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Effect of different Sulfur concentration on structural and magnetic properties of electrodeposited NiCoS magnetic thin films

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Abstract: Nano crystalline NiCoS alloy thin films were deposited on the copper substrate with different concentration of Sulfur by electrodeposition method. Electro deposited NiCoS thin films were subjected to the structural, mechanical and magnetic characterization analysis. The chemical composition of the coated films was analyzed by EDAX. The surface and structural morphology of the coated film were analyzed by using SEM and XRD. The mechanical properties of NiCoS films have been studied by VHT. The magnetic properties of thin films have been analyzed by VSM. The electroplated NiCoS thin films were strongly adherent to the copper substrate .The SEM pictures of NiCoS thin films shows that the deposits of thin films are crack free, uniform and bright surface with fine grain size. All the electro deposited NiCoS films exhibit FCC crystalline structure with crystalline size in the order of nano scale. The VSM result of NiCoS thin films shows that the NiCoS thin films coated withhigh concentration of sulfur have highest saturation magnetisation value with lower coercivity. Due to highest magnetisation value with low coercivity, NiCoS thin films can be used for the manufacturing of MEMS and NEMS devices.
Keywords : Electrodeposition ,thin films, characterization, crystalline size,X-ray diffraction, temperature , surface morphology,micro hardness.

1. Introduction

The most commonly used magnetic materials in MEMS and NEMS are soft magnetic materials, such as nickel cobalt based alloys(1-3). The most significant application of soft magnetic materials is in magnetic recording heads. The important requirement for high quality thin film recording heads are high magnetic saturation, low coercivity, high permeability, near zero magnetostriction, high electrical resistance and good corrosion resistance (4). The combination of low coercivity, relatively high magnetic saturation and good corrosion resistance has led to the use of electroplated NiCo films in microscopic sensors, actuators and systems .The electroplated magnetic thin films of the iron group metals (Ni,Co,Fe) have been developed due to its potential applications in MEMS (5-7).

In the recent years, electrodeposition of ferromagnetic alloys has given much attention as an effective method for the fabrication of micro devices and sensors due to its ability to fill up patterns of high aspect ratio properties as compared with the conventional vacuum deposition techniques such as CVD and PVD (8-12). So the electrodeposition method has been chosen for coating the NiCoS thin films in this current investigation. In power electronics industry, CoNiS thin films are the suitable materials for the production of super capacitors. The ternary nickel cobaltsulfides have been investigated as novel super capacitor electrode materials with improved magnetic and electrochemical performance .Also sulfur is a stress reducing agent (2). In this present work, the effect of different concentration of sulfur on CoNi thin films isanalyzed. This paper summarizes the synthesis and characterization of electroplated nanocrystalline NiCoS thin films with different concentration of sulfur.

2. Experimental Part

The working conditions and bath composition of NiCoS alloy thin film are shown in Table 1.The NiCoS thin films are successfully coated by electrodeposition method. In this investigation, Copper and stainless steel substrates act as cathode and anode respectively. A copper plate and stainless steel of size 1.5 cm as breath and 7.5cm as length were used as substrates. Both cathode and anode were washed with soap and soaking in 15% H_2SO_4 for 2 minutes. The reagent grade chemicals and triple distilled water were used to prepared electroplating bath. The pH value of the bath was adjusted to 6 by adding few drops of ammonia solution. The NiCoS thin films were electro deposited on the copper substrate by applying a current of 15 mA for 15 minutes and varying the thiourea concentration (10,20,30 g/lit of Thiourea) at 30˚C. The cathode was carefully removed from the bath after 15 minutes and dried for few minutes. The surface morphology of the NiCoS thin films was analyzed with the help of Scanning electron microscope(SEM). The film composition and structural characters of thin films were measured by Energy-dispersive X-ray Spectroscopy (EDAX) andX-ray diffraction (XRD) respectively. The hardness of NiCoS thin films was measured by Vickers Hardness Test (VHT).The magnetic property of NiCoS thin films film was measured by Vibrating Sample Magnetometer (VSM).The thicknesses of the films were determined by cross sectional view of SEM images. The electrodeposition bath details of NiCoS thin films are given in table 1.

Table 1: Electrodeposition bath details of NiCoSthin films

S. No	Name of the chemicals and parameters	Datag/L
1.	Nickel Sulphate	30
2.	Cobalt Sulphate	15
3.	Thiourea	10,20,30
4.	Tri Sodium citrate	40
5.	Citric acid	10
6.	Boric acid	10
7.	pH value	6
8.	Time Duration	15 min
9	Temperature	30˚C
10.	Current density	2 mA/cm^2

Result and Discussion

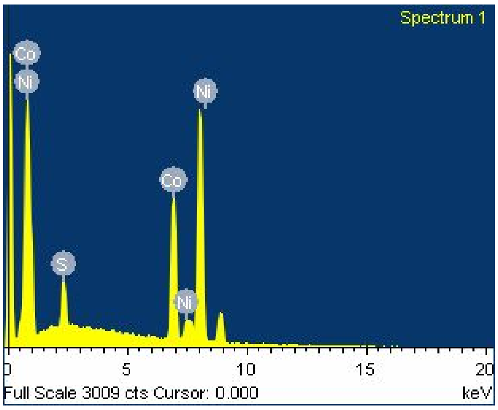
3.1 Composition of the Electro Deposited NiCoS Thin Films

The chemical composition of the electroplated NiCoS thin films is analyzed by EDAX spectrum. The EDAX spectrum of NiCoS thin films is shown in fig 1. The EDAX data of thin films are shown in Table 2.

Table 2: EDAX analysis of NiCoS thin films

S. No	Thiourea (g)	Co Wt%	Ni Wt%	S Wt%
1.	10	80.32	11.00	8.68
2	20	66.97	14.84	18.18
3	30	58.84	22.56	18.59

EDAX result showed that the films obtained with higher concentration of thioureahave high sulfur content. The highest sulfur content of 18.59wt% was obtained with high thiourea concentration. EDAX result showed that Ni content increases with increasing the thiourea concentration. The maximum Ni content of 22.56wt% was obtained for NiCoS thin films with high thiourea concentration. The weight percentage of Co decreases while increasing the thiourea concentration. Ammonia solution is used to correct the pH value of the bath solution only and its effect on the film was ignored.



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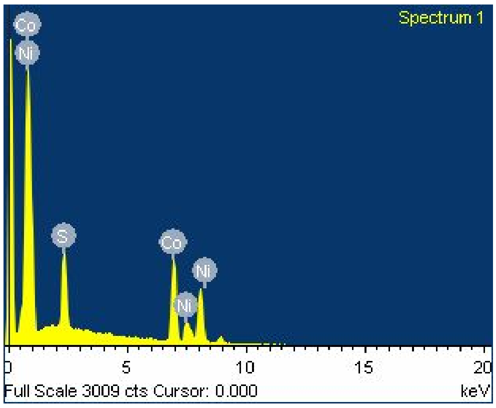

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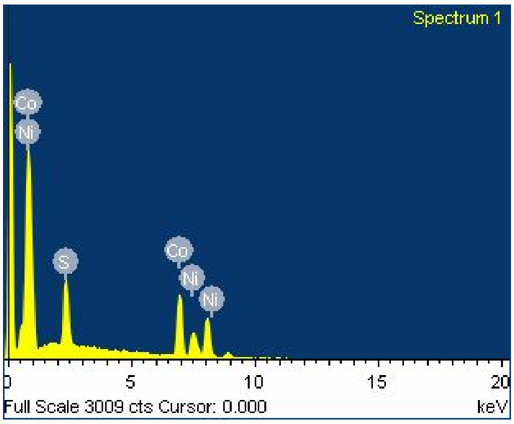

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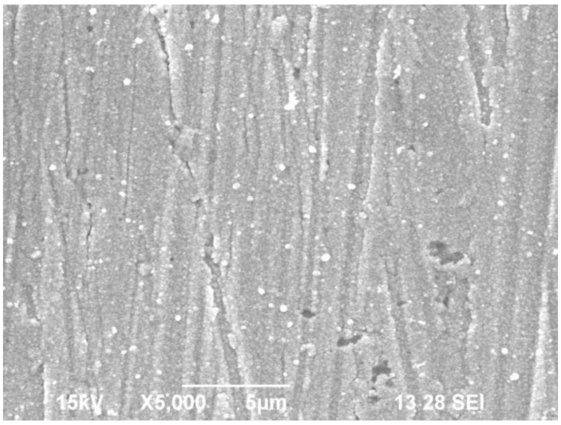
Figure 1: EDAX spectrum of NiCoS thin films for different concentration of thiourea(a) 10 g/l (b) 20 g/l (c) 30 g/l

3.2 Surface Morphology of NiCoS Thin Films

The surface morphology of the electroplated NiCoS thin films with different thiourea concentration is analyzed by using SEM pictures and are shown in fig 2.The electroplated thin films are smooth, uniform and adherent with substrate. The thin films are crack free, bright and uniform. From SEM analysis we conclude that the formation of thin films on the copper substrate is uniform in nature.

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

S.No	Thiourea (g)	Film Thickness µm
1	10	4.3
2	20	4.1
3	30	4.9



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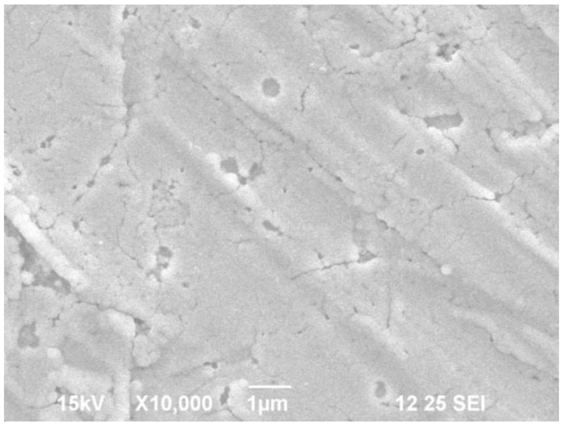

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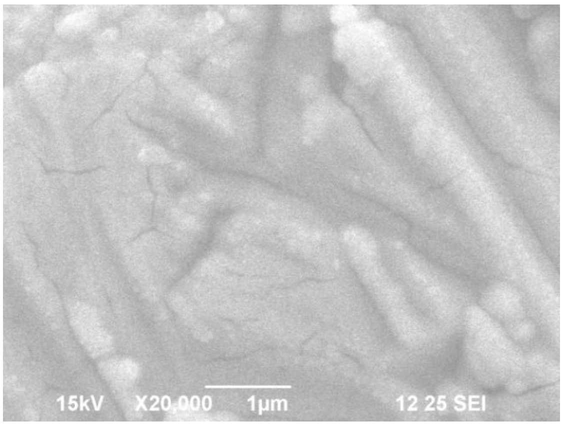

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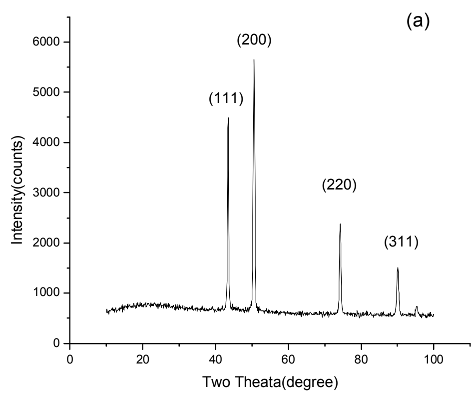
Figure 2: SEM images for Electro deposited NiCoS thin film for different concentration of thiourea(a) 10 g/l (b) 20 g/l (c) 30 g/l

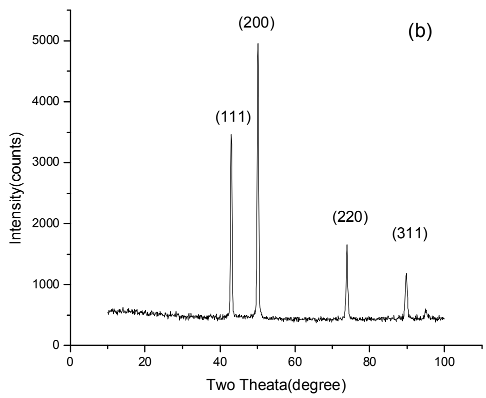
3.3 Structural Properties of NiCoS Thim Films

The crystalline sizes of the coated thin films are calculated by using Scherrer's formula.

$D=0.954\lambda/\beta\cos\theta$

Where, θ is the Bragg's angle,λ is the X-ray wavelength and β is the full width at half maximum intensity of the diffraction peak located at 2θ. X- ray diffraction patterns of electro deposited NiCoS alloy thin films obtained with different concentration of thioureaare shown in fig 3.The XRD data's of NiCoS thin filmswith different concentration of thiourea are compared with standard JCPDS data and are found to have FCC crystalline structure with four predominant peaks of (111) ,(200), (220) and (311). The crystal size of NiCoS alloy films is tabulated as shown in table 4.





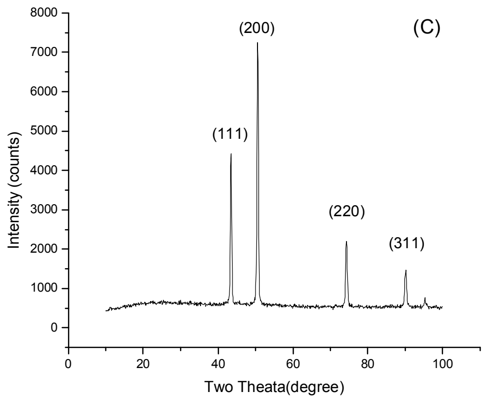


Figure 3: XRD pattern of electrodeposited NiCoSthin film with different concentration of thiourea(a) 10 g/l (b) 20 g/l (c) 30 g/l

From XRD analysis, It is concluded that the films have nano crystalline phase.When concentration of thiourea is increased, the crystalline size of NiCoS thin films decreases during electrodeposition. This is due to increase of nickel concentration. This may be due to stress difference with electrodeposited NiCoS films. The dependence of crystalline size with different concentration of thiourea is shown figure 4.

Table 4: Crystalline size of NiCoS alloy thin films

S. No	Thiourea (g)	2Θ (deg)	d (A^0)	Particle size, D (nm)	Strain (10^{-3})	Dislocation density (10^{14} / m^2)	Thickness (µm)
1	10	50.524	1.8049	20.72	1.7462	23.29	4.3
2	20	50.544	1.8039	20.47	1.7762	23.82	4.1
3	30	50.5644	1.80366	20.04	1.8059	24.90	4.9

3

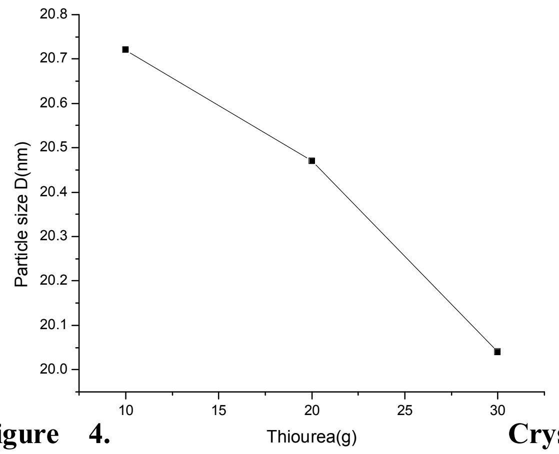


Figure 4. Crystalline Size as a function of thiourea concentration

3.4 Mechanical Properties of NiCoS Thin Films

The hardness of NiCoS films was examined by using Vickers hardness tester. The results show that the hardness increases with increasing concentration of sulfur. This may be due to lower stress associated with electrodeposited NiCoS films. The hardness of NiCoS thin films has been shown in table 5.The dependence of Vickers hardness and concentration of thiourea is shown fig 5.

Table 5. Mechanical Properties ofElectro deposited NiCoS thin film

S.No	Thiourea (g)	Crystalline size D nm	Vickers Hardness (VHN)
1	10	20.72	39
2	20	20.47	41
3	30	20.04	46

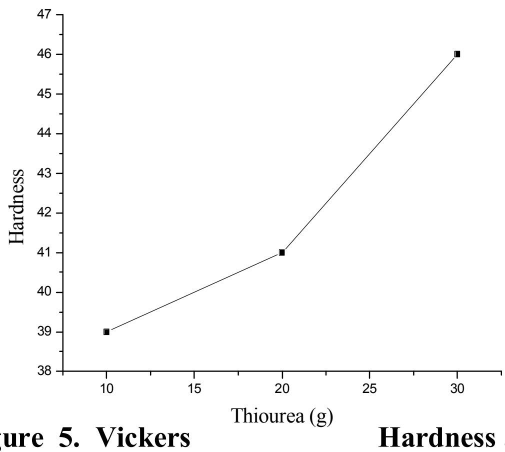


Figure 5. Vickers Hardness as a function of thiourea concentration

4. Magnetic Properties of NiCoS Thin Films

The magnetic properties of the electrodeposited NiCoS films have been observed from VSM and are tabulated as shown in Table 6.The magnetic hysteresis loops of NiCoS alloy thin films for different concentration of thiourea are shown in Figure 6.

Table 6. Soft Magnetic Properties of NiCoS deposits

S.No	Thiourea (g)	Coercivity H_s (G)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Squareness $S(M_r/M_s)$
1	10	292.70	476.88×10^{-6}	149.55×10^{-6}	0.3136
2	20	70.912	482.07×10^{-6}	53.174×10^{-6}	0.1103
3	30	54.291	704.00×10^{-6}	51.235×10^{-6}	0.0727

The film coated for high thiourea concentration exhibits the higher magnetization. It was observed that the magnetization increases from 476.88×10^{-6}emu/cm^{2}to 704.00×10^{-6}emu/cm^2. From that we concluded the film prepared with high thiourea concentration exhibits a higher value of saturation magnetization and lower coercivity. Coercivity and crystal size of the films were gradually decreased with increasing nickel content for NiCo based magnetic thin films. Grain size of the film plays an important role to decide the coercivity (14-15). The magnetic properties can be changed by decreasing the grain size. Coercivity of the films is also affected by other factors such as film stress and impurities etc.

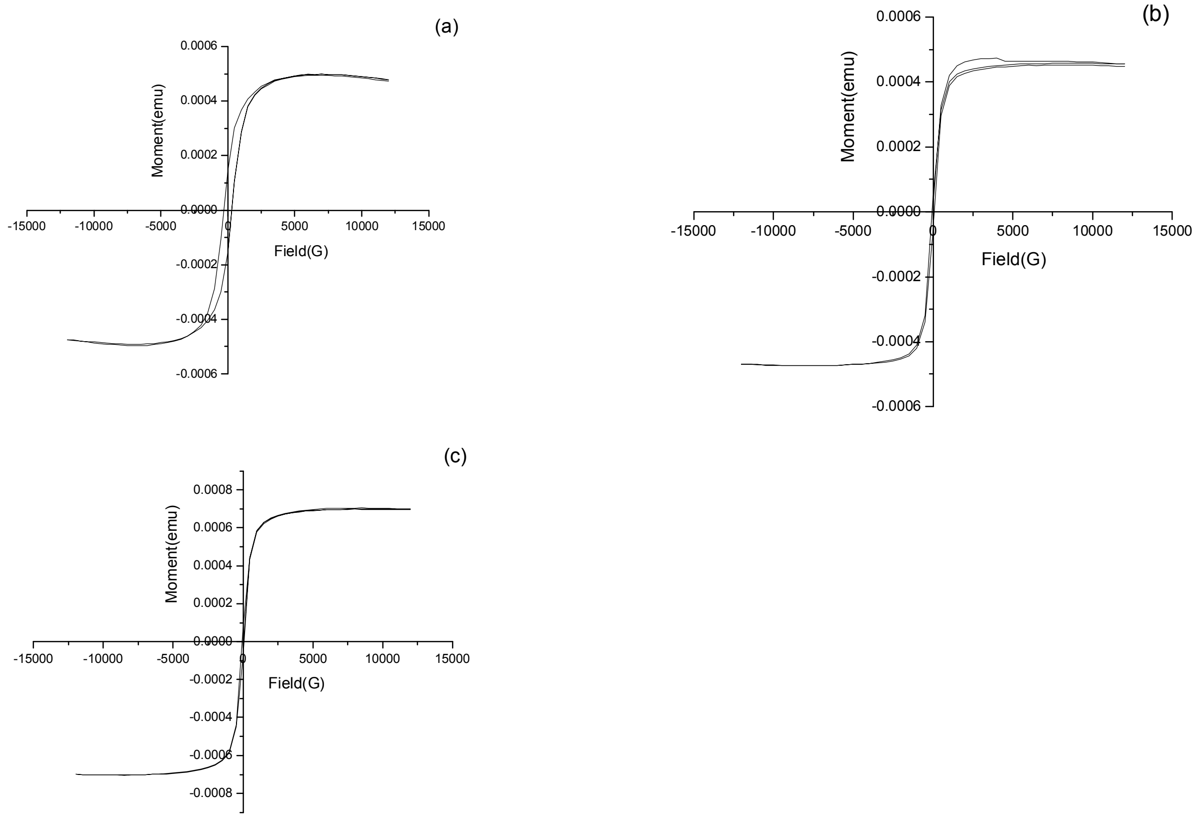


Figure 6. Magnetic Hysteresis loops for NiCoS thin film for different concentration of thiourea(a) 10 g/l (b) 20 g/l (c) 30 g/l

Particularly magnetic film stress strongly affects the coercivity. For NiCo based films, compressive stress leads to high coercivity while tensile stress reduces the coercivity. Normally NiCo based thin films have low magnetostriction value. The dependence of coercivity, saturation magnetization and concentration of thiourea are shown in Figure 7.

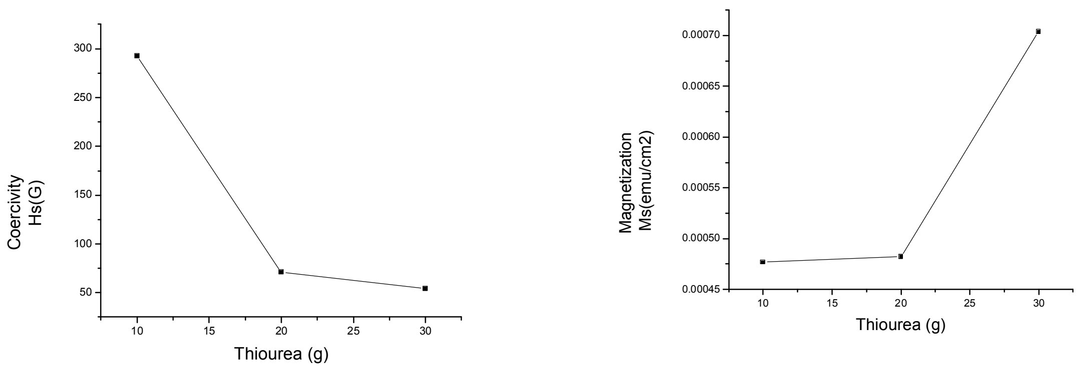


Figure 7. Thiourea concentrationas a function of (a) Coercivity Saturation Magnetization

Coercivity of the films was gradually decreased with increasing Ni content. From EDAX results of NiCoS thin films, it is concluded that Ni content increases with increasing concentration of thiourea and Co content decreases with increasing concentration of thiourea. The film stress is reduced because of increase in Ni content. From VSM results ,we conclude that due to low stress and smaller crystalline size of the NiCoS thin films obtained with high concentration of thiourea have higher saturation magnetization with lower coercivity.

By analyzing the results, it can be seen that the best soft magnetic properties have been obtained for the electroplated NiCoS films with high concentration of thiourea.

5. Conclusion

The NiCoS magnetic thin films were successfully synthesized by electro deposition with different concentration of thiourea. The nano crystalline films obtained with different concentration of thiourea are crack free, bright and uniform. FCC was the dominant structure of electro deposited NiCoS thin films. The crystalline sizes of the deposits are in the nano scale. Hardness is increases with increasing thiourea concentration. The film coated for high thiourea concentration exhibits the higher magnetization. It was observed that the magnetization increases from 476.88×10^{-6}emu/cm^2 to 704.00×10^{-6} emu/cm^2. The coercivity of the NiCoS thin films reduces from 292.70 G to 54.291 G. This is due to low film stress associated with NiCoS. The development of nickel cobalt sulfides with controllable composition by electrodeposition method and their application as positive electrodes improve super capacitors with excellent energy storage properties. The NiCoS thin films can be used in various electronic devices, MEMS and NEMS.

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