Preparation and characterization of ferrous manganese thin films for magnetic storage devices

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The nanocrystalline nature of Ferrous Manganese (Fe-Mn) thin film coatings was obtained from sulphate baths at different current densities on the copper substrate. The effects of current density on structure, surface morphology, elemental composition, magnetic properties, and mechanical properties of electrodeposited Fe-Mn magnetic films were studied. The structural and surface properties of Fe-Mn thin films were studied using an X-ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). The chemical compositions of the deposited films were investigated using Energy Dispersive X-ray Spectroscopy (EDAX). The magnetic properties of the thin films were studied with the aid of a Vibrating Sample Magnetometer (VSM). The electrodeposited Fe-Mn films were found to be nanocrystalline in nature due to the increase in current density. The deposits of Fe-Mn thin films were found to have a crack-free and smooth surface at low current densities. The films have good adherence to the copper substrate.

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1. Introduction

The hard magnetic thin films were synthesized by the electrodeposition method, which is a dominant manufacturing technology compared to chemical vapor deposition, physical vapor deposition, direct current sputtering, and radio frequency sputtering [1]. Ferromagnetic alloys such as Fe, Ni, and Co have been versatile materials in recent technological applications due to miniaturization, cost-competitiveness, high performance packaging, ease of maintenance, and quality deposits [1-5]. Electrodeposition has become the preferred technique in the electronics industry. The current developments in steel research depend on Fe-Mn alloys with up to 30% Mn for their greatly improved strength and ductility [6]. Fe-Mn hard magnetic materials are widely used in MEMS devices such as microactuators, sensors, micromotors, recording media, magnetic data storages, magnetic shielding, and magnetic writing heads [7-10]. There are few literary reports on magnetic thin film preparation with sulphate-based ferromagnetic materials such as ferrous sulphate, nickel sulphate, and cobalt sulphate. The majority of these works concentrate only on studying the regularity of the deposition of nickel–manganese and cobalt–manganese alloys, though an iron–manganese coating was considerably cheaper than nickel and cobalt. It is characterized by higher physicochemical properties compared to pure iron [11-16].

In the present study, we investigated in detail the effects of various current densities and deposition times on the structural and magnetic properties of ferrous manganese thin films.

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2. Experimental

2.1. Synthesis and Deposition

Fe-Mn thin films were prepared by the electrodeposition method using a copper substrate as a cathode and pure stainless steel as an anode. The sizes of the copper plate were 1.5 cm in breadth and 7cm in length and the same size of stainless steel was used. The electrodes, such as the cathode and anode, were cleaned using concentrated sulphuric acid (H_2SO_4) and rinsed with de-ionized water to remove foreign particles present on the substrate. Then they were cleaned with acetone to completely remove the impurities. Finally, the substrate was thoroughly rinsed with doubly distilled water.

Fe-Mn magnetic thin films were prepared from a bath containing 0.1 M of ferrous sulphate ($FeSO_4.7H_2O$), 0.1 M of manganese II sulphate ($MnSO_4.H_2O$), 0.3 M of tri-sodium citrate ($Na_3C_6H_5O_7.2H_2O$), 0.16 M of boric acid (H_3BO_3), and 0.3 M of ammonium sulphate ($(NH_4)_2SO_4$). Using dilute NaOH or H_2SO_4, the pH value of the bath was adjusted to 8. A regulated power supply supplied dc current for electrodeposition. The deposited films were coated at various current densities (20 mA cm^{-2}, 25 mA cm^{-2} and 30 mA cm^{-2}) and different deposition times (15, 30 and 45 minutes).

2.2. Characterization

Structural studies were carried out using XRD. The crystalline sizes of the deposited Fe-Mn were investigated using XRD data. The structural morphology of the Fe-Mn thin films is studied with the aid of Scanning Electron Microscope (SEM). The chemical composition of the deposits was investigated by Energy Dispersive X-ray spectroscopy (EDAX). The hardness of the coating film was calculated using Vicker's hardness tester by diamond intender method. The thickness of the deposit was measured using a digital micrometer (Mitutoyo, Japan). Adhesion of the film was tested by bent test and scratch test. The magnetic properties like magnetic saturation (M_s), coercivity (H_c), and retentivity (M_r) of Fe-Mn films were studied with a Vibrating Sample Magnetometer (VSM).

3. Result and Discussion

3.1. Thickness Study

The thickness of electrodeposited Fe-Mn films is tabulated as shown in Table 1. The data in table 1 clearly indicate that the thickness of the films increases with an increase in deposition time and current density. The magnetic properties of the films also increase with the increase in film thickness.

Table 1. Effect of the thickness and magnetic properties of electrodeposited Fe-Mn magnetic thin films with different current densities and different deposition times.

S. No.	Current density (mA cm^{-2})	Deposition time (mins)	Thickness of deposit (µm)	Magnetic saturation (x10^{-3}emu)	Remanent polarization (x10^{-3}emu)	Coercivity (Oe)	Squareness
1		15	2.3	2.415	0.097	85.33	0.040
2	20	30	2.6	8.489	0.507	96.35	0.060
3		45	2.7	10.896	0.799	131.73	0.073
4		15	3.0	4.683	0.181	101.50	0.039
5	25	30	3.1	9.674	0.539	111.43	0.060
6		45	3.3	23.215	1.618	139.63	0.070
7		15	3.4	10.189	0.427	119.14	0.042
8	30	30	3.7	17.164	0.913	138.82	0.053
9		45	3.8	26.779	2.042	158.84	0.076

3.2. Surface analysis

3.2.1. Structural analysis

The electrodeposited Fe-Mn films were obtained from the bath containing the current densities of 20 mA cm^{-2}, 25 mA cm^{-2}, and 30 mA cm^{-2} with a deposition time of 45 minutes. They were analyzed by XRD studies and shown in Fig. 1. The data obtained from the XRD pattern were compared with the standard JCPDS data and were found to have a cubic nature in Mn (111) (JCPDS card number 88-2327), Fe (222) (JCPDS card number 01-1267), Mn (332) (JCPDS card number 20-0180) and a hexagonal nature in Fe (008) (JCPDS card number 50-1275) planes. The presence of sharp peaks in the XRD pattern reveals that the films are crystalline in nature.

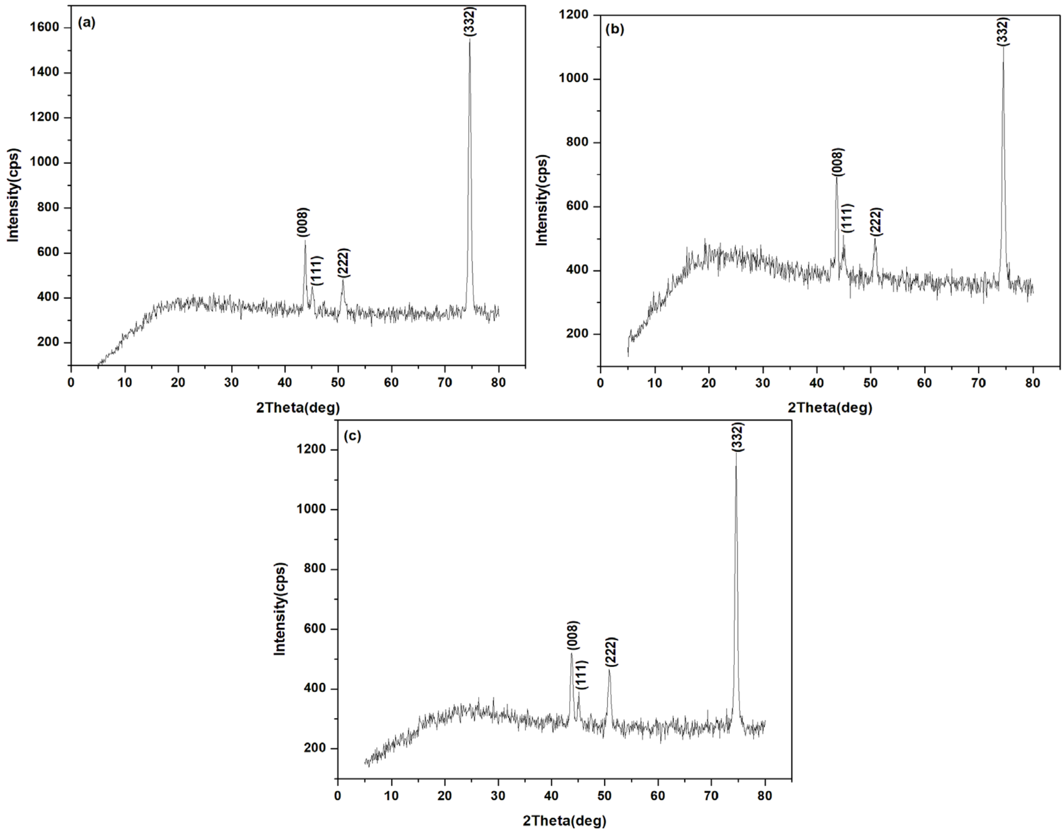

Fig. 1. XRD images of electrodeposited Fe-Mn films for 45 min deposition time at the current densities of a) 20 mA cm^{-2}b)25 mA cm^{-2} and c) 30 mA cm^{-2}.

Table 2.The crystalline size, strain, dislocation density, and composition of electrodeposited Fe-Mn thin films for 45 minutes of deposition time.

Current density (mA cm^{-2})	Crystalline size (nm)	Strain 10^{-4}	Dislocation Density ($10^{14}/m^2$)	Vicker Hardness Number (VHN)	Film Composition (at %)	
					Fe	Mn
20	18.3054	3.9860	3.004	139.535	96.50	3.50
25	17.5796	4.2133	3.3325	149.0797	91.36	8.64
30	16.7802	4.3842	3.6072	161.9913	87.37	12.63

3.2.2. Morphological observation

SEM images of electrodeposited Fe-Mn films are shown in Fig. 2. It shows that the prepared films had a uniform orientation and a smooth crack-free surface. At low current density, the film has a cone-like structure, and the crystalline nature of the deposited magnetic thin film mostly depends on the presence of ferrous and manganese.

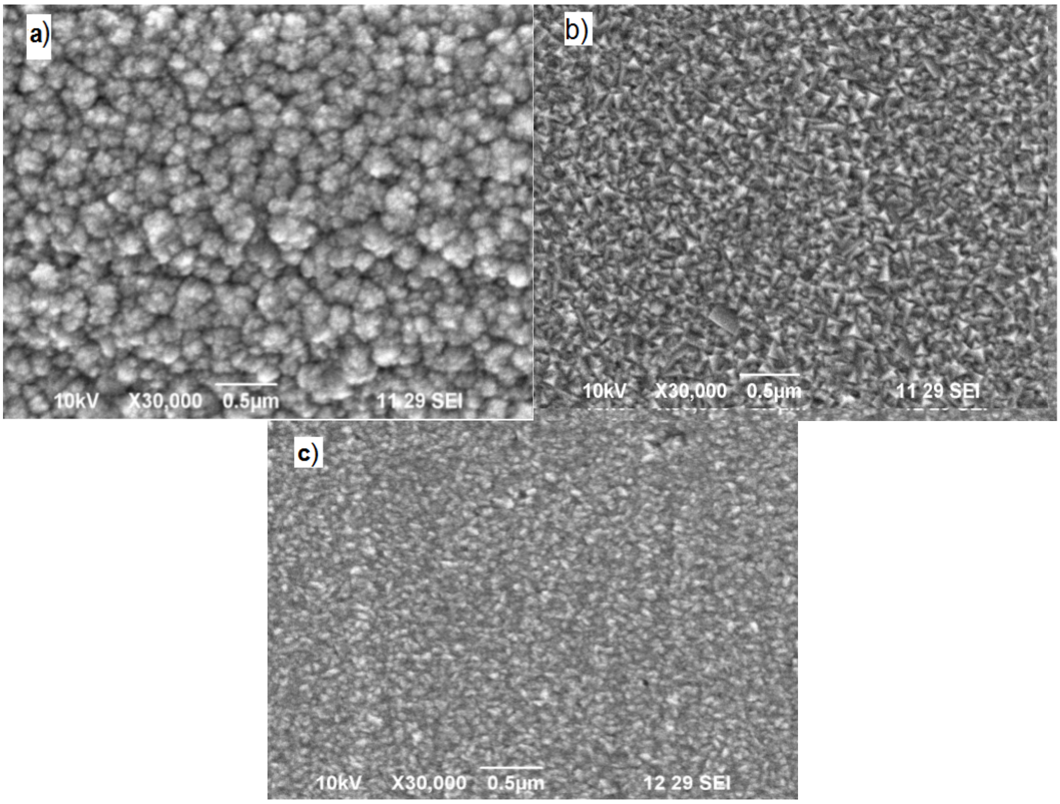

Fig. 2. SEM images of electrodeposited Fe-Mn films for 45 minutes deposition time at the current densities of a) 20 mA cm^{-2}b) 25mA cm^{-2} and c) 30 mA cm^{-2}.

3.3. Mechanical properties

The hardness of electrodeposited Fe-Mn magnetic films was examined using a Vickers hardness tester by the diamond intender method and the values are displayed in Table 2. When the current density increases from 20 mA cm^{-2} to 30 mA cm^{-2}, the hardness values increase from 139.535 VHN to 161.9913 VHN. This is due to the presence of stress in the film. A bend test and a scratch test revealed that the adhesion of the film to the substrate was good.

3.4. Composition of the electrodeposited Fe-Mn thin films

The chemical composition of the Fe-Mn films was analysed by EDAX, and it is shown in Fig 3. The percentage of the electrodeposited film composition is tabulated in Table 2. The EDAX result showed that the increase in current density decreased the percentage of ferrous and increased the percentage of manganese.

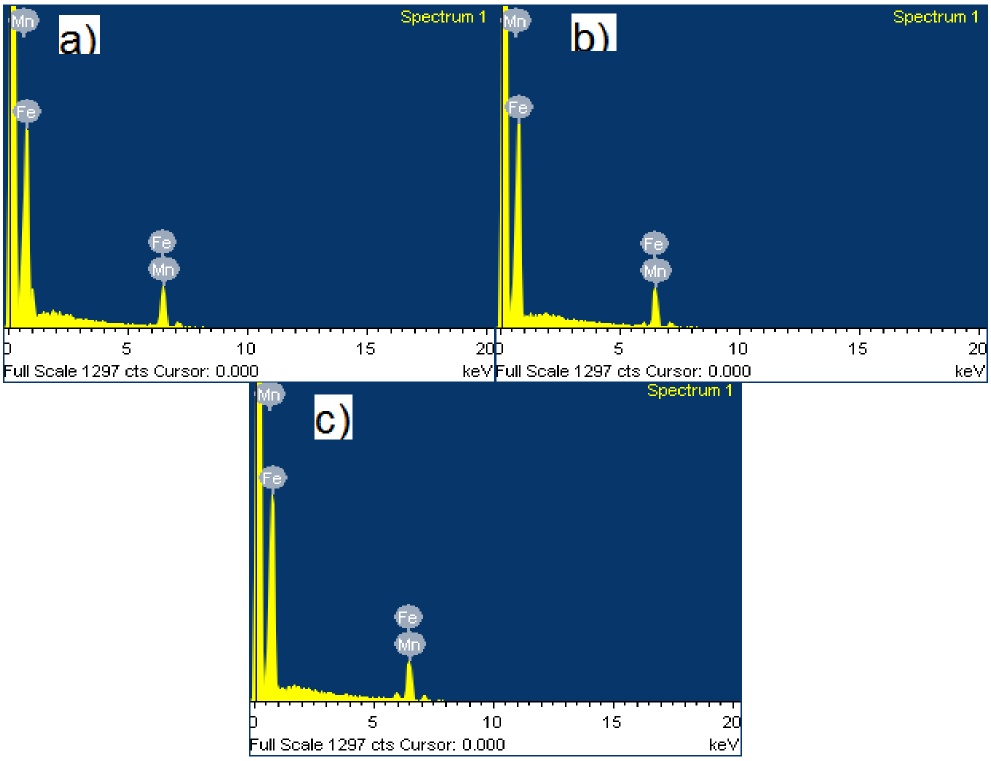

Fig.3. EDAX spectrum of electrodeposited Fe-Mn thin films for 45 minutes deposition time at the current densities of a) 20 mA cm^{-2}b) 25mA cm^{-2} and c) 30 mA cm^{-2}.

3.5. Magnetic Studies

The VSM images of Fe-Mn magnetic thin films are shown in Fig 3.

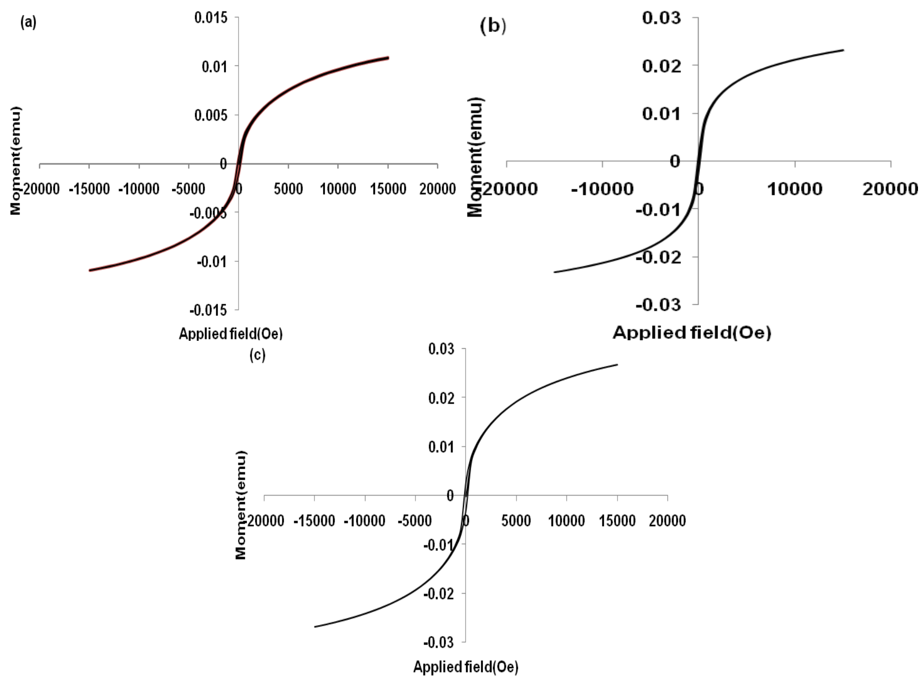

Fig. 3. VSM images of electrodeposited FeMn films for 45 minutes deposition time at the current densities of a)20 mA cm^{-2}, b) 25 mA cm^{-2}and c)30 mA cm^{-2}

On increasing the current density from 20 mA cm^{-2} to 30 mA cm^{-2} the magnetic saturation and the remanent polarization increase from 2.415 x 10^{-3} emu to 26.779 x 10^{-3} emu and from 0.097 x 10^{-3} emu to 2.042 x 10^{-3} emu, respectively. It shows that the increase in current density increases the magnetic properties of the films.

4. Conclusions

The Fe-Mn electromagnetic thin films were successfully synthesized by electrodeposition at room temperature. The nanocrystalline nature of thin films is obtained at room temperature with a crack free, bright, uniform film and good adhesion. The crystalline sizes of the Fe-Mn films are in the nano scale range. The crystalline size of the film decreases from 18 nm to 16.8 nm when the current density increases from 20 mA cm^{-2} to 30 mA cm^{-2}. The maximum average crystalline size of Fe-Mn magnetic films was found around 18 nm. The maximum hardness of magnetic thin films was found to be around 162 VHN. High coercivity and remanent values were observed as 158.84 Oe and 2.042 x 10^{-3} emu respectively, in the bath, which contained a current density of 30 mA cm^{-2} and a deposition time of 45 minutes. Due to the higher magnetic properties of electrodeposited Fe-Mn thin films, it may be used in various electronic devices, including high-density storage of recording media, magnetic writing heads, magnetic data storage, magnetic shielding, and MEMS.

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