Effect of annealing temperature on magnetic properties of nano crystalline Ni-Fe-W-S thin films in Diammonium Citrate bath

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The nano crystalline Ni-Fe-W-S thin films were deposited by electro deposition method in diamminoum citrate bath at 40˚C. Annealing of the deposited thin film was performed at 200˚ C temperature for 1 hour. The effect of annealing on the magnetic and structural properties of the product film was investigated by using Vibrating Sample Magnetometer (VSM) and X-ray diffractometer (XRD). Elemental composition and surface morphology of the films were studied using Energy Dispersive X-ray spectroscopy (EDAX) and Scanning Electron Microscope (SEM) respectively. Mechanical properties such as Hardness and adhesion of the films were also studied. Due to the improvement of soft magnetic properties in the 200˚C annealed film, the saturation magnetization is enhanced by 0.10935 emu/ cm^2 (coercivity decreased to 32 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 4.5703 Tesla. Hardness of the annealed film increased from 147 VHN to 155 VHN. Enhanced nano crystalline grains with size of 30.6 nm were observed in the annealed films. 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.

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1. Introduction

Electro deposited Permalloy (NiFe) is the best known thin film alloy in MEMS applications[1], because of their highest 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 [2]. 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 highly corrosion resistant metal and also bears high mechanical strength [3]. The Low stress thin film alloys with improved magnetic properties are very much used in magnetic recording heads and MEMS [4]. The best known stress reducing agents [5] for nickel based electro deposition are sulfur containing organic additives (saccharin, thiourea, benzene sulfonic acid etc).

Magnetic Properties of nano crystalline soft magnetic alloys have usually been correlated to structural evolution with heat treatment [6]. Nano crystallization can be induced by annealing the sample at high temperature [7-11]. In this paper, a new approach annealing treatment is proposed to make further enhancement of soft magnetic properties like saturation magnetization, magnetic flux density on electro deposited Ni-Fe-W-S thin films [12].

This paper reports the preparation of Ni-Fe-W-S thin films by electro deposition method. In order to 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 were studied and are reported here.

2. Experimental part

2.1 Electro deposition of NiFeWS thin films

NiFeWS thin film was electrodeposited on Copper substrate using relavant salts in Diammonium 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 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 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.

2.2 Annealing of NiFeWS thin films

The Ni-Fe-W-S thin films were electro deposited at bath temperature of 40˚C was annealed at 200˚C for 1 hour in a Muffle furnace (ranges from 0 to 1100˚C). The annealing temperature exceeds 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 cby 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.	Diammonium Citrate	70
6.	Citric acid	5.5
7.	Boric acid	10
8.	pH value	8
9.	Temperature	40˚C
10.	Current density	1 A/dm^2

2.3 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 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.

$$D = \frac{0.94\ 5\lambda}{\beta\ cos\theta} \qquad (1)$$

The strain (ε) was calculated from the relation

$$\varepsilon = \frac{\beta\ cos\theta}{4} \qquad (2)$$

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

$$\delta = \frac{1}{D^2} \qquad (3)$$

Magnetic properties (Coercivity, Magnetization, and retentivity) were studied using Vibrating Sample Magnetometer.

The Magnetic Flux density in the films ae calculated in Tesla using the relation

$$B_s = \frac{4\pi M_s \rho}{m} \qquad (4)$$

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

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

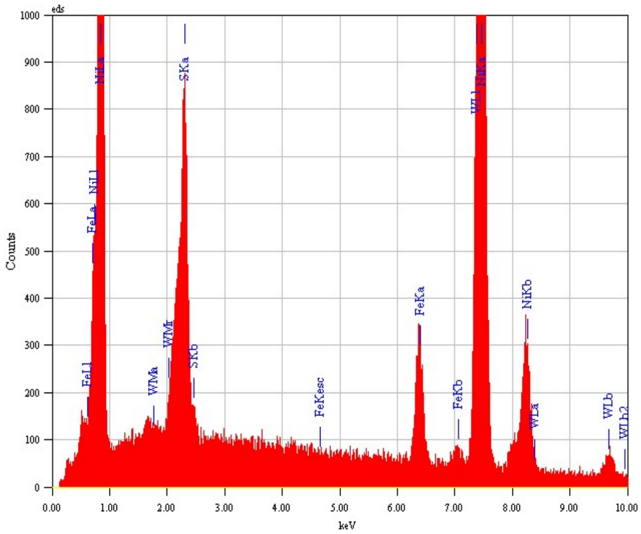
Where M_r is the Retentivity

Hardness of the as deposited and annealed film was measured by Vickers Hardness Test (VHN).

3. Results and discussion

3.1 Composition of the electro deposited NiFeWS thin films

The electrodeposited NiFeWS alloy films were smooth, uniform, adherent. The composition of the deposited NiFeWS film from Diammonium Citrate and annealed film was obtained from the EDAX analysis shown in Fig. 1.



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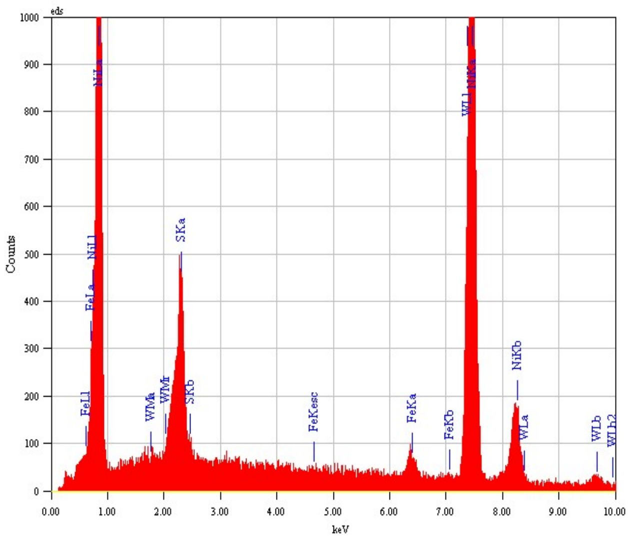

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Fig. 1. EDAX Spectrum of Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) After 200˚C annealing.

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 get 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.

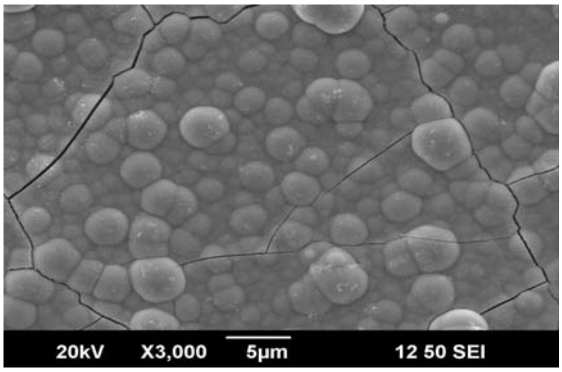
Table 2. Results of EDAX analysis

No	Temperature ˚C	Ni Wt%	Fe Wt%	W Wt%	S Wt%
1	40	85.81	8.02	0.70	5.45
2	200(after annealing)	84.36	7.10	0.54	7.10

3.2 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 Diammonium Citrate bath and annealed at 200˚ C are shown in Fig. 2.

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 having smaller crystallites and granular. This is due to uniform crystal orientation during electro deposition. Hence the film has low stress.



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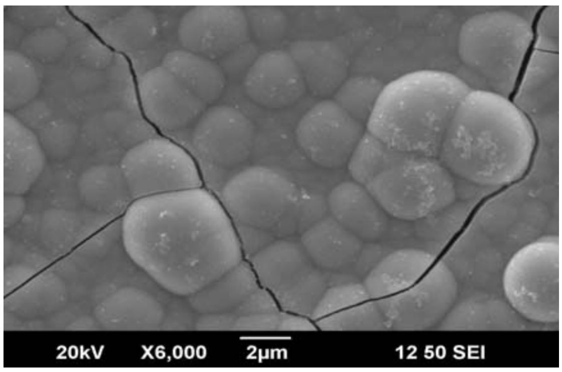

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Fig. 2. SEM images of Electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) After 200˚C annealing.

3.3 X-ray diffraction of the deposits

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

Electrodeposited NiFeWS film from Diammonium Citrate bath at 40˚ C and annealed at 200˚ C was subjected to XRD studies. Films obtained from Diammonium Citrate bath at temperature 40˚C and annealed at 200˚ C were studied for their structural characteristics as shown in Figure 3. The crystalline size of as deposited and annealed (at 200˚ C) NiFeWS alloy films obtained from Diammonium Citrate bath are tabulated as shown in Table 3. The dependence of crystalline size with annealing 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)	51.078	1.7888	9.2746	32.8	11.0951	9.2910
2	After annealing (annealed at 200˚C)	50.982	1.7899	9.3029	30.6	11.8932	10.6796

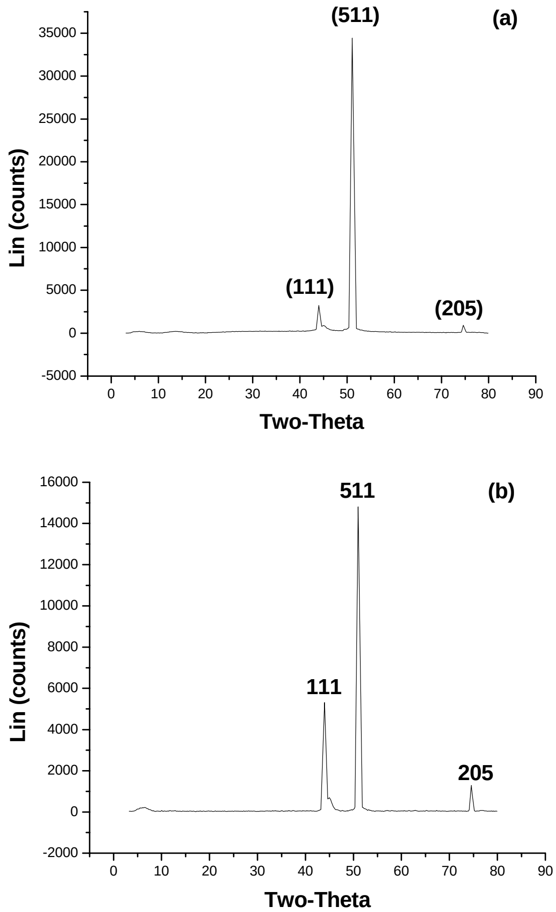

Fig. 3.XRD pattern of Electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) After 200˚C annealing.

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 32.8 nm for the film deposited from 40˚C bath temperature. But after annealing at 200˚ C for one hour the crystalline size decreased to 30.6 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 0.280˚ to 0.302˚, providing that the annealing procedure results in a smaller crystalline size. The strain built in the film gets released after annealing.

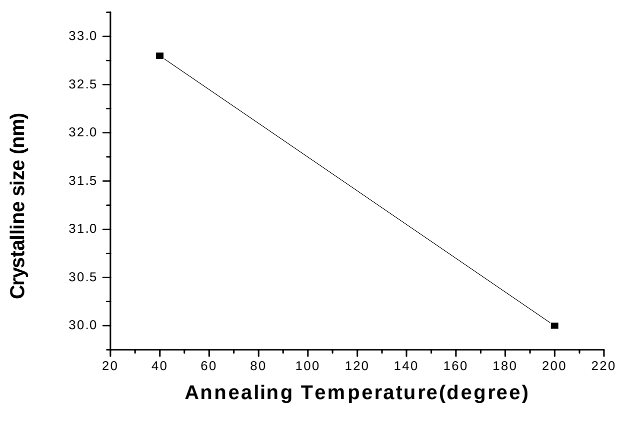

Fig. 4. Crystalline Size as a function of annealing temperature.

3.5 Mechanical Properties

3.6 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 is tested by bend test and scratch test. It showed that as deposited (at 40˚ C) and annealed (200˚ C) film having 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 (VH|N)
1	Before annealing (as deposited at 40˚C)	32.8	147
2	After annealing (annealed at 200˚C)	30.6	151

The results show that the hardness increases with annealing temperature. After annealing hardness of the film increases from 147 VHN to 155 VHN. This may be due to lower stress associated with electrodeposited Ni-Fe-W-S film in Diammonium Citrate bath. The dependence of Vickers hardness and annealing temperature is shown Fig. 5.

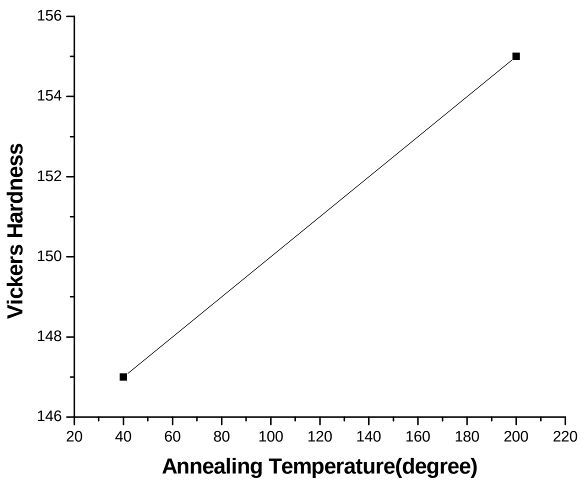

Fig. 5. Vickers Hardness as a function of annealing temperature.

3.7 Magnetic properties of the deposits

The hysteresis loop parameters, saturation magnetization (M_s), Coercivity (H_c), retentivity (M_r), 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 Diammonium Citrate bath at temperature 40˚C and annealed at 200˚C is shown in Fig. 6.

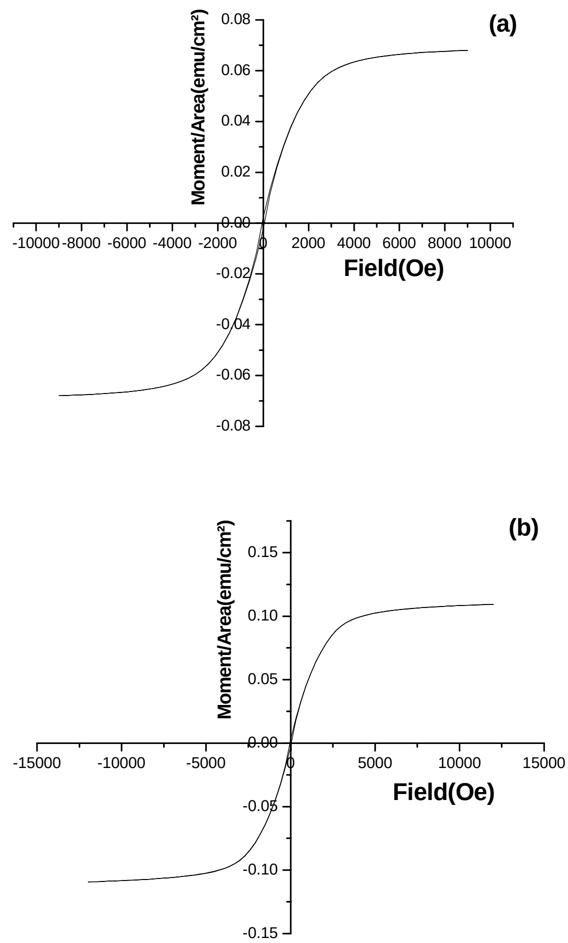

Fig. 6. Magnetic Hysteresis loops of Electro deposited Ni-Fe-W-S thin film (a) as-deposited film (at 40˚C) (b) After 200˚C annealing.

The magnetic properties of the as deposited annealed NiFeWS thin films have been 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 (O_e)	Magnetization M_s (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)	40.588	0.067986	2.1315×10^{-3}	2.6078	0.03135
2	After annealing (annealed at 200˚C)	32	0.10935	2.09×10^{-3}	4.5703	0.01911

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 [13]. 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 [14].

3.8 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 depends on film stress very sensitively and compressive stress lead to high coercivity but the tensile stress reduces coercivity [15]. 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 at high diammonium 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 42.588 Oe and saturation magnetization value of 67.986×10^{-3} emu/ cm^2. The retentivity value of as deposited film is 2.1315×10^{-3} emu/cm^2. After annealing at 200˚C, the annealed film exhibits lower coercivity of 32 Oe with higher magnetization of 0.10935 emu/ cm^2. The corresponding rententivity value decreased from 2.1315×10^{-3} emu/ cm^2 to 2.09×10^{-3} emu/ cm^2.The Squareness (S) decreases from 0.03135to 0.01911 as the annealing temperature increases.

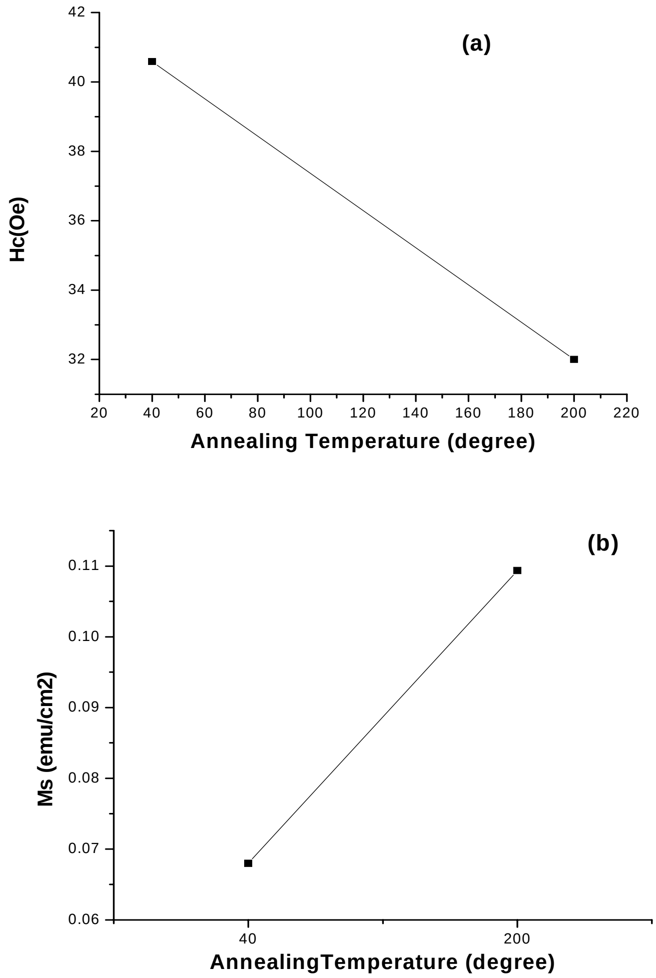

Fig. 7. Annealing Temperature as a function of (a) Coercivity (b) Saturation Magnetization.

The variation in magnetic properties can be attributed to the structural changes occurring in the film with annealing treatment. The drop in coercivity from 42.588 Oe to 32 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 67.986 × 10^{-3} emu/ cm^2 to 0.10935 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. 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 enhanced soft magnetic properties have been obtained from the electroplated nano crystalline films at annealed temperature 200˚ C.

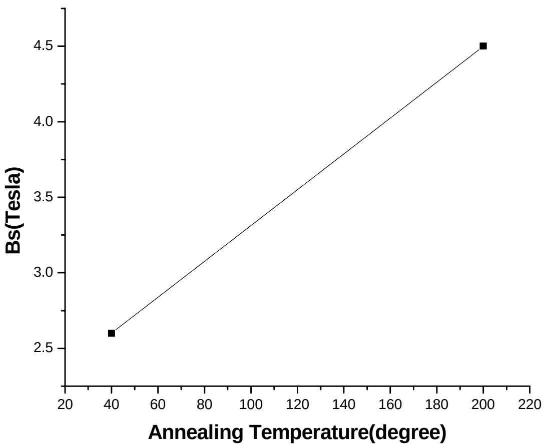

Fig. 8. Annealing Temperature as a function of Saturation Magnetic flux Density.

4. Conclusion

Ni-Fe-W-S film with soft magnetic properties can be obtained at bath temperature of 40˚C by electro deposition process from Diammonium Citrate bath. The coercive and saturation magnetization values of the film were 40.588 Oe and 67.986 × 10^{-3} emu/ cm^2 respectively. The electro deposited NiFeWS thin films at 40˚ C was annealed at 200˚ C for one hour. The effects of annealing on structural, mechanical and magnetic properties of NiFeWS thin films were investigated. The coercivity of the annealed film was decreased from 40.588 Oe to 32 Oe. Saturation magnetization of the annealed film was fond to be increased from 67.986 × 10^{-3} emu/ cm^2 to 0.10935 emu/ cm^2. In this work, we have found that annealed film (at 200˚ C) exhibits enhanced magnetic properties. This is due to the film undergoes substantial stress relief and occurrence of nano crystalline at annealing temperature 200 ˚C. Hardness of the annealed film increased from 147 VHN to 155 VHN. Enhanced nano crystalline grains with size of 30.6 nm were observed in the annealed films. 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.

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