IJST (2013) 37A2: 181-187
Iranian Journal of Science & Technology

http://www.shirazu.ac.ir/en

An investigation on effects of annealing on magnetic properties of Ni-Fe-W-S electrodeposited coatings in tri sodium citrate bath

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Abstract

In the present investigation electrodeposited Ni-Fe-W-S nano crystalline thin films were prepared in tri sodium citrate bath at bath temperature of 40˚C. Annealing of the electro deposited thin film was performed at 200˚ C temperature for one hour. X-ray diffraction technique (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDAX), Vickers Hardness Test (VHN), and Vibrating Sample Magnetometer (VSM) were utilized to study the as-deposited and annealing effects on the structural and magnetic properties of the film. X-ray diffraction (XRD) result indicated that the as-deposited film had crystalline size of 31 nm. Annealing treatment of the coatings produced the enhanced crystalline size of 26.6 nm. Due to the improvement of soft magnetic properties in the 200˚C annealed film, the saturation magnetization is enhanced by 88×10^{-3} emu/ cm^2 (coercivity decreased to 14.6 Oe) compared with the case of as-deposited film at bath temperature of 40˚C. The magnetic flux density (Bs) of the annealed film was enhanced by 0.6328 Tesla. Hardness of the annealed film increased from 143 VHN to 151 VHN. This shows that the soft magnetic properties of Ni-Fe-W-S thin films are greatly enhanced by annealing at 200˚C which can be used in MEMS applications.

***Keywords**:* Tri sodium citrate; coating; annealing treatment; soft magnetic properties and hardness

1. Introduction

Soft magnetic thin films with a high magnetic moment are used in various applications, such as magnetic recording systems, high frequency plasma inductors and modern nonvolatile magnetic memory [1]. Electro deposited Permalloy (NiFe) is the best known thin film alloy in MEMS applications[2], because of its high saturation flux density, lower coercivity, higher saturation magnetization and lower magnetostriction. Due to their soft magnetic properties, Ni-Fe alloys have been used in various industrial applications which include high density recording media [3-4]. By adding other elements to these alloys ($Ni_{80}Fe_{20}$), the properties of these alloys can also be altered. W is a good candidate as it is a highly corrosion resistant metal and also bears high mechanical strength [5, 6]. The low stress thin film alloys with improved magnetic properties are very much used in magnetic recording heads and MEMS [7]. The best known stress reducing agents [8] for nickel based electro deposition are sulfur containing organic additives (saccharin, thiourea, benzene sulfonic acid etc). The deposited film exhibit grain sizes less than 100 nm. The nano structure materials have enhanced physical properties due to their increased volume fractions of grain boundaries. For magnetic materials considerable changes are expected in their magnetic behavior when the grain size approaches the domain wall thickness [9].

Magnetic properties of nano crystalline soft magnetic alloys have usually been correlated to structural evolution with heat treatment [10]. Nano crystallization can be induced by annealing the sample at high temperature [11-15].The main reasons for heat treatment are i) To eliminate any hydrogen embrittlement in the basic metal ii) to increase deposit hardness or abrasion resistance iii) To increase deposit adhesion in the case of certain substrate iv) to increase temporary corrosion resistance (or) tarnish resistance and v) To enhance the magnetic properties of the deposits [16]. In this paper, a new approach annealing treatment is proposed to make further enhancement of soft magnetic properties like saturation magnetization, coercivity, and magnetic flux density on electro deposited Ni-Fe-W-S thin films [17].

This paper reports the preparation of Ni-Fe-W-S thin films by electro deposition method. In order to

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Received: 4 October 2012 / Accepted: 19 February 2013

obtain enhanced magnetic properties of the films, annealing process was employed. The effects of annealing temperature on the structural, magnetic and mechanical properties of the Ni-Fe-W-S films in tri sodium citrate bath were studied and are reported here.

2. Experimental Part

Electro deposition of NiFeWS thin films

NiFeWS thin film was electrodeposited on copper substrate using relavant salts in tri sodium citrate bath at 40˚C temperature. The chemical composition and operating conditions of the electroplating bath are as shown in Table 1. A copper substrate of size (1.5 × 7.5 cm) as cathode and pure stainless steel of the same size as anode were used for electro deposition of NiFeWS thin films. An adhesive tape was used to mask off all the substrate except the area on which the deposition of films was desired. All the reagent grade chemicals were dissolved in triply distilled water. Copper and stainless steel electrodes were degreased and slightly activated with 5% sulphuric acid and then rinsed with distilled water just before deposition. The pH of solution was adjusted to 8 by adding few drops of ammonia solution. The film was galvanostically deposited on copper substrate by applying a constant current of 75 mA (1 A/ dm^2) for a period of 30 minutes at 40˚ C bath temperature.

Annealing of NiFeWS thin films

In order to study the enhanced properties of the Ni-Fe-W-S thin films, the as-deposited coatings were annealed at 200˚C for 1 hour in a Muffle furnace (ranges from 0 to 1100˚C). Then the sample was allowed to cool for 15 minutes. When the annealing temperature exceeded 250˚C, electro deposited Ni-Fe-W-S thin films were decomposed. So annealing temperature was optimized to 200˚C for these Ni-Fe-W-S thin films.

The structure and morphology of the as-deposited and annealed NiFeWS thin films were studied with the help of X-ray diffractometer (XRD) and scanning electron microscope (SEM) respectively. The magnetic properties were studied by using vibrating sample magnetometer (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 sodium citrate	70
6.	Citric acid	5.5
7.	Boric acid	10
8.	pH value	8
9.	Temperature	40˚C
10.	Current density	1A/dm^2

Characterization of NiFeWS alloy thin films

The chemical composition of the as deposited and annealed film was determined by using the EDAX analyzer attached in (JEOL 6390 model) scanning electron microscope (SEM). Surface morphological studies were carried out with scanning electron micrographs. The structural analysis of the films was carried out using a computer controlled Shimadzu X-ray diffractometer employing Cu K_α radiation. The scanning was carried out using θ-2θ scan coupling mode, the rating begins with 30 Kv, 20 mA.

The crystalline size (D) was calculated using the Scherrer’s formula from the full width half maximum (β) using the relation.

$$D = \frac{0.94\ 5\lambda}{\beta\ cos\theta}. \tag{1}$$

The strain (ε) was calculated from the relation

$$\varepsilon = \frac{\beta\ cos\theta}{4}. \tag{2}$$

The dislocation density (δ) was evaluated from the relation.

$$\delta = \frac{1}{D^2}\ . \tag{3}$$

Magnetic properties (coercivity, magnetization, and retentivity) were studied using vibrating sample magnetometer.

The magnetic flux density in the films is calculated in Tesla using the relation

$$B_s = \frac{4\pi M_s \rho}{m} \tag{4}$$

where M_s is the saturation magnetization (emu), ρ is the density of the film (g/cc) and m is the mass of the film.

The squareness (S) was calculated from the relation

$$S = \frac{M_r}{M_s} \qquad (5)$$

where M_r is the retentivity

Hardness of the as-deposited and annealed film was measured by vickers hardness test (VHN).

3. Results and Discussion

Composition of the electro deposited NiFeWS thin films

The electrodeposited NiFeWS alloy films were smooth, uniform, adherent. The composition of the as-deposited NiFeWS film from tri sodium citrate bath and annealed film was obtained from the EDAX analysis shown in Fig. 1.

The weight percentages of the electro deposited and annealed films are tabulated as shown in Table 2. EDAX result showed that the films obtained at 40˚C temperature have low sulphur content, so that the coercivity of films reduced and the magnetization values were increased. 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.

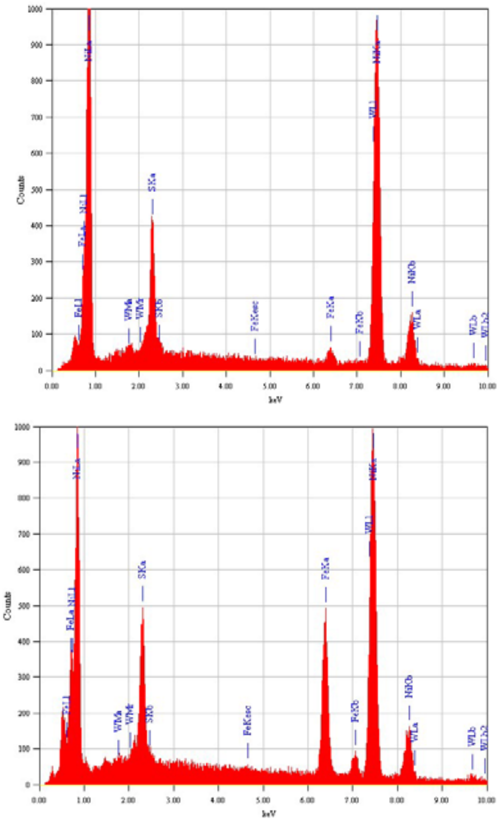

Fig. 1. EDAX spectrum of Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C)
(b) after 200˚C annealing

Table 2. Results of EDAX analysis

S.No	Temperature˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1	40	84.4	2.56	0.24	12.80
2	200(after annealing)	88.0	2.80	0.23	8.97

Morphology of the deposits

The surface morphologies of the as-deposited and annealed films are investigated by scanning electron microscopy (SEM). The SEM images of electrodeposited NiFeWS thin films from tri sodium citrate bath and annealed film at 200˚C are shown in Fig. 2.

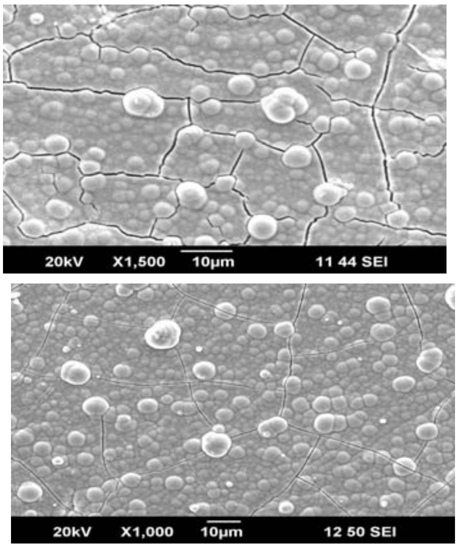

Fig. 2. SEM images of electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C)
(b) after 200˚C annealing.

The films obtained at 40˚C temperature have some micro cracks. This is due to the generation of internal stresses. After annealing the film was uniform and bright, the grain sizes were visible and very clear. Annealed film at 200˚C have smaller crystallites and granular. This is due to uniform crystal orientation during electro deposition. Hence the film has low stress.

X-ray diffraction of the deposits

Annealing effect on the structural properties of Ni-Fe-W-S thin films

Electrodeposited NiFeWS film from tri sodium citrate bath at 40˚C and annealed at 200˚C was subjected to XRD studies. Films obtained from tri sodium Citrate bath at temperatures 40˚C and annealed at 200˚ C were studied for their structural characteristics as shown in Fig. 3. The crystalline size of as-deposited and annealed (at 200˚C) NiFeWS alloy films obtained from tri sodium Citrate bath are tabulated as shown in Table 3. The dependence of crystalline size with annealed temperature is shown in Fig. 4.

Table 3. Crystal size of NiFeWS alloy thin films

S. No	Bath Temperature ˚C	2 θ (deg)	d (A^0)	Lattice parameter a (A^0)	Crystalline size D nm	Strain 10^{-4}	Dislocation density(10^{14} / m^2)
1	Before annealing (as deposited at 40˚C)	50.186	1.8164	9.2634	31	11.6913	10.4286
2	After annealing (annealed at 200˚C)	51.058	1.7874	9.2634	26.6	13.6747	14.1160

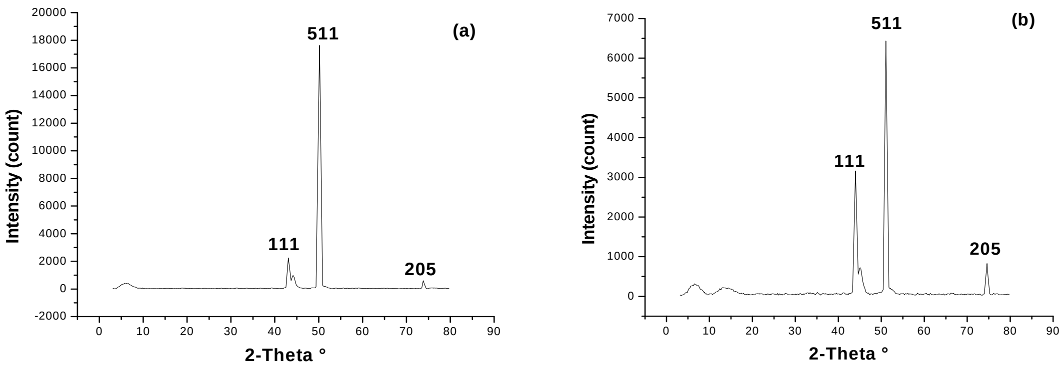

Fig. 3. XRD pattern of electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) After 200˚C annealing

The data obtained from the XRD pattern compared with the standard JCPDS data and were found to have FCC structure. The presence of sharp peaks in XRD patterns of as-deposited and annealed film reveals that the films are crystalline in nature. The peaks corresponding to (111), (511) and (205) reflections were observed in as-deposited and annealed films. The crystalline size is in the order of 31 nm for the film deposited from 40˚C bath temperature. But after annealing at 200˚C for one hour the crystalline size decreased to 26.6 nm. The grain sizes are in nano meter range. After annealing the NiFeWS thin films at 200˚C for 1 hour the full width half maximum (FWHM) increases from 0.296˚ to 0.347˚ for (511) plane, providing that the annealing procedure results in a smaller crystalline size. The strain built in the film gets released after annealing.

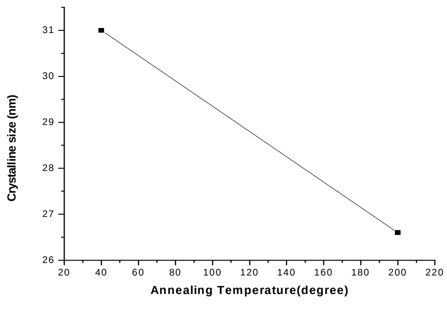

Fig. 4. Crystalline size as a function of annealing temperature

Mechanical Properties

Annealing effect on the mechanical properties of Ni-Fe-W-S thin films

Adhesion of the as deposited (at 40˚C) and annealed (200˚C) film with the substrate was tested by bend test and scratch test. It showed that as deposited (at 40˚C) and annealed (200˚C) film have good adhesion with the substrate. Hardness of the as deposited and annealed film was examined using a Vickers hardness tester by the diamond intender method. The results are tabulated and shown in Table 4.

Table 4. Mechanical properties of as deposited and annealed Ni-Fe-W-S thin film

S. No	Bath temperature (˚C)	Crystalline size D Nm	Vickers hardness (VHN)
1	Before annealing (as deposited at 40˚C)	31	143
2	After annealing (annealed at 200˚C)	26.6	151

The results show that the hardness increases with annealing temperature. After annealing, hardness of the film increases from 143 VHN to 151 VHN. 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 number and annealing temperature is shown Fig. 5.

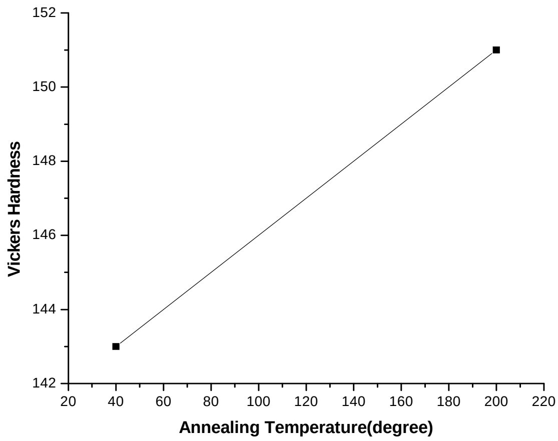

Fig. 5. Vickers hardness as a function of annealing temperature

Magnetic properties of the deposits

The hysteresis loop parameters, saturation magnetization (M_s), coercivity (H_c), retentivity (M_r), and magnetic flux density (B_s) of the as-deposited and annealed films were evaluated by using VSM. The magnetic hysteresis loops for NiFeWS alloy thin film prepared from tri sodium citrate bath at temperature 40℃ and annealed film at 200℃ is shown in Fig. 6.

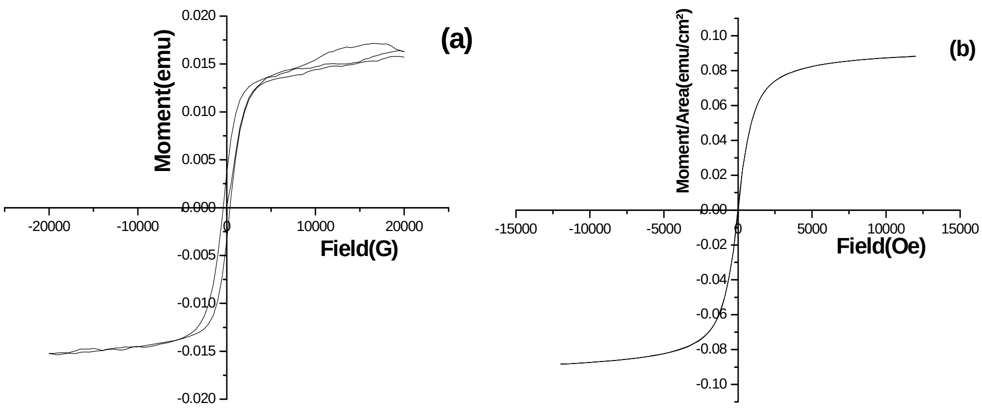

Fig. 6. Magnetic hysteresis loops of electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) after 200˚C annealing

The magnetic properties of the as-deposited and annealed NiFeWS thin films observed from VSM are tabulated as shown in Table 5.

Table 5. Soft Magnetic properties of as-deposited and annealed Ni-Fe-W-S thin films

S. No	Bath temperature (˚C)	Coercivity H_c	Magnetization $M_s \times 10^{-3}$ (emu/cm^2)	Retentivity M_r (emu/cm^2)	Magnetic flux density B_s (Tesla)	Squareness S
1	Before annealing (as deposited at 40˚C)	372.10 G	16.264	3.4002	0.4561	0.20906
2	After annealing (annealed at 200˚C)	14.677 (O_e)	88	1.1760	0.6328	0.01336

The crystalline nature of the material determines the magnetic properties of the materials. The saturation magnetization and coercivity are important parameters that determine the magnetic properties of soft magnetic materials [18-19]. The soft magnetic properties are strongly dependent on the microstructure of the thin films. The microstructure contribution to magnetization arises from morphology properties such as magnetic anisotropy, magnetostriction and coercivity [20].

Annealing effect on the magnetic properties of Ni-Fe-W-S thin films

The effect of film stress on coercivity should be considered because soft magnetic properties of iron based films depend on film stress very carefully and compressive stress leads to high coercivity, however, the tensile stress reduces coercivity [21]. This indicates that as the temperature of the bath increases the films may be under tensile stress and this leads to an increase in saturation magnetization. Many factors contribute to the development of stress in electro deposits including film composition, nature of the substrate surface, bath composition, bath temperature, current density, and deposit thickness etc. The high initial intrinsic stress in the film is associated with lattice mismatch and with the grain size of the underlying substrate. But at high tri sodium citrate bath temperatures, the electro deposited film has low stress. This is due to uniform crystal orientation during electro deposition.

The hysteresis loops of the as-deposited film and annealed film at 200˚C indicates the soft magnetic behavior of NiFeWS alloys. The B-H loop of NiFeWS thin film deposited at bath temperature of 40˚C indicates the coercivity value of 372.10 G and saturation magnetization value of 16.264 × 10^{-3} emu/ cm^2. The retentivity value of the as-deposited film is 3.4002 × 10^{-3} emu/cm^2. After annealing at 200˚C, the annealed film exhibits lower coercivity of 14.677 Oe with higher magnetization of 88 × 10^{-3} emu/ cm^2. The corresponding rententivity value decreased from 3.4002 × 10^{-3} emu/ cm^2 to 1.176 × 10^{-3} emu/ cm^2.The squareness (S) decreases from 0.20906 to 0.01336 as the annealing temperature increases.

The variation in magnetic properties can be attributed to the structural changes occurring in the film with annealing treatment. The drop in coercivity from 372.10 G to 14.677 Oe at 200˚C represents the onset of crystallization and exchange coupling between several grains. The coercivity drop at 200˚C suggested that, the films undergo substantial stress relief and occurrence of nano crystalline at that temperature. The corresponding magnetization and magnetic flux density were enhanced. So the enhanced saturation magnetization from 16.264 × 10^{-3} emu/ cm^2 to 88 × 10^{-3} emu/ cm^2 is found with increased annealing temperature which may be induced by strain relaxation and the particle size effect. Crystalline permalloy has very low magnetostriction. For this reason, nano crystalline NiFeWS films have very low magnetostriction and the intrinsic anisotropy was simultaneously minimized with highest possible permeability. So these films can be used for devices like magnetic recording heads. The effect of annealing temperature on saturation magnetization and magnetic flux density is shown in Fig. 7. By analyzing the present results it can be seen that the enhanced soft magnetic properties have been obtained from the electroplated nano crystalline films at annealed temperature 200˚ C.

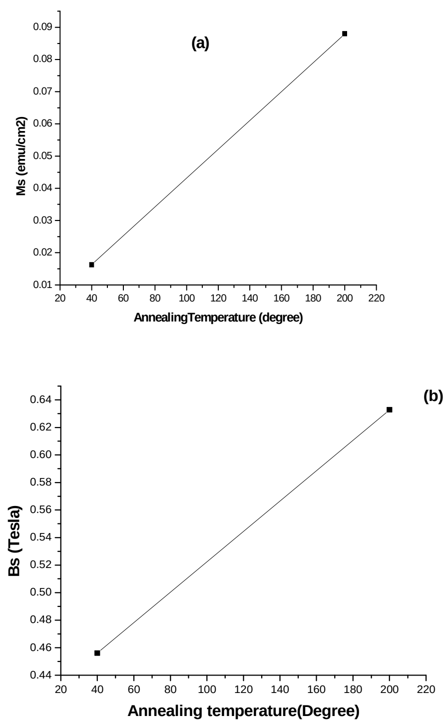

Fig. 7. Annealing temperature as a function of (a) saturation Magnetization (b) saturation magnetic flux density

4. Conclusion

Nano crystalline Ni-Fe-W-S electro deposited coating was deposited on Cu substrate. The annealing effects on structural and magnetic properties of the films were systematically studied. The results show that,

1. As-deposited Ni-Fe-W-S coatings in tri sodium citrate bath have crystalline size of 31 nm.

2. By applying heat treatment, the crystalline size reduces to 26.6 nm.
3. The coercivity of the annealed film was decreased from 372.10 G to 26.6 Oe. Saturation magnetization of the annealed film was found to increase from 16.264×10^{-3} emu/ cm^2 to 88×10^{-3} emu/ cm^2. Retentivity decreased from 3.4002×10^{-3} emu/ cm^2 to 1.1760×10^{-3} emu/ cm^2. The Squareness (S) decreases from 0.20906 to 0.01336 as the annealing temperature increases.
4. The magnetic flux density (Bs) of the annealed film was enhanced by 0.6328 Tesla. Hardness of the annealed film increased from 143 VHN to 151 VHN.
5. Proper annealing treatment can significantly enhance the structural and magnetic properties of the electro plated Ni-Fe-W-S thin film.
6. This shows that the soft magnetic properties of Ni-Fe-W-S thin films are greatly enhanced by annealing at 200˚C and can be used in MEMS applications.

References

[1] Chechenin, E. V., Khomenko E. V. & de Hosson, J. Th. M. (2007).*FCC/BCC* Competition and Enhancement of Saturation Magnetization in Nanocrystalline Co–Ni–Fe films. JETP Letters., *85***,** 212-215.

[2] Islam, M. A. & Moniruzzaman, M. (2009). Anomalous Electrodeposition Of Fe-Ni Alloy Coating From Simple And Complex Baths and its Magnetic Property. *IIUM Engg Journal*, *10*(2).

[3] Daheum, Kim., Park, D. Y., Yoo, B. Y., Sumodjo, P. T. A. & Myung, N. V. (2003). Magnetic properties of nanocrystalline iron group thin film alloys electrodeposited from sulfate and chloride baths. *Electrochim Acta*., *48*, 819-830.

[4] Celine, R. & Patrick, F. (2011). Electrodeposition of thin films and nanowires Ni–Fe alloys, study of their magnetic susceptibility. *J. Mater Sci*., *46*, 6046-6053.

[5] Zielinski, M. & Miekos, E. (2008).Influence of constant magnetic field on the electrodeposition of Co–Mo–W alloys. *J Appl Electrochem*, *38*, 1771-1778.

[6] Dong-Kuk, K., Sunghal L. & Heung S. S. (1999). Effect of Size and Shape of Tungsten Particles on Dynamic Torsional Properties in Tungsten Heavy Alloys. *Matal. mat Trans A*., *30*A, 1261.

[7] Selvakumari, T. M., Muthukumar, P. & Ganesan, S. (2010). Synthesis and characterization of nanocrystalline feptp films. *Dig J Nanomater Bios*., *5***,** 903-907.

[8] Sulztanu, N. & Fbrinza, J. (2004). Electrodeposited ni-fe-s films with high resistivity for Magnetic recording devices. *J. Optoelectron Adv Mat*., *6*, 641-645.

[9] Stephen, A., Ananth, M. V., Ravichandran, V. & Narashiman, B. R. V. (2000).Magnetic properties of electrodeposited nickel manganese alloys: Effect of Ni/Mn bath ratio., *J. Applied Electrochem*, *30*, 1313-1316.

[10] Hysen, T., Deepa, S., Saravanan, S., Ramanujan, R. V., Avasthi, D. K., Joy, P. A., Kulkarni, S. D. & Anantharaman, M. R. (2006). Effect of thermal annealing on Fe40Ni38B18Mo4 thin films. J. Phys D: *Appl. Phys*., *39*, 1993-2000.

[11] Hongtang Sun., Zewen Liu., Jiahao Zhao., Wang Li. & Jing Zhu. (2007). Low-Temperature Annealing Effect of RF Inductor with FeNi-SiO2 Granular Film. *IEEE, Transactions on magnetic*., *43*(8).

[12] Shajie Fang., Zhiyoung Pang., Fenggong Wang., Liang Lin. & Shenghao Han. (2011). Annealing Effect on Transport and Magnetic Properties of La0*:*67Sr0*:*33MnO3 Thin Films Grown on Glass Substrates by RF Magnetron Sputtering. *J. Mater. Sci. Technol*., *27*(3), 223-226.

[13] Haiwenxi., Bo Bian., Zailong Zhuang., David, E., Langhlin & White, R. M. (2000). Annealing Effect on Exchange Bias in Ni81Fe19/Cr50Mn50 Bilayers. *IEEE, Transactions on magnetics*, *36*(5).

[14] Tokumaru, R., Tamano, S., Goto, S., Madeswaran, S., Tokiwa, K. & Watanable, T. (2009). Effect of annealing on magnetic properties of Nd-Fe-B thin films prepared by ECR ion beam sputtering method. *J. Physics: Conference Series*., *191*, 012-021.

[15] Esther, P. & Joseph Kennady, C. (2010). Effect of sodium tungstate on the properties of electrodeposited nanocrystalline ni-fe-w films. *J. Non Oxide Glas*., *1*, 35-44.

[16] Rabizadeh, T., Allahkaram., S. R. & Zarebidaki, A. (2010). An investigation on effects of heat treatment on corrosion properties of Ni–P electroless nano-coatings. *Materials and Design*., *31*, 3174-3179.

[17] Kannan, R., Ganesan, S. & Selvakumari, T. M. (2012). Structural and magnetic properties of electrodeposited Ni-Fe-W-S thin films. *Optoelectron Adv Mat*., *6*, 383-388.

[18] Sundaram, K., Dhanasekaran, V. & Mahalingam, T. (2011).Structural and magnetic properties of high magnetic moment electroplated CoNiFe thin films. *Ionics*., *17*, 835-842.

[19] Xiang, Shen., Haiteng, Li., HaiHua, Li. & Jianghua, N. (2009). Effect of deposit conditions on magnetic parameters of electroless CoFeB films. *J. Mater Sci Mater Electron*, *20*, 272-275.

[20] Watanable, M., Nakayama, T., Watanable, K., Hirayama, T. & Onomura, A. T. (1996). Microstructure and Magnetic properties of High Coercive Fe-Pt alloy thin films. *Materials Transactions*, *JIM*, *37*, 489-493.

[21] Esther, P., Kennady, J. C., Saravanan, P. & Venkatachalam, T. (2009). Structural and magnetic propertiesof electrodeposited ni-fe-w thin films. *J. Non Oxide Glas*., *1*, 301-309.