INFLUENCE OF TRI SODIUM CITRATE BATH CONCENTRATION ON THE ELECTRO DEPOSITION OF Ni-Fe-W-S THIN FILMS

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In this present work, the Ni-Fe-W-S alloy thin films were electro plated from Tri Sodium citrate bath by varying the bath concentration at 60°C. The coated films were characterized by using EDAX, SEM, XRD, VHT and VSM. The SEM micrographs of the deposited Ni-Fe-W-S films exhibited smooth and uniform surface morphology. All the deposited Ni-Fe-W-S thin films have Nano crystalline structure (grain size's were calculated from Scherrer equations) and the FCC structure was the dominant microstructure of the NiFeWS alloy films. The VSM results of the Ni-Fe-W-S thin film reveals that the coated films have the best soft magnetic properties and are suitable for MEMS applications. The effects of citrate bath concentrations on magnetic properties were also discussed. The films coated from bath concentration of 0.3 mol / lit exhibits the lower coercivity and higher magnetization values. So that the citrate bath concentration was optimized to get excellent soft magnetic Ni-Fe-W-S alloy thin films.

(Received February 7, 2013; Accepted March 23, 2013)

Keywords: Tri sodium citrate, bath concentration, MEMS, coercivity and soft magnetic properties.

1. Introduction

The most commonly used magnetic materials in Micro Electromechanical Magnetic Systems (MEMS) are soft magnetic materials such as Permalloys (Permalloy is a nickel-iron magnetic alloy, with about 20% iron and 80% nickel content. Among the ferromagnetic materials NiFe based alloys considered as a very good choice for MEMS because of their highest saturation flux density, lower coercivity and lower magnetostriction [1-2]. The magnetic recording head is a key device for achieving high density magnetic recording, with soft magnetic thin films being used as core materials. For fabricating the magnetic recording head, electro deposition is the most suitable method. NiFe based thin films were most commonly fabricated by sputtering technique and electro deposition method. Electro deposition offers several practical advantages over sophisticated sputtering techniques in terms of cost and growth rate [3]. For fabricating MEMS devices magnetic properties such as high saturation magnetization, very low coecivity and anisotropy are needed for the purpose of minimizing hysteresis losses and hence avoid excessive power consumption and heating of the element [4].The Ni-Fe alloys with composition close to 80% Ni are very much used for producing the magnetic recording heads. Addition of alloying elements like W and Mo to NiFe alloys can reduce coercivity of the films and also improve corrosion resistance and other magnetic properties [5-6]. W is a good candidate as it is highly corrosion resistant metal and also bears high mechanical strength. Very few research works are

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documented about the structural and composition of electrodeposited crystalline NiFeW alloys [7-9].

The Low stress thin film alloys with improved magnetic properties are very much used in magnetic recording heads and MEMS. The best known stress reducing agents for nickel based electro deposition are sulfur [10-11]. The magnetic properties of NiFeW thin films are strongly depends on grain size and film stress. In order to decrease the grain size and film stress other elements were added to NiFeW alloy electro deposition bath. In this investigation Thiourea was (source material for Sulphur) tried. So we planned examine the electro deposited NiFeWS alloy thin films from Tri Sodium citrate bath for MEMS applications [12-13]. This article summarizes the results of electro deposited Ni-Fe-W-S films in Tri Sodium Citrate bath with different concentration.

2. Experimental Part

2.1 Electro deposition of NiFeWS thin films from Tri Sodium citrate bath

The bath composition of NiFeWS alloy thin film is shown in Table 1. Electro deposition was carried out by varying the Sodium citrate bath concentration (0.2, 0.3, 0.4, 0.5 mol / lit) at 60˚C. Copper substrate was cut out from a copper foil with thickness 0.1 mm and 7.5 cm in length and 1.5 cm as breath. A Cu substrate of size 1.5× 5 cm as cathode and pure steel of same size as anode were used for electro deposition experiments. An adhesive tape was used to mask off all the substrate except the area on which the deposition of films were desired. Analytical reagent grade chemicals were used to prepare bath. The bath pH was kept constant at 8 by adding few drops of ammonia solution. Copper and stainless steel electrodes were degreased and slightly activated with 5% sulphuric acid and then rinsed with distilled water just before deposition. The Cu surface was electrodeposited by dipping into a bath solution while applying a current of 75 mA/cm^2 for 30 minutes at different Tri Sodium citrate bath concentrations (0.2, 0.3, 0.4, 0.5 mol / lit).

The structure and morphology of the NiFeWS thin films were studied with the help of XRD and SEM. The magnetic properties were studied by using VSM. The film composition was measured by Energy-dispersive X-ray Spectroscopy (EDAX).Hardness of the film was measured by Vickers Hardness Test (VHN).The thicknesses of the films were determined by cross sectional view of SEM images.

Table 1. Composition and operating conditions of the electroplating bath from Sodium citrate bath.

S.No	Name of the chemical parameters	Data
1.	Nickel sulphate	60 g/l
2.	Ferrous sulphate	30 g/l
3.	Sodium tungstate	10 g/l
4.	Thiourea	7.5 g/l
5.	Tri Sodium citrate	(0.2, 0.3, 0.4, 0.5 mol / lit).
6.	Citric acid	5.5 g/l
7.	Boric acid	10 g/l
8.	pH value	8
9.	Temperature	60(˚C)
10.	Current density	1 A/dm^2

3. Results and discussion

3.1 Composition of the deposits

The electrodeposited NiFeWS alloy films were smooth, uniform and adherent. The composition of the NiFeWS film from Tri Sodium citrate bath was obtained from the EDAX analysis. The weight percentages of the films deposited with different Tri Sodium citrate bath are tabulated as shown in Table 2.

EDAX result showed that Ni content decreases with increasing the Tri Sodium citrate concentration. The maximum Ni content of 60.26 wt % was obtained for NiFeWS thin films from the Tri Sodium citrate bath concentration of 0.2 mol / lit. The weight percentage of Fe increases while increasing the bath concentration. The films obtained from Tri Sodium citrate bath have low Sulphur content. So that the coercivity of films get reduced and the magnetization values were increased. The lowest Sulphur content of 7.27 wt% was obtained at temperature 60˚C in Tri Sodium citrate bath (0.5 mol / lit). It is usual to ignore the effect of ammonia on the composition of the films, as it is a mild base which is used to adjust the pH of the solution. At low W dosage W ions are only complexed, as the dosage increases, the Ni Fe ions are also complexed. Metals are more difficult to plate out from the complexed ions, due to high activation energies and low diffusivities to the cathode.

Table 2. Results of EDAX analysis from Tri Sodium citrate bath

S.No	Citrate bath concentration (mol/lit)	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1.	0.2	60.26	26.02	0.7	13.02
2	0.3	58.86	30.92	0.94	9.28
3	0.4	54.31	37.54	0.86	7.29
4	0.5	53.98	37.87	0.88	7.27

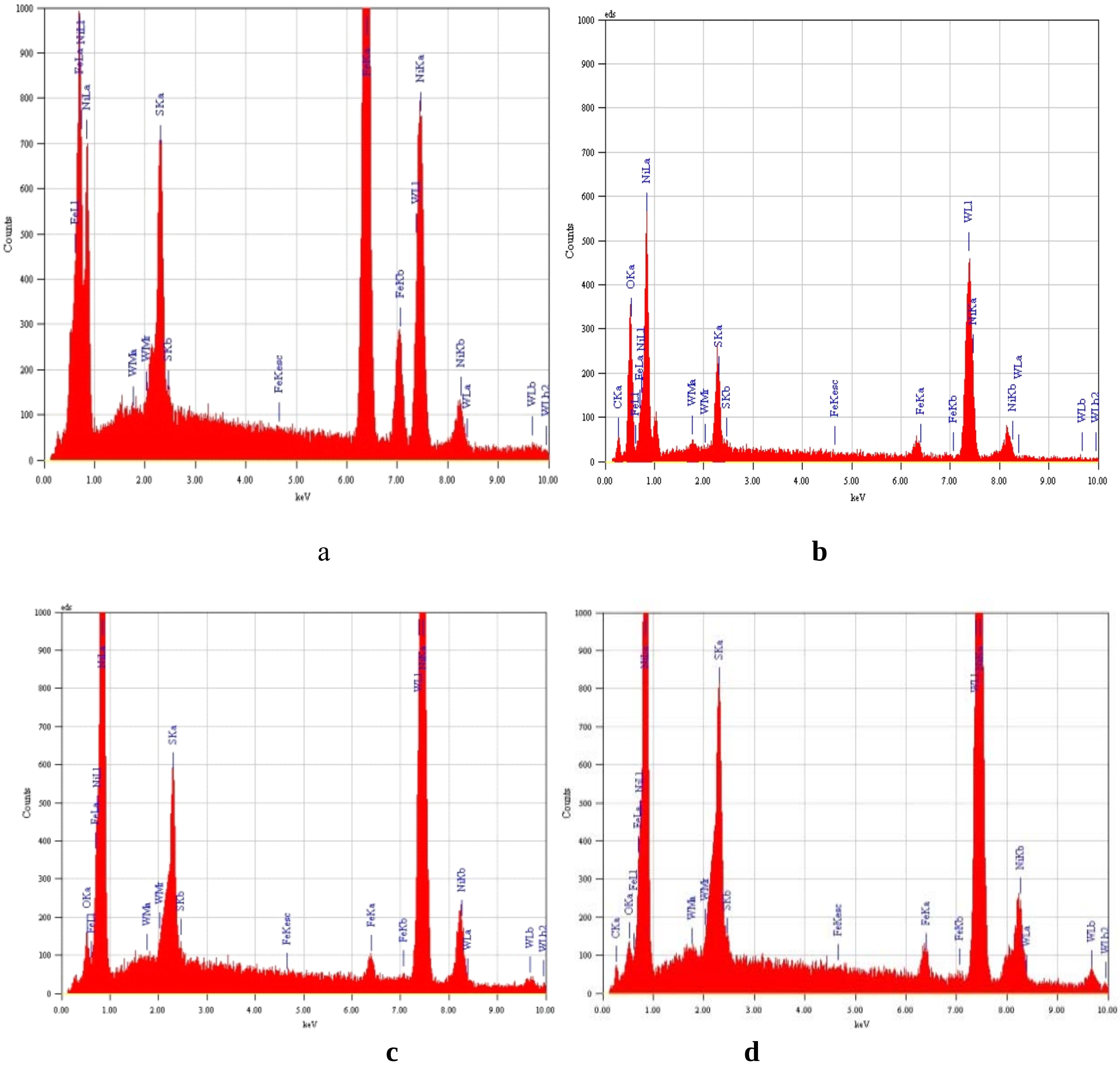


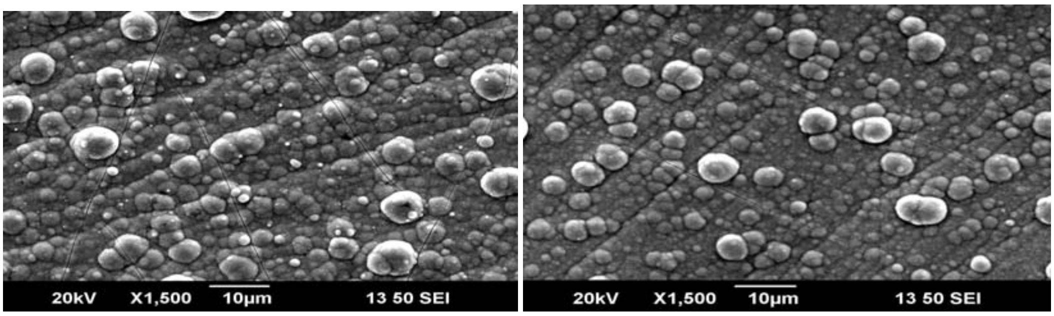
Fig 1. EDAX Spectrum of Electro deposited Ni-Fe-W-S thin film deposited from different citrate concentration (a) 0.2 mol / lit. (b) 0.3 mol / lit. (c) 0.4 mol / lit. (d) 0.5 mol / lit.

3.2 Morphology of the deposits

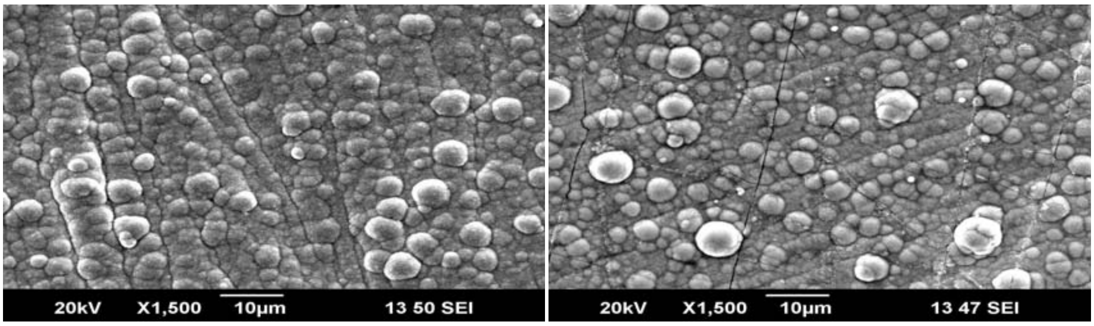
The SEM images of electrodeposited NiFeWS thin films from Tri Sodium citrate bath are shown in Fig 1.The films obtained from low citrate concentration have some micro cracks. This is due to the generation of internal stresses resulting in the formation of micro cracks. The film obtained from higher citrate bath concentration (0.5 mol/ lit) of Tri Sodium citrate bath has uniform morphology and there is no observable micro void on the film surface. The low pH baths in electro deposition of thin films can lead to the formation of micro voids which affects the film properties. So in this investigation the bath pH value is 8 which leads to form uniform surface morphology. The films obtained at higher temperature are crack free and grain boundaries can be seen among the crystal grains. The variation of surface morphology may be related to the change in the preferred orientation of the microstructure. Hence the film has low stress. As Tri Sodium citrate bath concentration increased, the grain size is decreased and the film surface becomes smoother. Thicknesses of the deposited NiFeWS films were determined from cross sectional view of SEM images and are shown in Table 3.

Table 3.Film thickness from cross sectional view of SEM images

S.No	Citrate bath concentration (mol/lit)	Crystalline size D nm	Film Thickness µm
1	0.2	28.90	1.88
2	0.3	24.49	1.92
3	0.4	23.37	1.12
4	0.5	29.34	1.66



(a) **(b)**



(c) **(d)**

Fig 1. SEM images for Electro deposited Ni-Fe-W-S thin film deposited from different citrate concentration (a) 0.2 mol / lit. (b) 0.3 mol / lit. (c) 0.4 mol / lit. (d) 0.5 mol / lit.

3.3 X-ray diffraction of the deposits from Tri Sodium Citrate Bath

The crystal structure of the electro deposited NiFeWS alloy thin films was determined by XRD analysis. X-ray diffraction patterns of various NiFeWS films obtained by varying the concentration of Tri Sodium citrate bath at 60˚C temperature were shown in Fig 2. The presence of sharp peaks in XRD pattern reveals that the films are crystalline in nature. Crystalline size of the deposits were calculated from the XRD pattern using the formula

$$D = \frac{0.94\ 5\lambda}{\beta cos\theta}$$

These values clearly show that the crystalline sizes of the NiFeWS deposits obtained by electro deposition process are in the nano scale. The crystal size of NiFeWS alloy films obtained from Tri Sodium Citrate bath are tabulated as shown in Table 4. The XRD patterns of NiFeWS films revealed the existence of FCC phase with (111), (511) and (205) diffraction peaks. The crystalline size decreases with increase in bath concentration. The grain growth and its size are sensitive to the deposition parameters such as the rate of depositions, bath temperature and bath concentration. During electro deposition, if atoms are located on irregular crystallographic positions of a growing cluster, they can lead to the nucleation of the other phase and consequently decreasing the grain size.

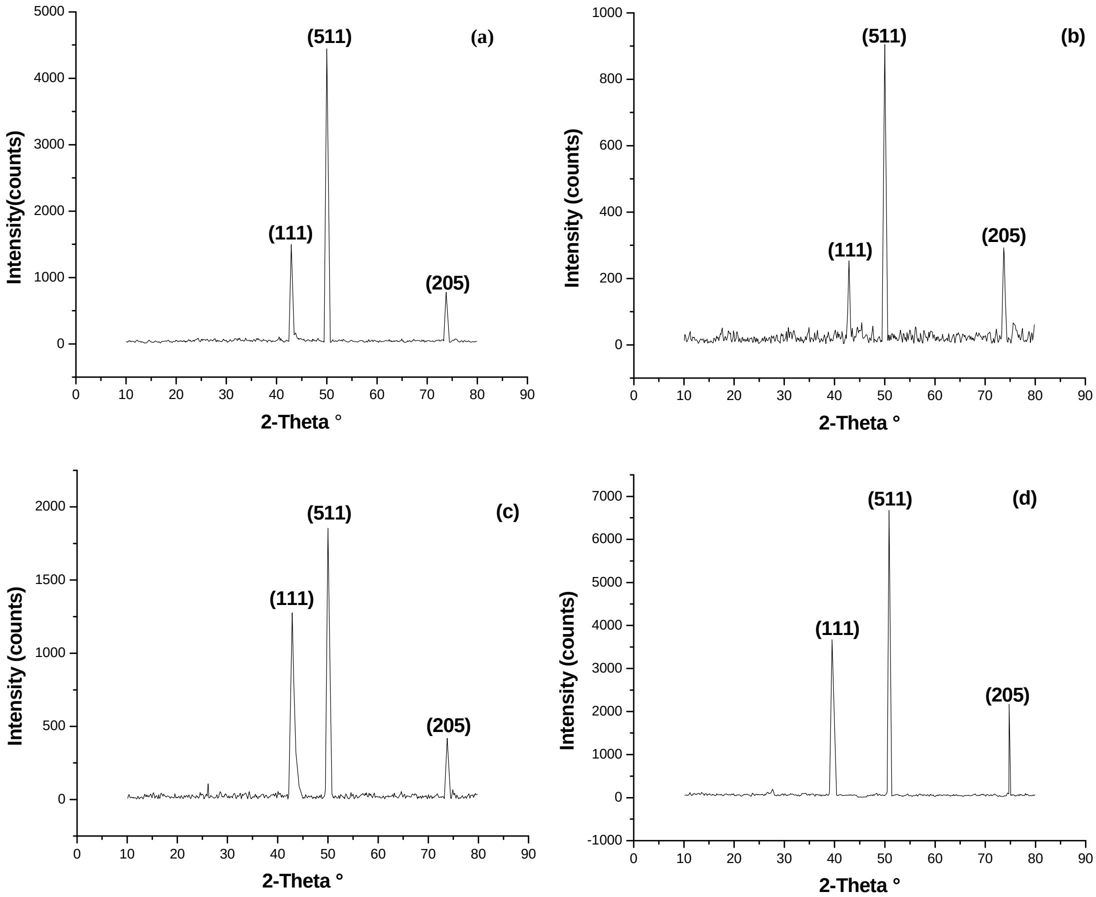


Fig 2.XRD pattern of Electro deposited Ni-Fe-W-S thin film deposited from different citrate concentration (a) 0.2 mol / lit. (b) 0.3 mol / lit. (c) 0.4 mol / lit. (d) 0.5 mol / lit.

Table 4.Structural characteristics of NiFeWS alloy thin films from Tri Sodium Citrate Bath

S.No	Citrate bath concentration (mol/lit)	2 θ (deg)	Lattice parameter a (A^0)	Crystalline size D nm	Strain 10^{-4}	Dislocation density(10^{14} / m^2)	Film Thickness µm
1	0.2	50.02	9.4661	28.90	12.528	11.9730	1.88
2	0.3	50.02	9.4661	24.49	14.780	16.6733	1.92
3	0.4	50.02	9.4661	23.37	15.492	18.3098	1.12
4	0.5	50.86	9.2242	29.34	12.338	11.6166	1.66

3.4 Mechanical Properties

Adhesion of the film with the substrate is tested by bend (bending the film with substrate to 180˚) test and scratch test. Draw equal lines by pin and paste an adhesive tape over the scratch and pull it. If the film comes with tape then the adhesion is poor. This test showed that the film is having good adhesion with the substrate. Hardness of the films was examined using a Vickers hardness tester by the diamond intender method. The results are tabulated and shown in Table 5. The results show that the hardness varied with increasing the concentration of Tri Sodium citrate bath. This may be due to lower stress associated with electrodeposited Ni-Fe-W-S film in Tri Sodium citrate bath. The dependence of Vickers hardness and Bath concentration is shown Fig 3.

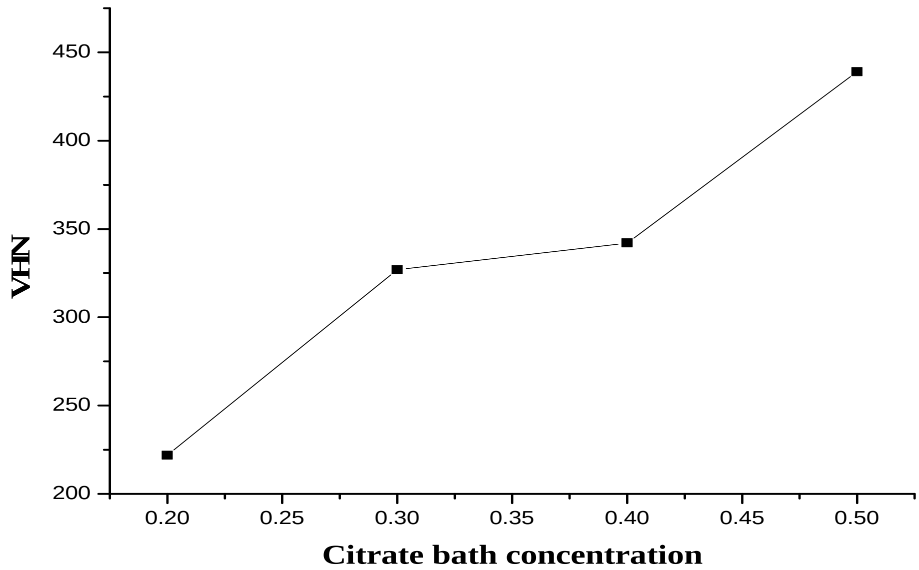


Fig 4. Vickers Hardness as a function of Citrate bath concentration.

Table 5. Mechanical Properties of Electro deposited Ni-Fe-W-S thin film from Tri Sodium Citrate Bath

S.No	Citrate bath concentration (mol/lit)	Crystalline size D Nm	Vickers Hardness (VH)
1	0.2	28.90	222
2	0.3	24.49	327
3	0.4	23.37	342
4	0.5	29.34	439

3.5 Magnetic properties of the deposits

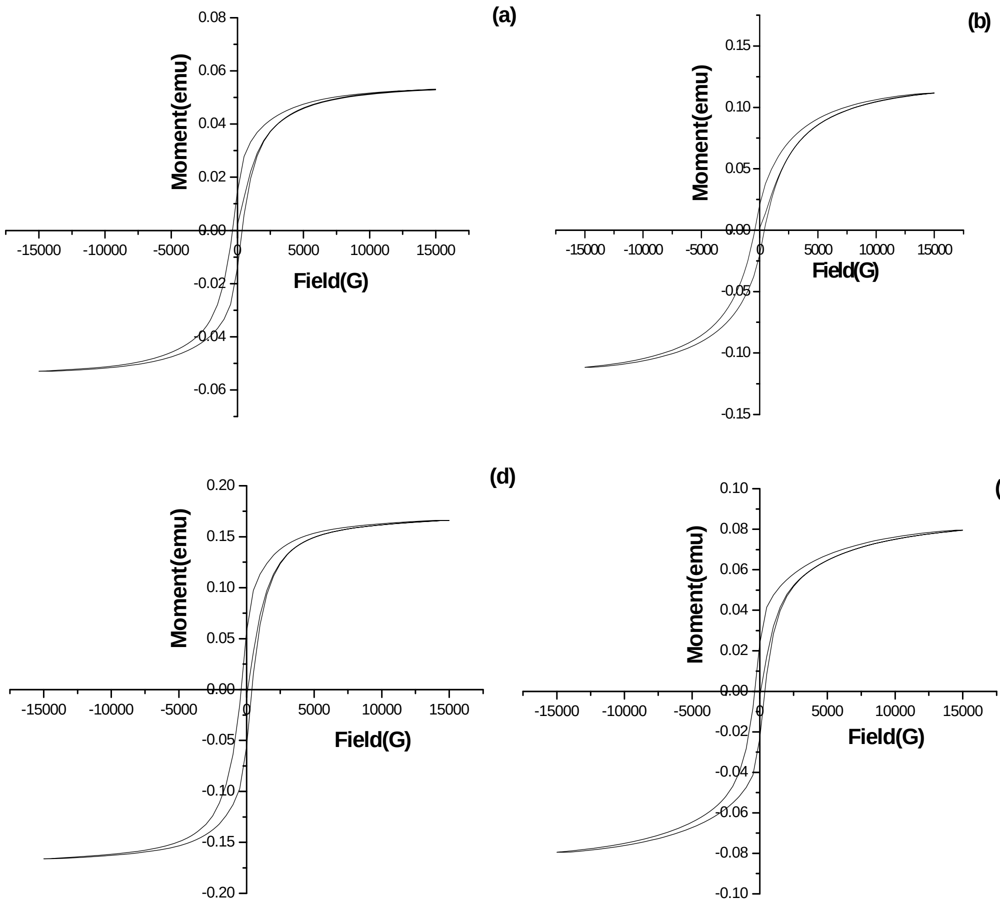


Fig 4. Magnetic Hysteresis loops for Ni-Fe-W-S thin film deposited from different citrate concentration (a) 0.2 mol / lit. (b) 0.3 mol / lit. (c) 0.4 mol / lit. (d) 0.5 mol / lit.

The magnetic properties of the electrodeposited NiFeWS films have been observed from VSM are tabulated as shown in Table 6.The magnetic Hysteresis loops for NiFeWS alloy thin films prepared from different Tri Sodium citrate bath concentrations at temperature 60°C is shown in Fig 4.

The film coated under the temperature of 60 ˚C and citrate concentration of 0.3 mol / lit exhibits the higher magnetization and magnetic flux density. It was observed that the magnetization and coercivity of the film was 0.17167 emu/cm^2 and 303.83 Gauss. From that we concluded the films prepared at bath concentration of 0.3 mol / lit (60˚C) exhibits a higher value of saturation magnetization and magnetic flux density.

Table 6. Soft Magnetic Properties of Ni-Fe-W-S deposits from Tri Sodium Citrate Bath.

S.No	Citrate bath concentration (mol/lit)	Coercivity H_c (G)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Squareness S (M_r / M_s)
1	0.2	407.78	53.047×10^{-3}	13.985 ×10^{-3}	0.2636
2	0.3	303.83	0.17167	19.102 ×10^{-3}	0.1113
3	0.4	368.30	79.516×10^{-3}	23.150 ×10^{-3}	0.2911
4	0.5	393.59	0.1661	26.090 ×10^{-3}	0.1570

Among the magnetic properties coercivity is crucial for the NiFe based thin films because it is well known to posses low coercivity that could be used in soft magnetic applications. The coercivity is highly affected by the grain size of the films. If the grain size is large enough to have multiple domains, magnetization of ferromagnetic materials occurs via domain wall movement. If the grain size is in the nano meter range, where it is smaller than the effective domain-wall width, the magnetic properties can be changed. Below the magnetic exchange length, the smallest grain size for magneto crystalline anisotropy governing the magnetization process, the H_c shows a steep decrease with decreasing grain size [14-16]. Coercivity could be affected by not only grain size but also several factors such as impurities, film stress, crystalline anisotropy etc.

Among these, film stress affects the coercivity strongly. The effect of film stress on coercivity should be considered because soft magnetic properties of iron based films depends on film stress very sensitively and compressive stress lead to high coercivity but the tensile stress reduces coercivity [17-18]. This indicates that as concentration of the bath increases the films may be under tensile stress and this leads to increase in saturation magnetization. Crystalline Permalloy has very low magnetostriction. Due to this nano crystalline NiFeWS films have very low magnetostriction and the intrinsic anisotropy was simultaneously minimized with highest possible permeability. So that these films can be used for devices like magnetic recording heads. The dependence of coercivity with citrate bath concentration is shown Fig 5.

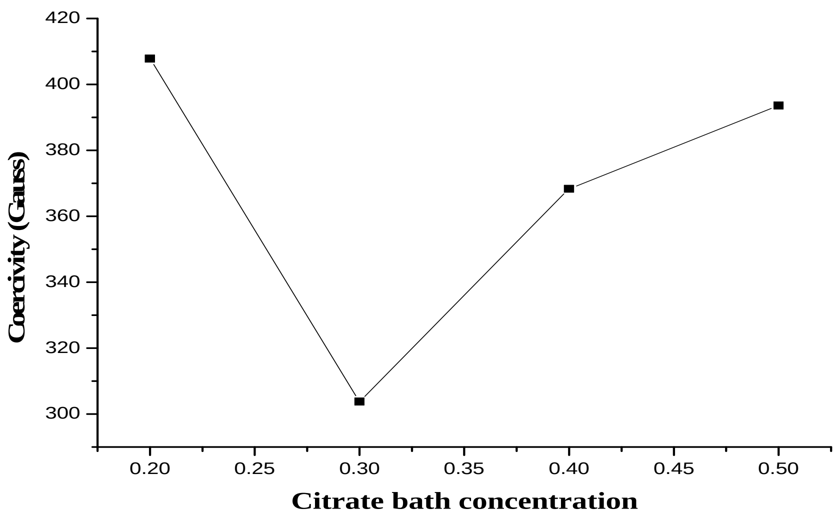


Fig 5. Citrate bath concentration as a function of Coercivity

Variation in coercivity with increase in bath concentration is caused by relaxation of lattice distortion. The low coercivity obtained at Tri Sodium citrate bath concentration of 0.3 mol / lit may be due to decrease in strain and dislocation density of the NiFeWS films. The presence of W, a non magnetic alloying element, affects the saturation magnetization by means of dilution mechanism. Coercivities of the films were gradually decreased with increasing Ni content for Ni-Fe based films. When the Ni content is higher than 48 at %, Coercivity decreased as grain size decreased by possessing the predominant microstructure FCC. From VSM results of NiFeWS thin films, it is concluded that Ni content of the films are above 48 at % with increasing the bath concentration. The film stress is reduced because of increase in Ni content. Because of low stress and smaller crystalline size the NiFeWS thin films obtained at 60˚C bath temperature (concentration of 0.2 mol / lit) have higher saturation magnetization with lower coercivity. By analyzing the present results it can be seen that the best soft magnetic properties have been obtained for the electroplated nano crystalline films from Tri Sodium citrate bath concentration of 0.3 mol / lit at 60˚C temperature. So we conclude that the Tri Sodium citrate bath concentration of about 0.3 mol / lit is optimized to obtain good soft magnetic NiFeWS films.

4. Conclusion

In this study we have presented the report of nano crystalline Ni-Fe-W-S alloy thin films. The Ni-Fe-W-S thin films were synthesized from electro deposition process on to copper substrate with different citrate bath concentration at the current density of 1 A / dm^2. Increase in the concentration of citrate bath will affect the soft magnetic properties of Ni-Fe-W-S thin films. The electro plated Ni-Fe-W-S films from citrate bath concentration of 0.3 mol / lit have low coercivity and high magnetization values. It was observed that the magnetization and coercivity of the film was 0.17167 emu/cm^2 and 303.83 Gauss. This is due to nano crystalline microstructure and low film stress associated with NiFeWS. Hardness of this magnetic thin film also affected by increasing the bath concentration. Because of their soft magnetic properties, these films can be used in various electronic devices including high density recording media, magnetic actuators, magnetic shielding, magnetic writing heads high performance transformer cores and MEMS.

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