Development of nano structured Ni rich Ni-Fe-W-S films for micro electro mechanical system applications

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Nano crystalline Ni rich Ni-Fe-W-S alloy thin films were electrodeposited on copper substrate from different citrate bath at 50˚C.The structural, chemical composition, surface morphology and magnetic properties of the electro deposited Ni-Fe-W-S thin films were studied. The chemical compositions of the films were carried out by using Energy Dispersive X-ray spectroscopy (EDAX). The structural and morphology of the films were detected by using X-ray diffractometer (XRD) and Scanning Electron Microscope (SEM) respectively. The Mechanical properties of the films were analyzed by using Vickers Hardness Test (VHN).In this report; vibrating sample magnetometer (VSM) has been used as a tool to investigate the magnetic properties on the electrodeposited Ni-Fe-W-S films. The deposits of Ni-Fe-W-S thin films were found to be smooth, adherence to the substrate. All the electro deposited films exhibit FCC crystalline structure with crystalline size in the order of Nano scale. The study of Coercivity, Saturation magnetization and magnetic flux density of the films from Tri Sodium, Diamminoum and Tri Potassium citrate bath are also reported. Electro deposited Ni-Fe-W-S thin films from various citrate bath exhibit good soft magnetic properties and are suitable for various electronic devices including high density recording media, magnetic actuators, magnetic shielding, and high performance transformer cores.

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1. Introduction

In recent years, electrodeposited Nano crystalline magnetic thin films have been developed due to their potential applications in power electronics, sensors, actuators, core material for writing elements in recording heads. Magnetic thin films must have good adhesion, low stress, corrosion resistance with great magnetic properties.Electro deposited Permalloy ($Ni_{80}Fe_{20}$) is the best known thin film alloy in magnetic thin film recording heads and MEMS applications [1-3]. The Ni-Fe alloys are the most versatile from all the known soft magnetic materials for magnetic storage [4-5], Because of their highest saturation flux density, lower coercivity and lower magnetostriction. Due to their soft magnetic properties, Fe-Ni alloys have been used in industrial applications. Typical examples of applications that are based on the soft magnetic properties include read-write heads magnetic actuators, magnetic shielding, and high performance transformer cores. The Ni-Fe alloys with composition close to 80% Ni are very much used for producing the magnetic recording heads. By adding other elements to these alloys ($Ni_{80}Fe_{20}$), the properties of these alloys can also be altered. Now the researchers show interest in electrodeposited alloys of W, Cr and Mo with nickel-iron metals, because of their enhanced and specific magnetic, electrical, mechanical, thermal and corrosion less 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 NiFeWalloys [6-9].

The Low stress thin film alloys with improved magnetic properties [10-14] are very much used in magnetic recording heads and MEMS.The best known stress reducing agents for nickel based electrodeposition are sulfur containing organic additives (saccharin, thiourea, benzene sulfonic acid etc).This article summarizes the result of electro deposition of Ni-Fe-W-S films deposited using Thiourea as the source of Sulphur in Tri Sodium citrate bath, Diammonium Citrate bath and Tri Potassium citrate bath at 50˚C.

2. Experimental part

2.1 Electro deposition of NiFeWS thin films

Nano crystalline Ni rich NiFeWS thin films were electrodeposited on Copper substrate using relavant salts in Tri Sodium, Diammonium, TriPotassium Citrate bath at 50˚C. The chemical composition and operating conditions of the electroplating path are as shown in Table 1. A copper substrate of size (1.5 × 7.5 cm) as cathode and pure stainless steel of 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 films were galvanostically deposited on copper substrate by applying a constant current of 75 mA (1 A/ dm^2) for a period of 30 minutes.

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, Diammonium, Tri Potassium citrate	70
6.	Citric acid	5.5
7.	Boric acid	10
8.	pH value	8
9.	Temperature	50˚C
10.	Current density	1 A/dm^2

3. Results and discussion

3.1 Composition of the deposits

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

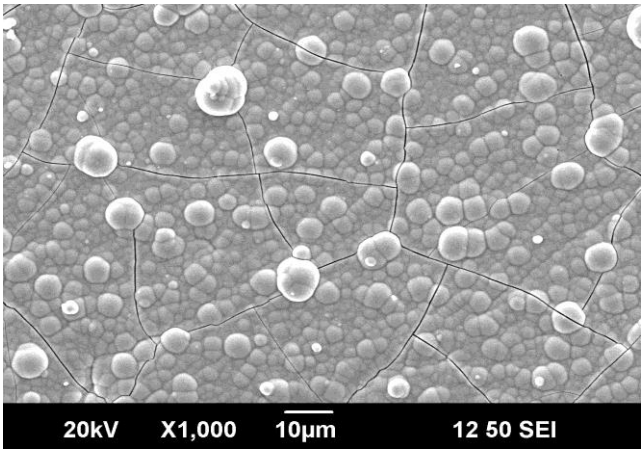
Table 2.Results of EDAX analysis.

S.No	Name of the citrate bath	Temperature ˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1	Tri Sodium Citrate	50	88.14	3.68	0.76	7.42
2	Diamminoum citrate	50	84.81	8.22	0.68	6.29
3	Tri Potassium citrate	50	84.62	8.98	0.71	5.69

EDAX result showed that the films obtained from various citrate baths have low Sulphur content. So that the coercivity of films gets reduced and the magnetization values were increased. The lowest Sulphur content of 5.69wt% was obtained at temperature 50˚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 Sodium, Diammonium and Tri Potassium citrate bath are shown in Fig. 2. The films obtained from various citrate baths at 50˚Ctemperature have some micro cracks. This is due to the generation of internal stresses resulting in the formation of micro cracks. The film obtained from Diammonium citrate bath at temperature (50˚c) having smaller crystallites and granular. The films obtained from Diammonium citrate bath are crack free and grain boundaries can be seen among the crystal grains. This is due to uniform crystal orientation during electro deposition. Hence the film has low stress.



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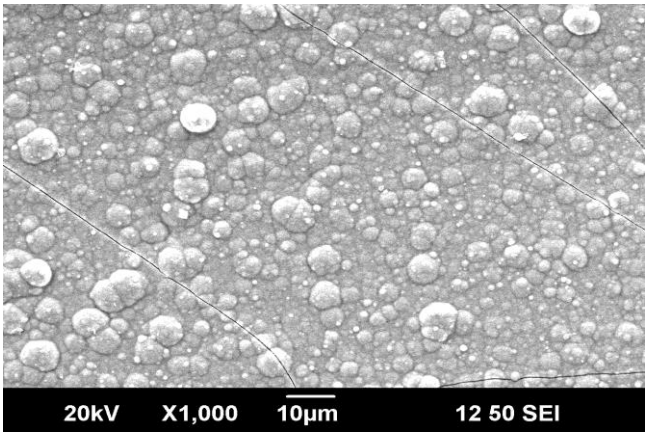

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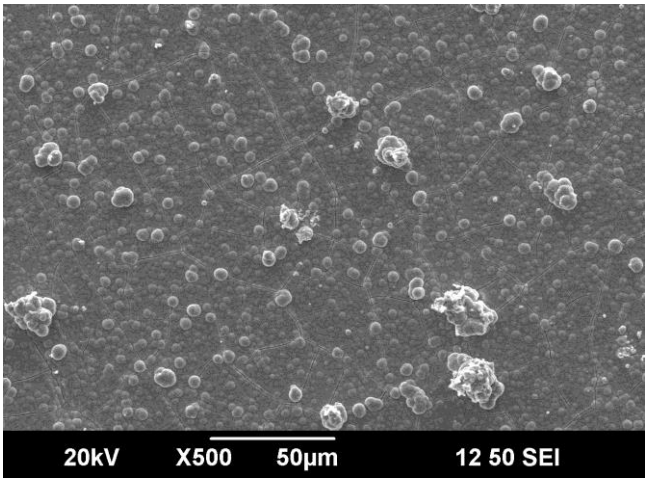

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Fig. 2. SEM images for Electro deposited Ni-Fe-W-S thin film from different citrate baths at 50˚C(a) Tri odium citrate bath (b) Diammoniumcitrate bath (c) Tri Potassium citrate bath.

3.3 X-ray diffraction of the deposits

Electrodeposited NiFeWS films from Tri Sodium, diammonium and Tri Potassium citrate baths were subjected to XRD studies. Films obtained from various Citrate bath at temperature 50˚C were studied for their structural characteristics as shown in Fig. 3.

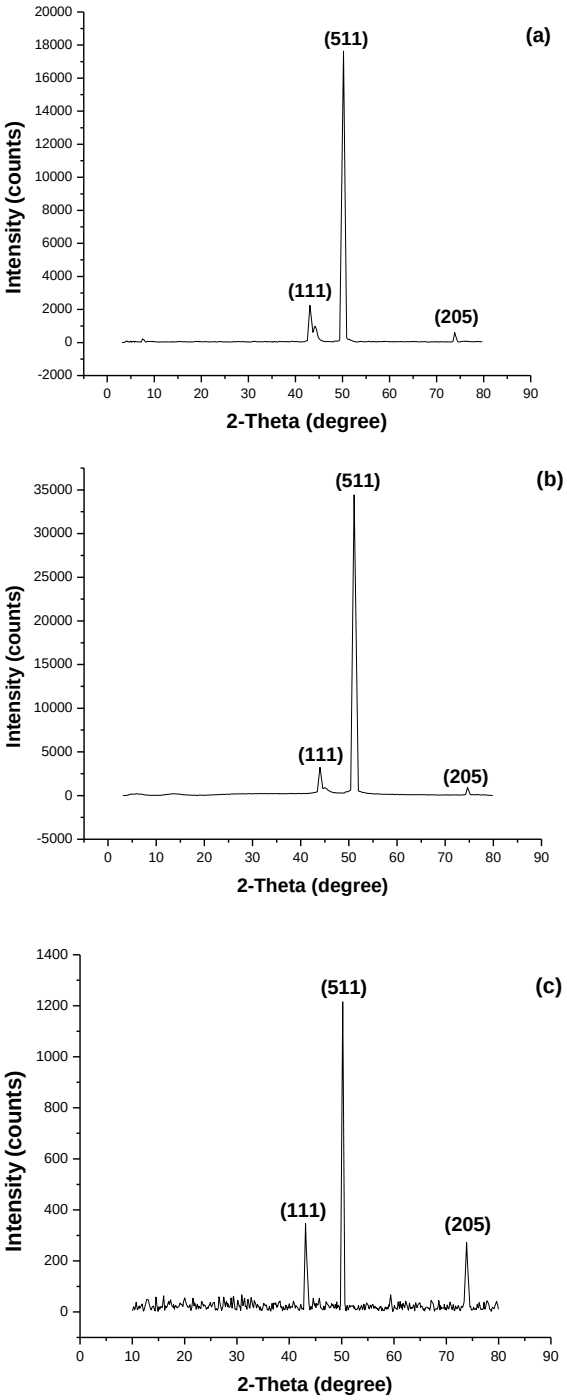

Fig. 3. XRD pattern for Electro deposited Ni-Fe-W-S thin film from different citrate baths at 50˚C(a) Tri odium citrate bath (b) Diamminoumcitrate bath (c) Tri Potassium citrate bath.

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 pattern reveals that the films are crystalline in nature. The peaks corresponding to (111), (511) and (205) reflections were observed in all the films. The crystalline size (D) of all the films were calculated using the Scherrer's formula from the full width half maximum (β) using the relation.

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

The grain sizes are in nano meter range.The crystal size of NiFeWS alloy films obtained from various Citrate baths are tabulated as shown in Table 3.

Table 3.Crystal size of NiFeWS alloy thin films.

S.No	Name of the citrate bath	Bath Temperature ˚C	2 θ (deg)	Lattice parameter a (A^0)	Crystalline size D Nm	Strain 10^{-4}	Dislocation density(10^{14} / m^2)
1	Tri Sodium citrate	50	50.204	9.4356	29.38	12.32	11.59
2	Diamminoum citrate	50	51.165	9.2746	31.41	11.53	10.14
3	Tri Potassium citrate	50	50.212	9.4356	30.57	11.84	10.70

3.4 Mechanical properties

Adhesions of the films from various citrate baths with the substrate are tested by bend test and scratch test. It showed that the films 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 4. The results show that the hardness value of different citrate baths,the variation in hardness may be due to lower stress associated with electrodeposited Ni-Fe-W-S film in different citrate bath.

Table 4. Mechanical properties of electro deposited Ni-Fe-W-S thin film.

S.No	Name of the citrate bath	Bath Temperature (˚C)	Crystalline size D Nm	Vickers Hardness (VHN)
1	Tri Sodium citrate	50	29.38	128
2	Diamminoum citrate	50	31.41	153
3	Tri Potassium citrate	50	30.57	198

3.5. Magnetic properties of the deposits

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 [15-17].We have planned to examine the saturation magnetization, magnetic flux density and Coercivity of electrodeposited NiFeWS alloy thin films from Tri Sodium, Diammonium and Tri Potassium citrate bath. The magnetic properties of the electrodeposited NiFeWS films from various citrate baths have been observed from VSM are tabulated as shown in Table 5.

Table 5.Soft magnetic properties of Ni-Fe-W-S deposits.

S.No	Name of the citrate bath	Bath Temperature (˚C)	Coercivity H_s (G)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Squareness S
1	Tri Sodium citrate	50	343.47	0.028519	3.5043×10^{-3}	0.1229
2	Diamminoum citrate	50	128.84	0.068988	2.2316×10^{-3}	0.0323
3	Tri Potassium citrate	50	132.28	0.089613	4.7311×10^{-3}	0.0528

The magnetic Hysteresis loops for NiFeWS alloy thin films prepared from Tri Sodium, Diammoniumand Tri Potassium citrate bath at temperatures 50˚C is shown in Fig. 4.

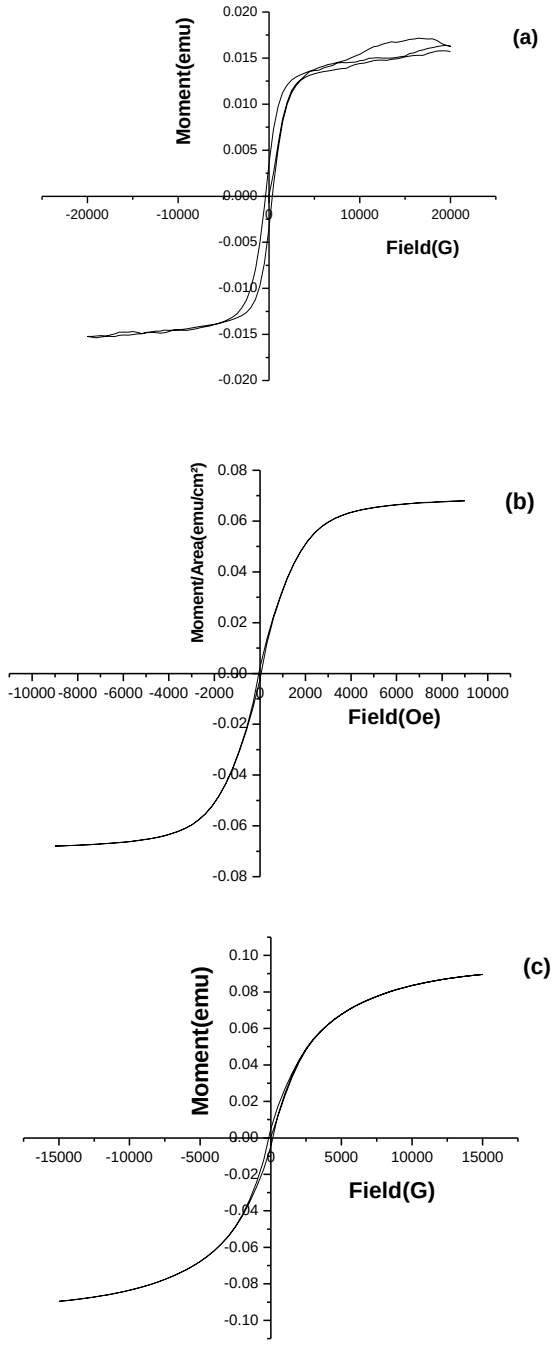

Fig. 4. Magnetic Hysteresis loops forNi-Fe-W-S thin film from different citrate baths at 50˚C(a) Tri odium citrate bath (b) Diamminoum citrate bath (c) Tri Potassium citrate bath.

The film coated under the temperature of 50˚C from Tri Potassium citrate bath exhibits the higher magnetization and Magnetic flux density. It was observed that the magnetization value is 0.089613 emu/cm^2 with coercivity value 132.28 (G).

The corresponding coercivity values of NiFeWSalloy thin films prepared from Tri Sodium, Diammonium, Tri Potassium citrate bath at temperatures 50 ˚C is shown in table and it was found to be low value in the unit of Gauss. 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. Many factors contribute to the development of stress in electro deposits including film composition, natures 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 the film from Tri Potassium citrate bath at temperature 50 ˚C, the electro deposited film has low stress. This is due to uniform crystal orientation during electro deposition. The films obtained from 50˚C are having high saturation magnetization when compared to the films obtained from room temperature. Crystalline Permalloyhas very low magnetostriction [18]. 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. 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 diammonium citrate bath.

The NiFeWS thin films obtained from Tri Potassium citrate bath having enhanced magnetic properties (High saturation magnetization, High magnetic flux density, low remanent value) when it is compared to the films obtained from Tri Sodium and Diammonium Citrate bath.

4. Conclusion

The nano crystalline NiFeWS alloy thin films from various citrate baths were synthesized by electro deposition method.The crystalline sizes of all the NiFeWS thin films are in the order of nano scale(average size = 30 nm).The films are smooth, uniform, adherent, low stress, crack free deposits from various citrate baths at 50˚C. It is found that from Vickers Hardness Test, the film obtained from Tri Potassium citrate bath at temperature 50℃ having higher value of Hardness (198 VHN). The NiFeWS thin films obtained from Tri Potassium citrate bath having enhanced magnetic properties when it is compared to the films obtained from Tri Sodium and Diammonium citrate

bath. It was observed that the magnetization value is 0.089613 emu/cm^2 with coercivity value 132.28 (G). We conclude that good soft magnetic property is observed in all the films. 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] T. E. Buchheit, S. H. Goods, P. G. Kotula, P. F. Hlava, Materials science and Engineering A, **432**, 149 (2006).

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

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

[4] IbroTabakovic, VenkateswaraInturi, Jeremy Thurun, Mark Kief, ElectrochemicaActa, **55**,6749 (2010).

[5] Tetsuya Osaka, Toru Asahi Jun Kawaji, Tokihiko Yokoshima, ElectrochemicaActa, **50**, 4576 (2005).

[6] R. Kannan, S. Ganesan, T. M. Selvakumari, J. Optoelectron. Adv. Mater.-Rapid Comm. **6**(3-4), 383 (2012).

[7] P. Esther, C. Joseph Kennady, P. Saravanan, T. Venkatachalam, J. Non-Oxide Glasses, **1**(3), 301 (2009).

[8] R. Kannan, S. Ganesan, T. M. Selvakumari, Digest J. Nanomaterials and Biostructures, **7**(3),1039 (2012).

[9] P. Esther, C. Joseph Kennady, P. Saravanan, T. Venkatachalam, J. Non-Oxide Glasses, **1**(3), 301 (2009).

[10] S. Mehrezi, M. HeydrazadehSohi, S. A. Seyyed Ebrahimi, Surface & Coatings Technology, **205**,740 (2011).

[11] N. G. Chechenin, E. H. du Marchie Van Voor thuysen, J. Magnetism and Magnetic Materials, **290-294**, 1539 (2005).

[12] Amaresh Chandrak Mishra, Physica B, **407**, 923 (2012).

[13] Bonkeup Koo, Bongyoung Yoo, Surface &Coatings Technology, **205**, 740 (2010).

[14] L. X. Phua, N. N. Phuoc, C. K. Ong, J. Alloys and Compounds, **520**, 132 (2012).

[15] Senoy Thomas, S. H. Al-Harthi, D. Sakthikumar, A. Al-omari, R. V. Ramanujam, Yasuhiko Yoshida, M. R. Anantharaman, J. Phys. D: Appl. phys, **41,** 155009(8pp) (2008).

[16] K. Sundaram, V. Dhanasekaran, T. Mahalingam, Springer Verlag Ionics **17**,835 (2011).

[17] T. M. Selvakumari, P. Muthukumar, S. Ganesan, Digest J.Nanomaterials and Biostructures, **5**(4), 903 (2010).

[18] H. Gavrila, V. Ionita, J. Optoelectron. Adv.Mater. **4**(2), 173 (2002).

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