International Journal of Thin Films Science and Technology

http://dx.doi.org/10/12785/ijtfst/020309

Development of High Performance Magnetic Ni-Fe-W-S Thin Film for Micro Electro Mechanical System.

R. Kannan[1,*], S. Ganesan[2], P.Esther[3] and C. Joseph Kennady[4]

[1]Department of Physics, KSR College of Engineering, Tiruchengode-637215, Tamil Nadu, India
[2]Department of Physics, Government College of Technology, Coimbatore-641001, Tamil Nadu, India
[3]Department of Physics, LRG Government Arts College for Women, Tirupur, Tamil Nadu, India
[4]Department of Chemistry, Karunya University, Coimbatore-641 114, Tamil Nadu, India

E-mail: kannanarjun13@gmail.com

Received: 19 Jul. 2013, Revised: 29 Jul. 2013; Accepted: 19 Aug. 2013
Published online: 1 Sep. 2013

Abstract: Electro deposition of NiFeWS thin films was carried out from Tri Potassium citrate bath at a constant current density (1 A/dm^2) and controlled pH of 8 by varying bath temperature. Physical properties such as surface morphology, microstructure and magnetic properties such as coercivity, saturation magnetization, magnetic flux density were investigated for electrodeposited NiFeWS soft magnetic thin films. The characteristics of the NiFeWS thin films were enhanced when the temperature of the bath increased. The SEM micrographs of the electrodeposited films at 80˚C exhibited no micro cracks and more uniform. According to X-ray diffraction pattern, the FCC structure was the dominant microstructure of the NiFeWS alloy films and all the electroplated films were exhibited Nano crystalline structure. The VSM results demonstrated that the coercivity of the nano crystalline NiFeWS films reduced with increasing the bath temperature and saturation magnetization increased with increasing the bath temperature. The hardness and adhesion of the electroplated films were also investigated. Reasons for variation in magnetic properties and structural characteristics were discussed.

Keywords: Potassium citrate, current density, micro cracks, adhesion and hardness.

1. Introduction

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 because with electro deposition it is possible to deposit high aspect ratio films of high thickness more than 1 micro meter on a substrate [1]. 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. NiFe based thin films were most commonly fabricated by sputtering technique and electro deposition method [2]. Electro deposition offers several practical Advantages over sophisticated sputtering techniques interms of cost and growth rate [3]. The magnetic properties necessary for fabricating MEMS devices are high saturation magnetization, very low coercivity and anisotropy in order to minimize 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 reduce coercivity of the films and also improve corrosion resistance and other magnetic properties. W is a good candidate as it is highly corrosion resistant metal and also bears high mechanical strength. Very few research works are documented about the structural and composition of electrodeposited crystalline NiFeW alloys [5-9].

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]. 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 Potassium citrate bath for MEMS applications. This article summarizes the results of electro deposited Ni-Fe-W-S films in Tri Potassium Citrate bath at different temperatures.

2. Experimental Part

The bath composition of NiFeWS alloy thin film is shown in Table 1. Electro deposition was carried out from Tri Potassium citrate bath at different temperatures (28, 40, 60, 80˚C). Copper substrate was cut out from a copper foil with thickness 0.1 mm and 7.5 cm^2 in area. 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 was 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 temperature (28, 40, 60, 80˚C).

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

S.No	Name of the chemical parameters	Data g/l
1.	Nickel sulphate	60
2.	Ferrous sulphate	30
3.	Sodium tungstate	10
4.	Thiourea	7.5
5.	Tri Potassium citrate	70
6.	Citric acid	5.5
7.	Boric acid	10
8.	pH value	8
9.	Temperature	28,40,60,80(˚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, adherent. The composition of the NiFeWS film from Tri Potassium citrate was obtained from the EDAX analysis. The weight percentages of the films deposited with different temperature are tabulated as shown in Table 2.

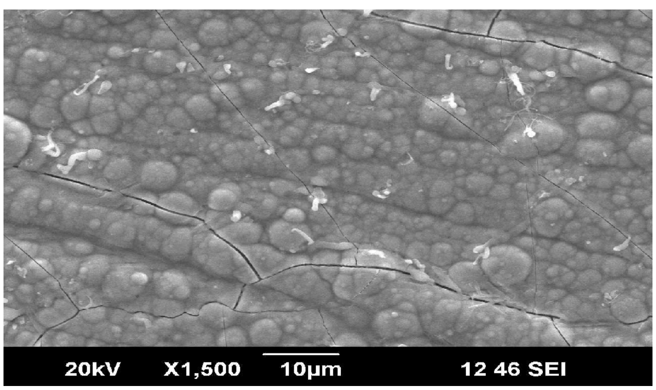
Table 2. Results of EDAX analysis

S.No	Temperature ˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1	28	21.07	70.97	0.45	7.51
2	40	31.71	61.24	0.62	6.43
3	60	46.15	47.09	0.58	6.18
4	80	81.14	12.44	0.82	5.60

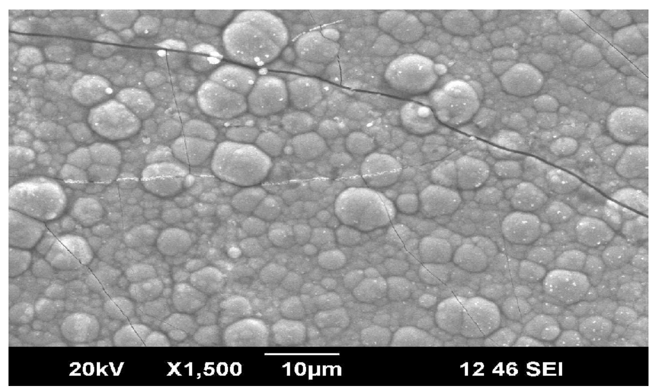
EDAX result showed that Ni content increases with increasing the bath temperature. The maximum Ni content of 81.14 was obtained for NiFeWS thin films at 80˚C bath temperature. The weight percentage of Fe decreases while increasing the bath temperature. The films obtained at higher temperature have low Sulphur content. So that the coercivity of films gets reduced and the magnetization values were increased. The lowest Sulphur content of 4.06wt% was obtained at temperature 80˚C in Tri Potassium citrate bath. 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.

3.2 Morphology of the deposits

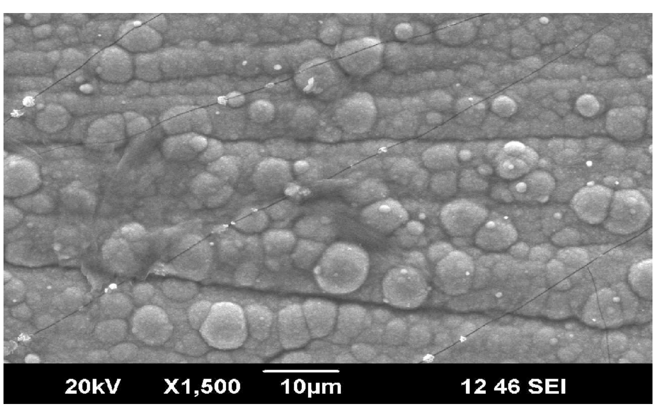
The SEM images of electrodeposited NiFeWS thin films from Tri Potassium citrate bath are shown in Figure 1. The films obtained at low temperature have some micro cracks. This is due to the generation of internal stresses resulting in the formation of micro cracks. The film obtained from higher temperature (80˚c) of Tri potassium 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. 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 Ni concentration is increased and at the same time Fe concentration is decreased, the grain size is decreased and the film surface become smoother [11]. Thicknesses of the deposited NiFeWS films were determined from cross sectional view of SEM images and are shown in Table 3.



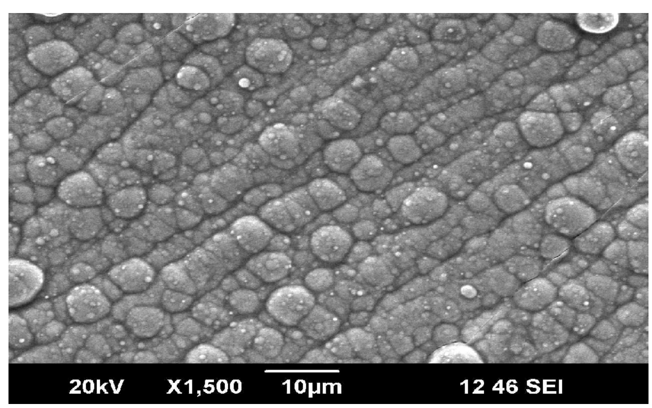
(a)



(b)



(c)



(d)

Figure 1. SEM images for Electro deposited Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

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

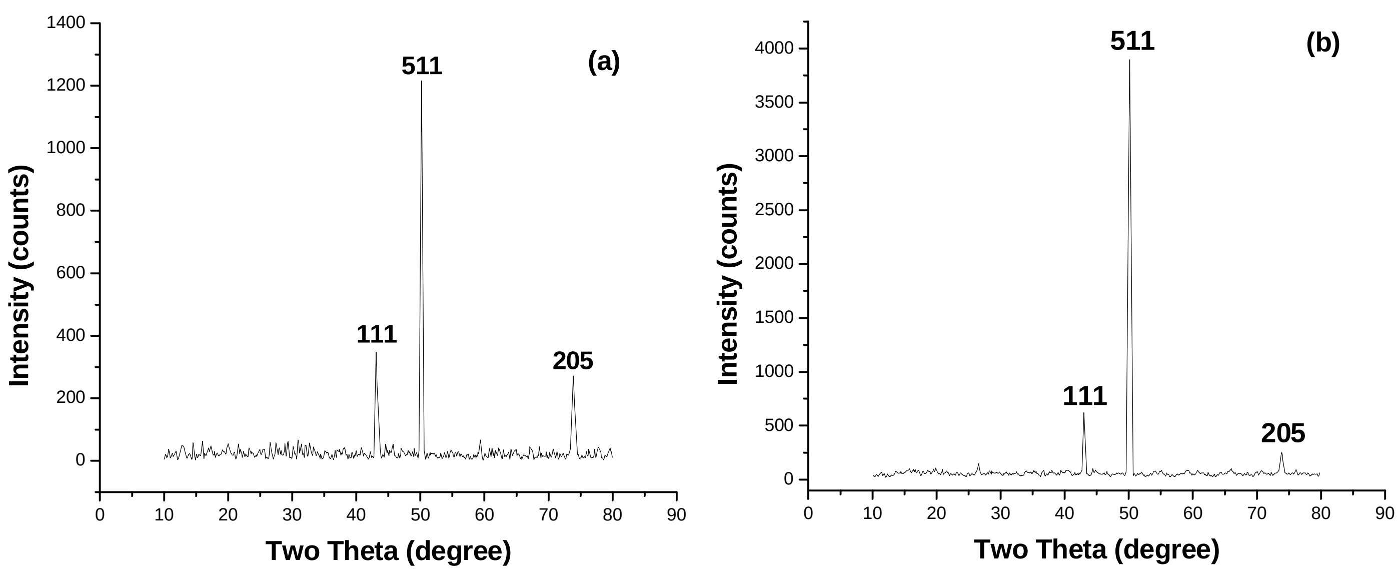
S.No	Bath Temperature ˚C	Crystalline size D nm	Film thickness µm
1	28	32.05	1.49
2	40	31.28	2.01
3	60	23.93	2.15
4	80	19.34	2.90

3.3 X-ray diffraction of the deposits

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 from Tri Potassium citrate bath at various temperatures like 28, 40, 60, and 80˚c were shown in Figure 2.

Table 4.Crystal size of NiFeWS alloy thin films

S.No	Bath Temperature ˚C	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	28	50.205	9.4356	32.05	11.295	10.220	1.49
2	40	50.134	9.4472	31.28	11.575	10.220	2.01
3	60	50.125	9.4532	23.93	15.129	17.463	2.15
4	80	50.281	9.4238	19.34	17.925	26.735	2.90



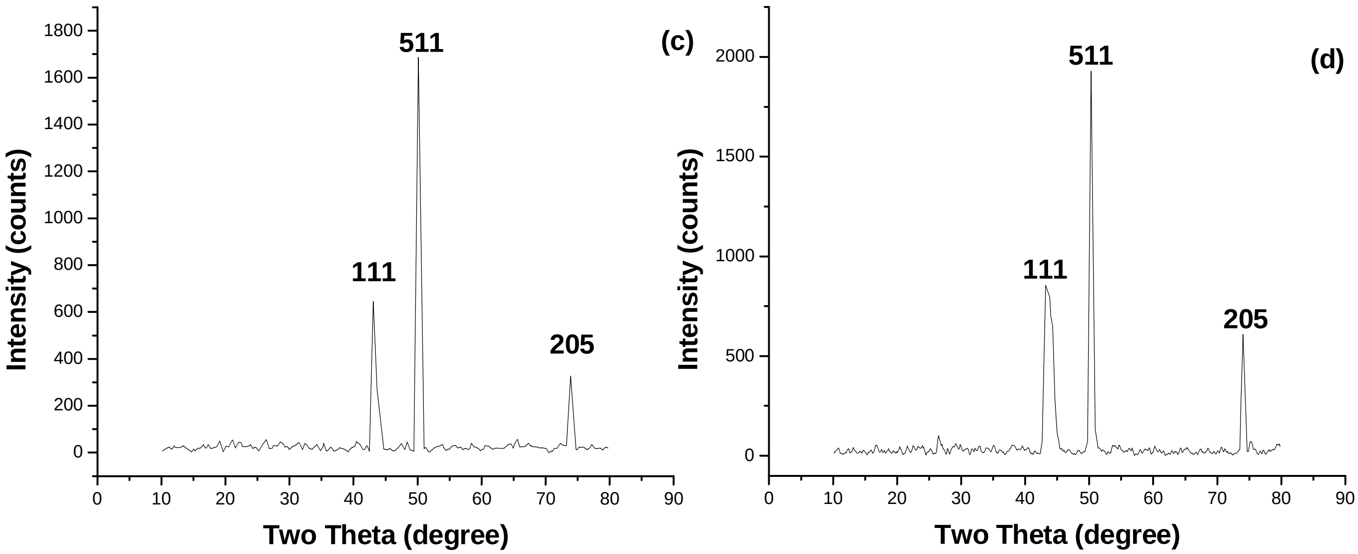


Figure 2.XRD pattern of Electro deposited Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

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 Potassium 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 (520) diffraction peaks.The crystalline size decreases with increase in bath temperature.

The grain growth and its size are sensitive to the deposition parameters such as the rate of depositions, bath temperature.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. The dependence of crystalline size and Bath temperature is shown Figure 3.

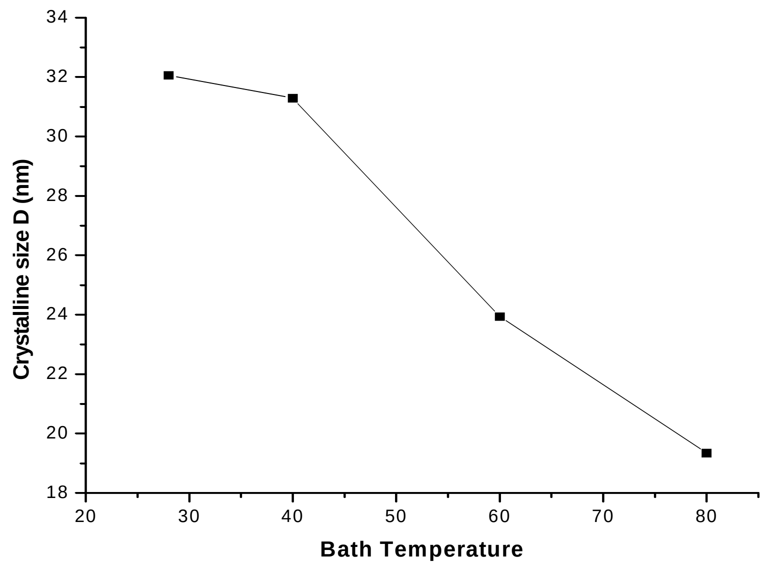


Figure 3. Crystalline Size as a function of Bath temperature

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 increases with increasing bath temperature. This is may be due to lower stress associated with electrodeposited Ni-Fe-W-S film in Tri Potassium citrate bath. The dependence of Vickers hardness and Bath temperature is shown Figure 4.

Table 5. Mechanical Properties of Electro deposited Ni-Fe-W-S thin film

S.No	Bath Temperature (˚C)	Crystalline size D Nm	Vickers Hardness (VH)
1	28	32.05	164
2	40	31.28	195
3	60	23.93	213
4	80	19.34	332

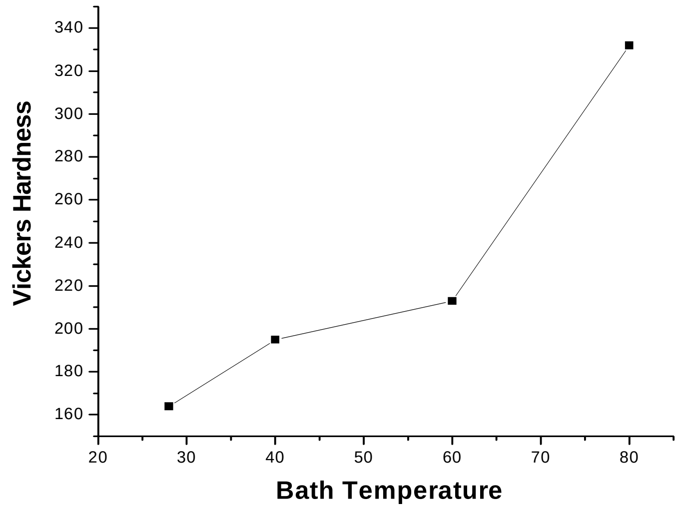


Figure 4. Vickers Hardness as a function of bath temperature

3.5 Magnetic properties of the deposits

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 Tri Potassium citrate bath at temperatures 28˚C, 40˚C, 60˚C and 80˚C is shown in Figure 5.

Table 6. Soft Magnetic Properties of Ni-Fe-W-S deposits

S.No	Bath Temperature (˚C)	Coercivity H_s (G)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Magnetic flux Density B_s (Tesla)	Squareness S
1	28	136.48	0.07572	0.03494	0.5822	0.04615
2	40	121.23	0.08961	0.04631	0.6772	0.05168
3	60	80.48	0.09391	0.06575	0.6816	0.07001
4	80	50.04	0.15691	0.06645	0.7324	0.04231

The film coated under the temperature of 80˚c exhibits the higher magnetization and Magnetic flux density. It was observed that the magnetization increases from 0.07572 emu/cm^2 to 0.15691 emu/cm^2. From that we concluded the films prepared at higher temperature (80˚C) exhibits a higher value of saturation magnetization and magnetic flux density.

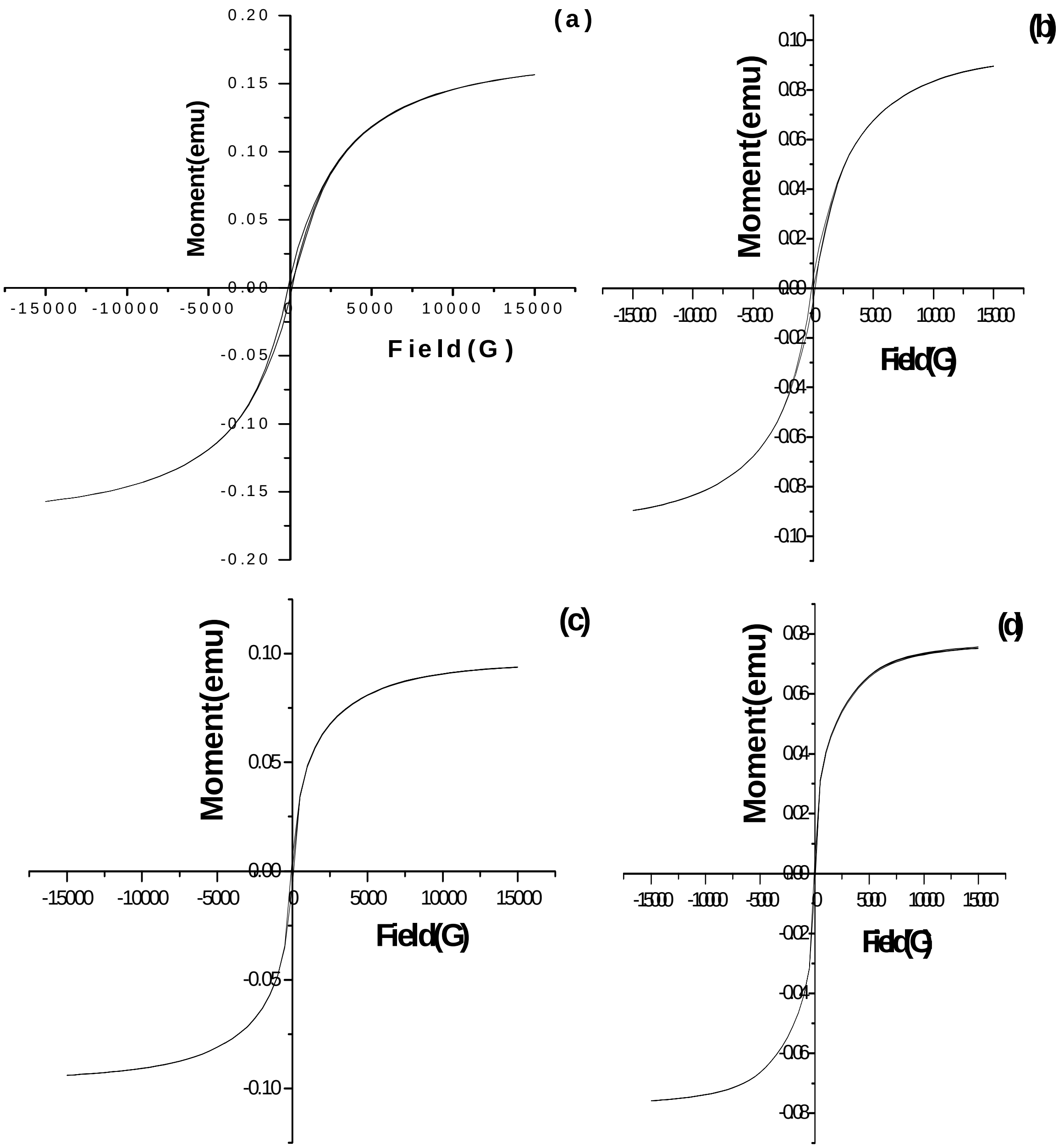
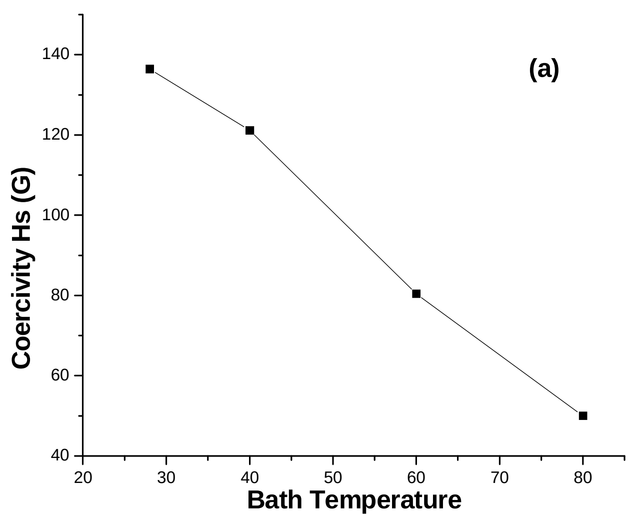


Figure 5. Magnetic Hysteresis loops for Ni-Fe-W-S thin film for different bath temperatures (a) 28˚C (b) 40˚C (c) 60˚C (d) 80˚C

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, Coercivity decreases as grain size increases. 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 [12-14]. 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 [15-16]. 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. This indicates that as temperature 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, saturation magnetization and Bath temperature is shown Figure 6.



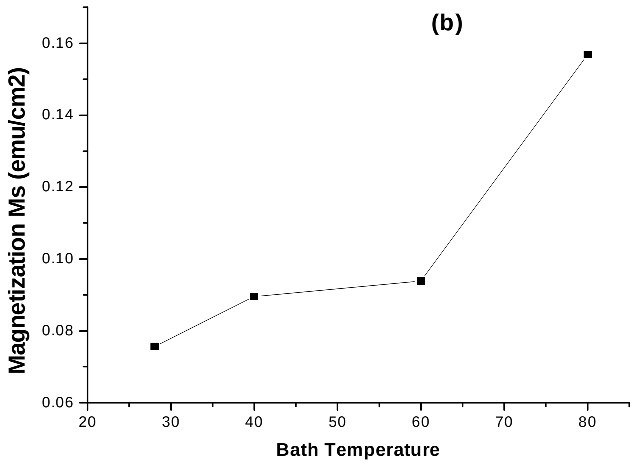


Figure 6. Bath Temperature as a function of (a) Coercivity (b) Saturation Magnetization

Coercivities of the films were gradually decreased with increasing Ni content. When the Ni content was 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 increases with increasing bath temperature and Fe content decreases with increasing the Tri Potassium citrate bath temperature. The film stress is reduced because of increase in Ni content. The decrease in Fe content of NiFeWS thin films reduces the film stress. Because of low stress and smaller crystalline size the NiFeWS thin films obtained at 80˚C bath temperature 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 at high temperature Tri Potassium citrate bath.

4. Conclusion

NiFeWS magnetic thin films were synthesized by electro deposition from Tri Potassium Citrate bath at different temperatures. The surface morphology was strongly affected by the bath temperature and composition of the deposits. The nano crystalline films obtained at 80˚C bath temperature are crack free and uniform. FCC was the dominant structure of electro deposited NiFeWS thin films. The crystalline sizes of the NiFeWS deposits obtained by electro deposition process are in the nano scale. When the temperature of Tri Potassium Citrate bath was increased to 80˚C, the magnetization values increases from 0.07572 to 0.15691 emu/cm^2. The coercivity of the NiFeWS thin films reduces from 136.48 to 50.04 Gauss. This is due to nano crystalline microstructure and low film stress associated with NiFeWS. Hardness of this magnetic thin film also increases by increasing bath temperature. 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.

References

[1]. Tetsuya Osaka, Toru Asahi, Jun Kawaji, Tokihiko Yokoshima. Electrochim.Acta. **50**, 4576 (2005).

[2]. L.X.Phua, N.N. Phuoc, C.K..Ong. J. alloy Compd. **520,** 132 (2012).

[3]. S. Esmail, M.E. Bahrololoom, K.L. Kavanagh. Mater Charact. **62**, 204 (2011).

[4]. S.Mehrizi, M.Heydarzadeh Sohi, S.A. Seyyed Ebrahimi. Surf Coat Tech. **205**, 4757 (2011).

[5]. R.KANNAN, S.GANESAN, T.M.SELVAKUMARI. J. Optoelectron Adv Mat – R.C. **6** (3- 4), 383 (2012).

[6]. R.KANNAN, S.GANESAN, T.M.SELVAKUMARI. Dig J Nanomater Bios. **7** (3),1039 (2012).

[7]. P.ESTHER, C.JOSEPH KENNADY, P.SARAVANAN, T.VENKATACHALAM. J. Non Oxide Glas. **1** (3), 301 (2009).

[8]. R.KANNAN, S.GANESAN, T.M.SELVAKUMARI, J. Optoelectron Adv Mat. **14 (** 9-10), 774 (2012).

[9]. P.ESTHER, C.JOSEPH KENNADY. J. Non-Oxide Glasses. **1**, 35 (2010).

[10]. T.M.Selvakumari, P.Muthukumar, S.Ganesan. Dig J Nanomater Bios. **5,**(4), 903- (2010).

[11]. Bonkeup Koo, Bongyoung Yoo. Surf Coat Tech. **205**, 740 (2010).

[12]. B.Y.Yoo, S.C. Hernandez, D.Y. Park, N.V.Myung. Electrochim.Acta. **51**, 6346 (2006).

[13]. C.D. Lokhande, S.S. Kulkarni, R.S. Mane, Oh-Shim Joo, Sung-Hawan Han. Ceram Int, **37**.335 (2011).

[14]. L.Perez, K. Attenborough, J. De Boeck, J.P.Celis, C.Aroca, P. Sanchez, E.Lopez, M.C. Sanchez. J. of Magn and Mag Mat. **242-245**, 163 (2002).

[15]. D.Niarchos. Sensors and Actuators A. **106**, 255 (2003).

[16]. Amaresh Chandra Mishra. Physica B.**407**, 923 (2012).