodeposition, these substrates were cleaned in alkaline electro cleaning bath and finally it was rinsed in the distilled water. The electrodeposition was done at different current densities and deposition time.

Electrodeposition of Co-Fe-W magnetic thin film was prepared from a bath containing 0.1M of cobalt sulfate ($CoSO_4.7H_2O$), 0.1M of ferrous sulfate ($FeSO_4.7H_2O$), 0.05M of sodium tungstate ($Na_2WO_4.2H_2O$), 0.3M of trisodium citrate ($Na_3C_6H_5O_7.2H_2O$), 0.16M of boric acid (H_3BO_3) and 0.3M of ammonium sulfate ($(NH_4)2SO_4$). The effect of Co, Fe and W content on prepared thin film was investigated at different current density (2.5mA cm^{-2}, 5mA cm^{-2}, 7.5mA cm^{-2}) and various deposition time (15, 30, 45 minutes). The constant pH value of 8.0 is maintained during the electrodeposition.

The thickness of the deposited films was measured using a digital micrometer (Mitutoyo, Japan). Magnetic properties of the deposited films were studied using vibrating sample magnetometer. The crystalline structure and surface morphology of the magnetic films were studied using an X-ray diffractometer (Rich Seifert, model 3000) and scanning electron microscope (JEOL) respectively. The crystalline size, strain, and dislocation density of the deposited Co-Fe-W film have been calculated from the XRD data. The percentage of Co, Fe & W content in the prepared magnetic thin film was obtained using EDAX. Vickers hardness tester (diamond indenter method) is used to determine the hardness of the prepared thin film. Followed by, adhesion of the films was tested by bend and scratch process.

3. Results and discussion

3.1. Thickness measurement

It is clearly observed that the magnetic thickness on the substrate is increases while increasing current density and deposition time (Table 1). Due to increasing of deposition time, the Co-Fe-W deposition on the substrate also increases. When the film thickness reached to the maximum, the electrode material shows the largest area-specific capacitance. Further the changes in the microstructure of Co-Fe-W have the opposite effect on the area-specific capacitance. From the Table 1, it can be clearly observed that the coercivity of the magnetic thin film decreases while increasing the current density and deposition time.

Table 1. Effect of the thickness and magnetic properties of Co-Fe-W electrodeposited films at different current densities and deposition time.

Current density ($mAcm^{-2}$)	**Deposition Time (mins)**	**Thickness of film (µm)**	**Magnetic saturation (emu)**	**Remanent polarization (emu)**	**Coercivity (Oe)**	**Squareness**
2.5	15	1.80	0.053	0.002	215.90	0.03
	30	2.33	0.031	0.015	207.71	0.48
	45	2.80	0.054	0.023	194.36	0.42
5	15	2.33	0.040	0.002	195.89	0.05
	30	2.67	0.082	0.009	146.98	0.10
	45	3.10	0.112	0.020	88.95	0.17
7.5	15	2.33	0.073	0.036	186.75	0.49
	30	3.03	0.033	0.006	178.36	0.18
	45	3.50	0.073	0.009	83.687	0.12

3.2. Structural analysis

XRD is another tool to analyze the structure and nature of the prepared thin films. The strain of the films was calculated from XRD data, using the formula,

$$\text{Strain } (\varepsilon) = (\beta \cos \theta)/4$$

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal. The distinction in lattice spacing leads to the variation in the crystalline size due to the change in dislocation density [26].

$$\text{Dislocation density } (\delta) = 1/ D^2$$

XRD studies performed for electrodeposited Co-Fe-W films which were prepared at different current density (2.5$mAcm^{-2}$, 5$mAcm^{-2}$, 7.5$mAcm^{-2}$) and maintained 45 minutes as a deposition time. Also, the XRD spectrum (Figure 1a-1c) reveals the existence of cubic crystalline structure of the prepared magnetic thin film. The data obtained from the XRD pattern were compared with the joint committee for powder diffraction studies data (JCPDS card number 65-7519). It is found that the crystalline size is around 21nm and observed that the grain size decreases while increasing the current density. Because an increase in the current density results in a higher potential which in turn increases the nucleation rate.

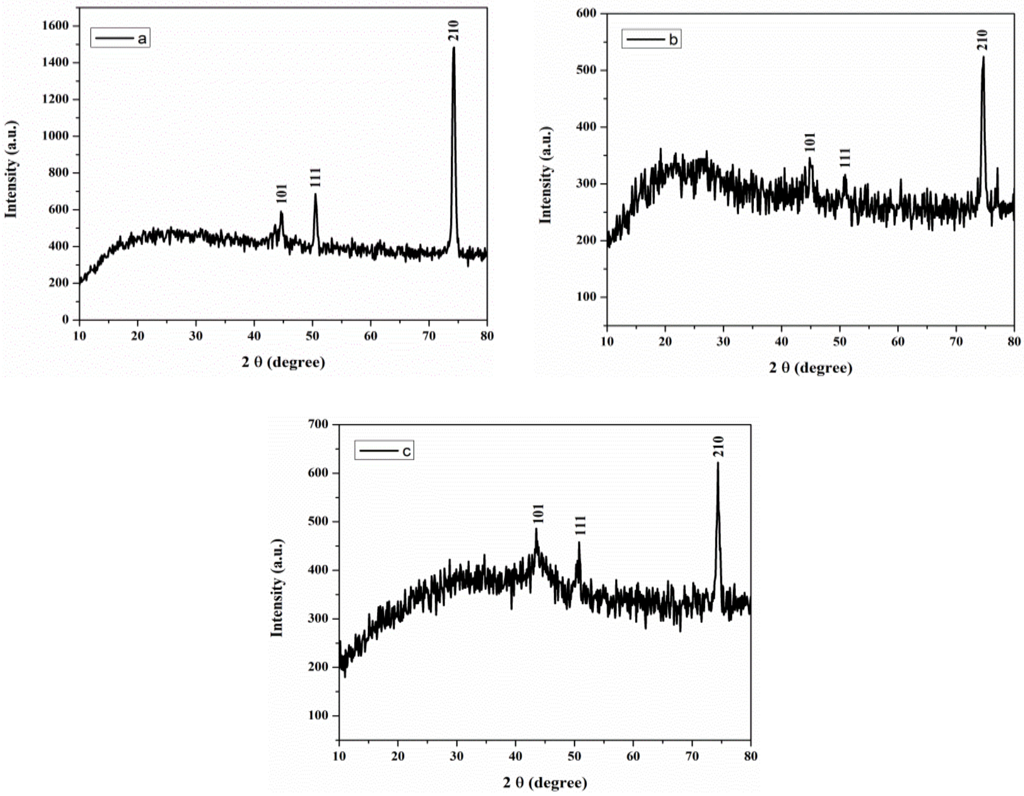


Fig. 1. XRD images of Co-Fe-W electrodeposited films at 45 mn deposition time at different current density of (a) 2.5mAcm^{-2}, (b) 5mAcm^{-2}and (c) 7.5mAcm^{-2}.

When the current density increases, both strain value (from 16.3709x10^{-4} to 19.9071 x10^{-4}) and dislocation density increases (from 20.2340x10^{14}/m^{2} to 29.9193x10^{14}/m^{2}). The calculated crystal size, strain value and dislocation density of Co-Fe-W alloy films are given in Table 2. The crystalline size of deposition decreases due to the onset orientation of crystals while current density increases. A crystalline size of the electrodeposition was calculated and found that in nano scale range from the XRD data using Debye-Scherrer formula [27]

$$\text{Crystalline size} = (0.945\ \lambda)/(\beta \cos\ \theta)$$

It is noticed that the crystalline size of the film decreases while increasing the strain and dislocation density. The dislocation density increases in the deposited film which is due to the formation of new dislocations. The consequent increasing and the overlapping between the strain fields of adjacent dislocations, gradually increases the resistance to further dislocation motion. This causes a hardening of the metal as the deformation progresses.

Table 2. Crystalline size, strain, dislocation density, hardness and composition of Co-Fe-W films at 45 minutes deposition time.

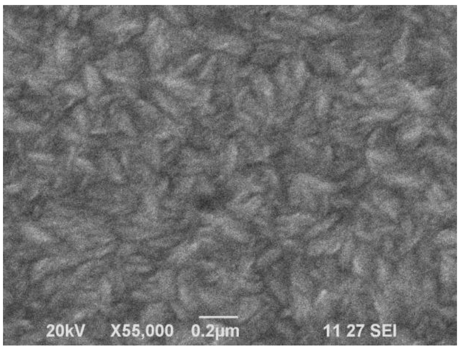
Current density (mA cm^{-2})	Thickness of the film (µm)	Crystalline size(nm)	Strain 10^{-4}	Dislocation Density (10^{14} / m^2)	Vicker Hardness Number (VHN)	Film Composition (wt%)		
						Co	Fe	W
2.5	2.80	22.231	16.3709	20.2340	150	35.64	57.47	6.89
5	3.10	22.091	16.4747	20.4912	169	40.93	49.37	9.71
7.5	3.50	18.282	19.9071	29.9193	212	41.83	42.88	15.29

3.3. Elemental Analysis

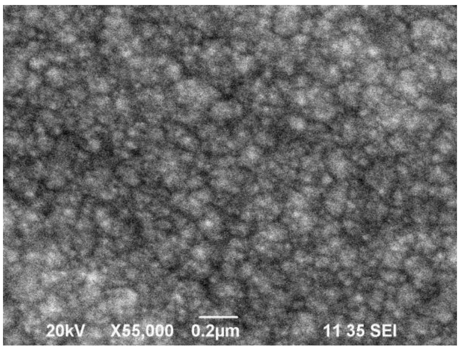
An energy-dispersive X-ray analyzer (EDAX) gives the elemental composition of magnetic thin films. Table 2 shows the weight percentage of Co, Fe and W at different current densities. From the result, it is found that the thin film prepared at 7.5mAcm^{-2} show a high content of tungsten which is more useful to prepare the high corrosive resistance material at different applications. The highest ferrous content of 57.47 wt% was found at a current density of 2.5mAcm^{-2}. Further, the current density increases, the content of cobalt and tungsten also increases. The higher cobalt content of 41.83 wt% was found at a current density of 7.5mAcm^{-2} in the prepared thin films

3.4. Morphological observation

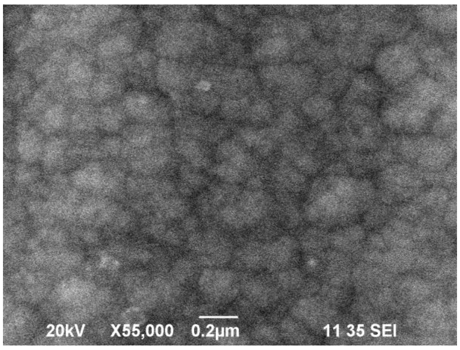
Figure (2a-2c) shows the SEM image of electrodeposited Co-Fe-W thin films at various current densities (2.5mAcm^{-2}, 5mAcm^{-2}, 7.5mAcm^{-2} for 45 minutes deposition time). The crystalline of magnetic thin film mainly depends on the presence of the amount of cobalt, ferrous, and tungsten. SEM image is a clear evidence for the crack-free and homogeneous morphology of the prepared thin films.



(a)



(b)



(c)

Fig. 2. SEM images of Co-Fe-W films electrodeposited at 45 minutes (a) 2.5mAcm^{-2}, (b) 5mAcm^{-2} and (c) 7.5mAcm^{-2}.

3.5. Mechanical Properties

Co-Fe-W coated thin films were tested to identify their hardness number using Vickers hardness tester and the corresponding values are depicted in Table 2. The hardness values of thin films prepared for current density *2.5mA*cm^{-2}, 5mAcm^{-2} and 7.5mAcm^{-2} for 45 *minutes* deposition time are evaluated as 150, 169 and 212 VHN respectively. So, the hardness test shows that the micro hardness increases while increasing current density due to lower stress associated with thin films. Bend test and scratch test were done to confirm the good adhesion of the film.

3.6. Magnetic Studies

The VSM images of Co-Fe-W electrodeposited thin films are shown in Figure 3(a), 3(b) and 3(c). On increasing the current density from 2.5mA cm^{-2} to 7.5mAcm^{-2} the magnetic saturation is increased from 0.031emu to 0.112emu. From table 1, it is observed that while increasing current density from 2.5mAcm^{-2} to 7.5mAcm^{-2}, the coercivity decreases from 215.90Oe to 83.968Oe. It is concluded that films obtained at higher current density reveal a high value of magnetization and a low value of coercivity. The magnetic hysteresis loop measurement shows that the films are having an easy magnetic direction orientation along in-plane, with high saturation and low coercivity. Surface and microscopic magnetization measurements proved that the deposition potential modifies the film roughness and influences on the magnetic domain formation.

The enhanced value of saturation magnetization and reduced value of coercivity promote magnetic properties of alloy coating. The magnetization and other important magnetic properties of coercivity can be changed by decreasing the grain size of deposition. The film stress is reduced by increasing current density. The Co-Fe-W thin films prepared at 7.5mAcm^{-2} have lower coercivity and higher magnetization due to low-stress formation during deposition. So it is concluded that the soft magnetic nature of Co-Fe-W thin films are enhanced by increasing current density. Due to the soft-magnetic properties of these films, it shows a strong dependence on the film deposition bias voltage, which presumably changes the microstructure of the films and the related magnetic anisotropy.

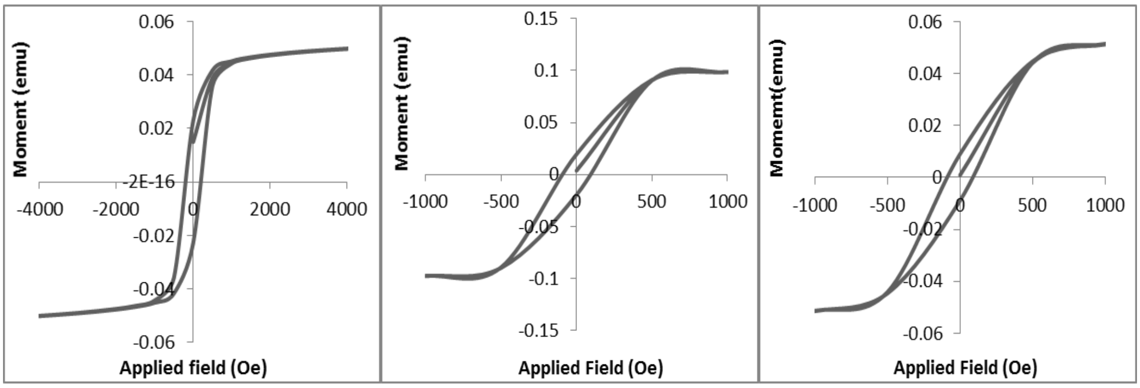


Fig. 3. VSM images of Co-Fe-W films electrodeposited for 45 minutes at (a) 2.5mA cm^{-2}, (b) 5mA cm^{-2} and(c) 7.5mA cm^{-2}.

4. Conclusions

At constant PH (8.0), Co-Fe-W thin film with different current densities was prepared by electrodeposition. Bright and uniformly coated thin films confirm the added advantages in the thin film technology. The XRD results reveal the existence of cubic crystal structure of the prepared thin film. The crystalline size of deposits decreases due to onset orientation of crystal while increasing current density. When current density is increased from 2.5mA cm^{-2} to 7.5mAcm^{-2} the magnetic saturation increased from 0.053 emu to 0.073 emu. Also, the coercivity decreases from 215.90 Oe to 83.687 Oe. This is due to nano crystalline structure of deposits. The Co-Fe-W shows good hard magnetic properties when electrodeposited in lower current density. On addition of tungsten (W) with increase in current density, the film character is changed to soft magnetic character and it enhances magnetic, mechanical and structural properties. The hardness of the film also increases in current densities which are having lower coercivity value and lower remanent values. On increases current density the films are lower stress which are used in MEMS devices and this alloy films can also be used memory devices.

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