Structural and magnetic properties of electrodeposited Ni-Fe-W-S thin films

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Nano crystalline Ni-Fe-W-S alloy thin films were deposited by electro deposition method on copper substrate with different concentration of bath at 50℃ and 80℃ temperatures. The structural, chemical composition, surface morphology and magnetic properties of the electro deposited Ni-Fe-W-S thin films were studied. The chemical composition of the film was 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 magnetic properties of the electro deposited Ni-Fe-W-S thin films were studied by using Vibrating Sample Magnetometer (VSM). The deposits of Ni-Fe-W-S thin films were found to be smooth, nano crystalline, adherence to the substrate. All the electro deposited films exhibit primitive FCC crystalline structure with crystalline size in the order of nano scale. Ni-Fe-W-S alloy thin films prepared at high temperature (80℃) were found to have higher magnetization value with lower coercivity (71.102×10^{-3} emu, 338.66 G and 89.33×10^{-3} emu, 332.80 G). Electro deposited Ni-Fe-W-S thin films 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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Keywords: Ni-Fe-W-S alloy thin films, Magnetic properties, Chemical composition and magnetization

1. Introduction

Electrodeposited alloys of iron group metals have been widely used in industry, mainly as the materials for magnetic storage devices and electronics [1]. There has been great research interest in the development and characterization of iron-nickel (Fe-Ni) thin films due to their operational capacity, economic interest, magnetic and other properties [2-5]. 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 for magnetic storage, magnetic actuators, magnetic shielding, and high performance transformer cores [6]. Mostly CoNiFe magnetic thin films have been analyzed because of its potential application in computer read-write heads and also in microelectromechanical systems (MEMS) [7]. The thin films on the write heads are deposited mostly using electro deposition technique. Electrodeposited Permalloy ($Ni_{80}Fe_{20}$) is the best known iron group thin films in computers and MEMS, because of its high magnetic saturation, low coercivity and low magnetostriction. The coercivity and permeability of these films are in the order of 1 to 5 Oe and 500 to 1000[8] respectively. As iron is the most corrosion susceptible metal among the magnetic elements, corrosion is still a major issue in the development of a soft magnet with good chemical stability and high Bs. Now the researchers show interest in electrodeposited alloys of W, Cr and Mo with iron group metals [9-11], because of their enhanced and specific magnetic, electrical, mechanical, thermal and corrosion less properties. W is a good additive 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 amorphous and crystalline iron group W alloys [12].

The electro deposition conditions such as physical conditions (bath temperature, current density, deposition time) and chemical conditions (pH value, addition of complexing agent) determine the microstructure (crystallite size, uniformity, and adherence) which in turn influence the physical and chemical properties of the films. This article summarizes the result of electro deposition of Ni-Fe-W-S films deposited using Thiourea [13] as the source of Sulphur in Tri sodium Citrate bath. The effects of Thiourea on the properties of Ni-Fe-W-S deposits including elemental composition, magnetic properties, surface morphology and structure have been studied. We adapted the deposition based on sodium citrate electrolytes, since the wide range of W deposited composition with high deposit hardness, fine texture and smooth surface morphology. So far, the magnetic properties of Ni-Fe-W-S thin films in trisodium citrate bath are not analyzed.

2. Experimental part

2.1 Electro deposition of NiFeWS thin films

NiFeWS thin films were deposited using two different concentrations of relavant salts at different temperatures. The chemical composition and operating conditions of the electroplating bath are as shown in Table 1. A copper substrate of size (7.5 × 1.5 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 film was desired. All the reagent grade chemicals were dissolved in triple 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 60 mA (1 A/ dm^2) for a period of 30 minutes. 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).

Table 1. Composition and operating conditions of the electroplating bath.

Bath identification	Bath concentration (g/l)		Temperature ˚C	pH	Current density A/dm^2
B-I	Nickel sulphate	60			
	Ferrous sulphate	30	50		
	Sodium tungstate	10		8	
	Thiourea	7.5			1
	Tri sodium citrate	70	80		
	Citric acid	5.5			
	Boric acid	10			
B- II	Nickel sulphate	75			
	Ferrous sulphate	37.5	50		
	Sodium tungstate	12.5		8	1
	Thiourea	9.5			
	Tri sodium citrate	87.5	80		
	Citric acid	7			
	Boric acid	12.5			

2.2 Characterization of NiFeWS alloy thin films

The chemical composition of the 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 analyses of the films were 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) were calculated using the Scherrer's formula from the full width half maximum (β) using the relation.

$$D = \frac{0.945\,\lambda}{\beta\,\mathrm{Cos}\theta} \tag{1}$$

The strain (ε) was calculated from the relation

$$\varepsilon = \frac{\beta\,\mathrm{Cos}\theta}{4} \tag{2}$$

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.

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 was obtained from the EDAX analysis. The weight percentage of the films deposited with two different concentrations of bath and different temperature are tabulated as shown in Table 2.

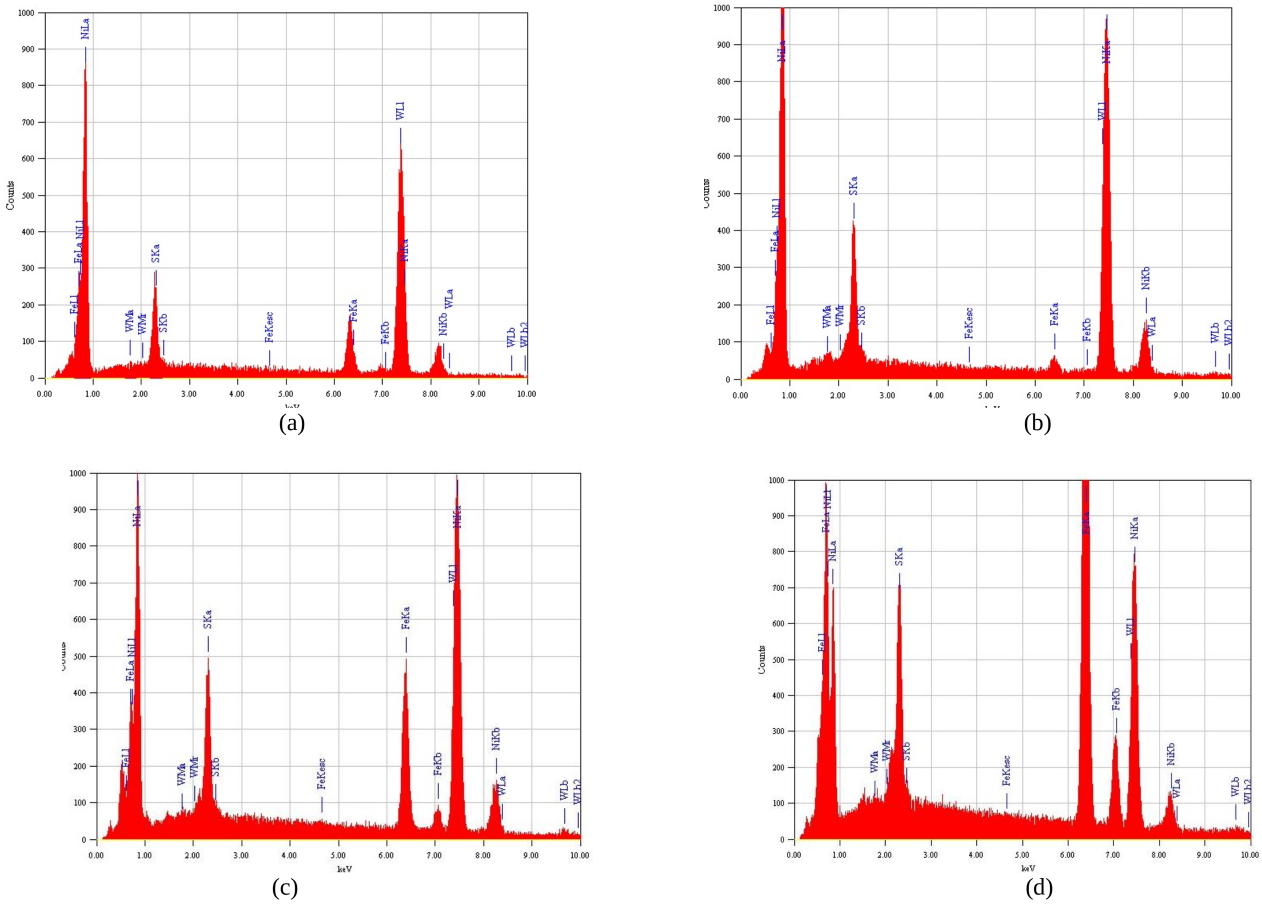


Fig. 1. EDAX spectrum of NiFeWS films electrodeposited at 1 A/dm^2 from bath I & II with (a) at 50˚C, (b) at 80˚C, (c) 50˚C, (d) 80˚C.

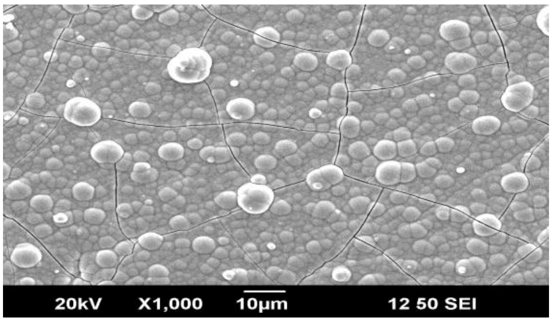
EDAX result showed that the films obtained at higher temperature have low Sulphur content. So that the coercivity of films get reduced and the magnetization values were increased. The lowest Sulphur content of 5.39 wt% was obtained at temperature 80˚C of bath I. It is usual to ignore the effect of ammonia on the composition of the films, as it is a mild base which is used to adjust the pH of the solution.

Table 2. Results of EDAX analysis.

Bath identification	Sample identification	Temperature ˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
Bath – I	A	50	89.24	2.58	0.79	7.39
	B	80	88.11	5.01	1.774	5.39
Bath -II	C	50	69.72	23.21	0.5	6.57
	D	80	34.16	59.91	0.34	5.6

3.2 Morphology of the deposits

The SEM images of electrodeposited NiFeWS thin films are shown in Fig. 2. The films obtained at low temperature have some micro cracks. This is due to the generation of internal stresses resulting in the formation of microcracks. The film obtained from higher temperature (80˚C) bath have small crystallites and granular. The films obtained at higher temperature are crack free and grain boundaries can be seen among the crystal grains. Hence the films have low stress.



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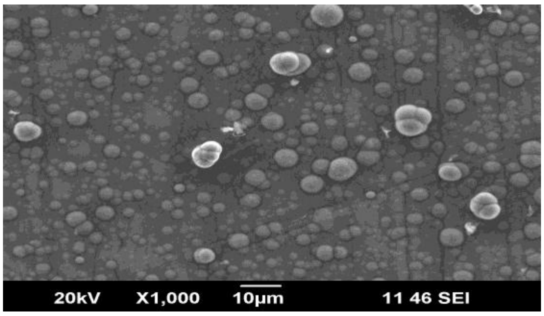

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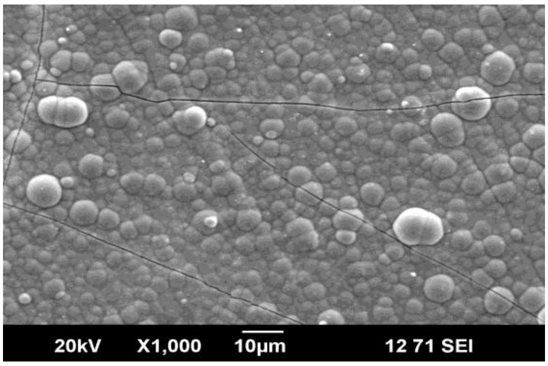

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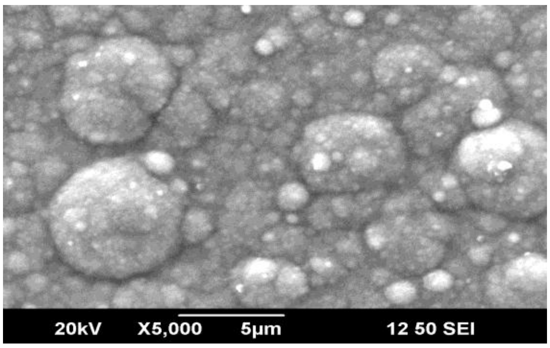
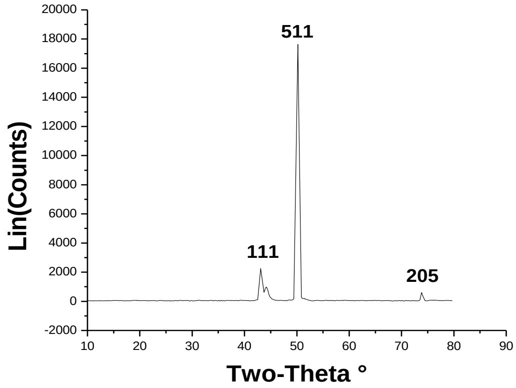


(d)

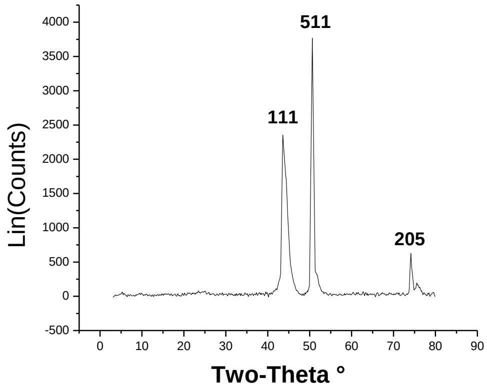
Fig. 2. SEM images of NiFeWS films electrodeposited at 1 A/dm^2 from bath I & II with (a) at 50˚C, (b) at 80˚C, (c) 50˚C, (d) 80˚C.

3.3 X-ray diffraction of the deposits

Electrodeposited NiFeWS films were subjected to XRD studies. Films obtained from bath I and bath II at temperatures 50˚C and 80˚C were studied for their structural characteristics as shown in Fig. 3.



(a)



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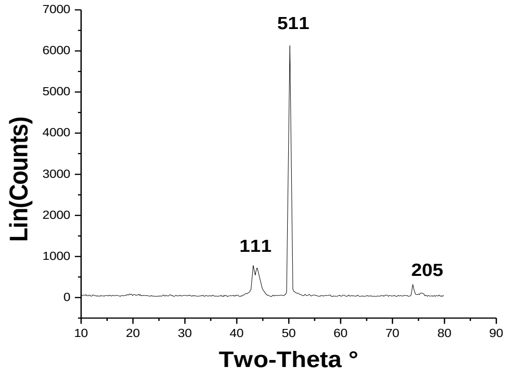

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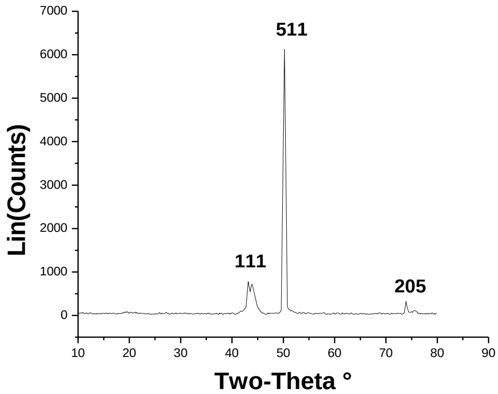


(d)

Fig 3. XRD patterns of NiFeWS films electrodeposited at 1 A/dm^2 from bath I & II with (a) at 50˚C, (b) at 80˚C, (c) 50˚C, (d) 80˚C.

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 decreases with increase in temperature of the bath.

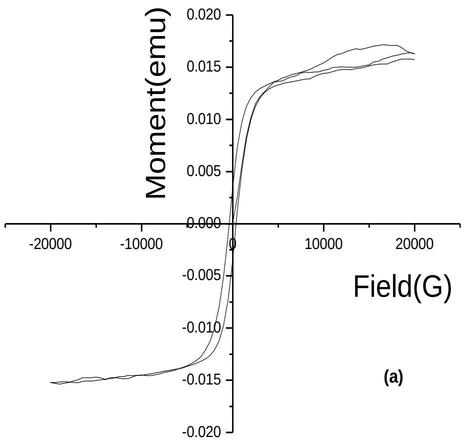
The crystal size of NiFeWS alloy films obtained from bath I and bath II are tabulated as shown in Table 3. The lowest crystalline size of NiFeWS thin film was obtained from bath I at temperature 80˚C and it is tabulated as shown in Table 3.

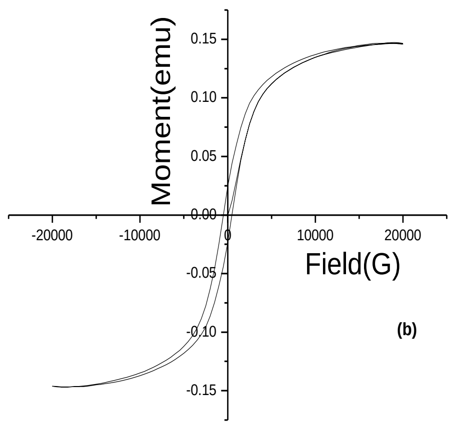
Table 3. Crystal size of NiFeWS alloy thin films.

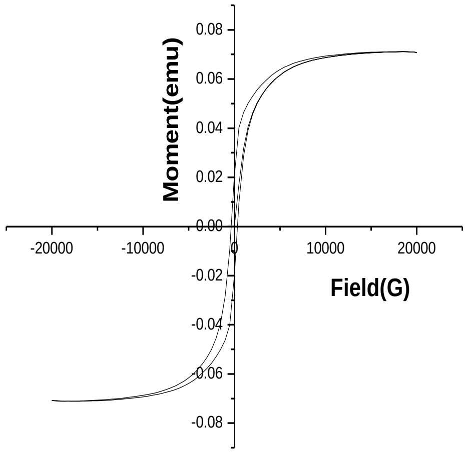
Bath identification	Sample identification	Temperature ˚C	2 θ	d A^0	Crystalline size D nm	Strain 10^{-4}	Dislocation density(10^{14} / m^2)
Bath – I	A	50	50.186	1.8164	30.966	11.69	10.42
	B	80	50.606	1.2406	23.85	15.17	17.58
Bath –II	C	50	50.217	1.8149	32.393	11.17	9.531
	D	80	50.236	1.8143	32.390	11.17	9.531

3.4 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 [7], [14]. We have planned to examine the saturation magnetization and coercivity of electrodeposited NiFeWS alloy thin films. The magnetic properties of the electrodeposited NiFeWS films have been observed from VSM are tabulated as shown in Table 4.







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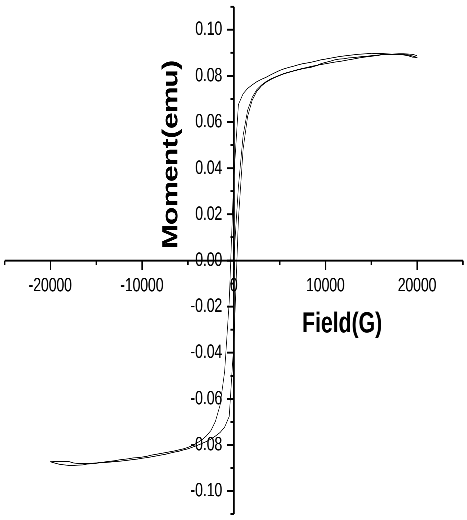

(d)

Fig. 4. Hysteresis loops of NiFeWS films electrodeposited at 1 A/dm² from bath I & II with (a) at 50˚C, (b) at 80˚C, (c) 50˚C, (d) 80˚C.

Table 4. The magnetic properties of the electrodeposited NiFeWS films.

Bath identification	Sample identification	Temperature ˚C	Coercivity G	Retentivity 10^{-3} emu	Magnetization 10^{-3} emu
Bath – I	A	50	372.10	3.4002	16.264
	B	80	338.66	19.821	71.102
Bath -II	C	50	485.64	23.534	0.14703
	D	80	332.80	35.231	89.33

The dependence of the coercivity and magnetization on temperature for the NiFeWS films were found from the Table 4.

The variation of saturation magnetization and coercivity for NiFeWS alloy thin films prepared at temperatures 50℃ and 80 ℃ of bath I & bath II is shown in Fig. 4. The film coated under the temperature of 80˚c exhibits the lower coercivity and higher magnetization. It was observed that the magnetization increases from 16.264×10^{-3} emu to 71.102×10^{-3} emu in bath I and from 0.14703×10^{-3} emu to 89.33×10^{-3} emu in bath II. From that we concluded the films prepared at higher temperature (80˚C) exhibits a higher value of saturation magnetization with lower value of coercivity. This is due to the fact that the crystalline size attains the minimum level of 24 nm. The best magnetic behavior arising with minimum crystalline size is due to the origin of nanoregion for this film. From Fig. 4 we conclude that the NiFeWS film exhibits the soft magnetic property effectively at higher bath temperature.

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 decrease in coercivity.

By analyzing the present results it can be seen that the best soft magnetic properties have been obtained for the electroplated deposits at high temperature bath.

4. Conclusion

The deposition of NiFeWS alloy thin films have been carried out by using electro deposition technique. The structural, compositional, morphological and magnetic properties were studied. The electro deposited NiFeWS thin film exhibits FCC cubic structure. The crystalline size of NiFeWS thin films are in the order of nano scale. The films obtained at temperature of 80˚c have crystalline size nearly 24 nm. SEM data of NiFeWS thin film reveals that the films are smooth, uniform, adherent. From VSM data we concluded that increase in temperature of the bath reduces the coercivity and increases the saturation magnetization. The NiFeWS alloy thin films electrodeposited under 80˚c temperature of the bath has higher magnetization value with lower coercivity (71.102×10^{-3} emu, 338.66 G and 89.33×10^{-3} emu, 332.80 G). So that the soft magnetic property is observed in higher temperature of bath (80˚C). Because of its higher magnetization and lower coercivity, these films can be used in various electronic devices including high density recording media, magnetic actuators, magnetic shielding, and high performance transformer cores.

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