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Effect of bath temperature on structural and magnetic properties of electrodeposited NiCoS magnetic thin films

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Abstract: Nano crystalline Ni-Co-S alloy thin films were deposited on the copper substrate at different temperature by electrodeposition method. Electro deposited Ni-Co-S thin films were subjected to the structural, mechanical and magnetic characterization analysis. The chemical composition of the coated films was analysed 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 analysed by VSM. The electroplated NiCoS thin films were strongly adherent to the copper substrate The SEM pictures of NiCoS thin films show that, the deposits of thin films are crack free, uniform and bright surface with fine grain size. All the electro deposited Ni-Co-S 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 at high bath temperature 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: Thin films, characterization, electrodeposition, crystalline size , temperature ,X-ray diffraction, Micro hardness, , Surface morphology.

1. Introduction

Electrodeposition has become the dominant manufacturing technology in many new applications such as micro electromechanical system (MEMS) devices, nano electromechanical system (NEMS) devices, data storage media and magnetic recording head. Electrodeposited nickel is one of the most widely used materials in the fabrication of micro machines such as micro cantilevers, micro gears and their components (3-5). The most commonly used magnetic materials in MEMS and NEMS are soft magnetic materials, such as NiCo ,NiFe and NiP (4-6) .The combination of low coercivity (low hysteresis loss), relatively high magnetic saturation and good corrosion resistance has led to the use of electroplated NiCo films in microscopic sensors, actuators and systems (7). The use of NiCo as the soft film can be improved by adding a third element with NiCo alloy. In power electronics industry, CoNiS thin films are the suitable materials for the production of super capacitors. Sulfur is the suitable stress reducing agent for NiCo based thin films. It is important to develop new electrode materials with desirable super capacitor properties, such as high electrical conductivity, porous structure, large capacitance and good electrochemical stability. The development of ternary nickel cobalt sulfides with controllable composition by electrodeposition method and their application as positive electrodes improve super capacitors with excellent energy storage properties In this current investigation, the electrodeposition method has been chosen for coating Ni-Co-S thin films. In this work, thiourea is used as a source material for Sulfur . In

this present work we have analyzed the effect of S on CoNi thin films with different temperature. This paper summarizes the synthesis and characterizations of electroplated Ni-Co-S thin films.

2. Experimental part

The working conditions and bath composition of Ni-Co-S 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 Ni-Co-S thin films were electro deposited on the copper substrate by applying a current of 15 mA for 15 minutes at 30˚C,50˚C ,70˚C and 90˚C. The cathode was carefully removed from the bath after 15 minutes and dried for few minutes. The surface morphology of the Ni-Co-S 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) and X-ray diffraction (XRD) respectively. The hardness of NiCoS thin films was measured by Vickers Hardness Test (VHN). 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. Electroplating bath details of NiCoS thin films

S.No	Name of the chemicals	(g/L)	Temperature (^{0}C)	Current density	pH
1	Nickel Sulphate	30	30,50,70,90	2 mA/cm^2	6
2	Cobalt Sulphate	15			
3	Thiourea	10			
4	Tri Sodium citrate	40			
5	Citric acid	10			
6	Boric acid	10			

3. Results and Discussion

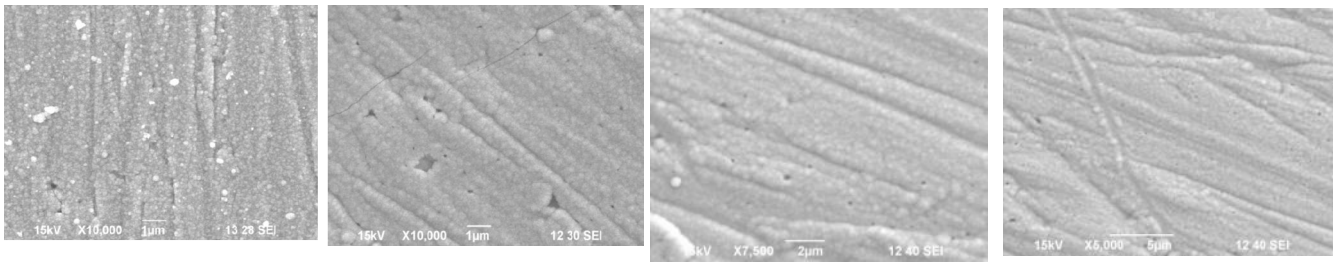
3.1 Composition of electrodeposited thin films

The chemical composition of the electroplated thin films is analyzed by EDAX spectrum. The EDAX data's of thin films are shown in Table 2. EDAX result showed that the films obtained at higher temperature have high sulfur content. The highest sulfur content of 33.13 wt% was obtained at temperature 90˚C. EDAX result showed that Ni content increases with increasing the bath temperature. The maximum Ni content of 26.92 wt% was obtained for NiCoS thin films at 90˚C bath temperature. The weight percentage of Co decreases while increasing the bath temperature. Ammonia solution is used to correct the pH value of the bath solution only and its effect on the film was ignored.

Table.2 Results of EDAX analysis

S. No	Bath Temperature (^{0}C)	Ni wt %	Co wt %	S wt %
1	30	80.32	11.00	8.68
2	50	66.16	20.56	13.28
3	70	60.23	25.08	14.69
4	90	39.95	26.92	33.13

3.2 Morphological observation



(a) (b) (c) (d)

Fig.1. SEM images of NiCoS films electrodeposited at (a) 30^0C (b) 50^0C (c) 70^0C (d) 90^0C

The surface morphology of the electroplated Ni-Co-S thin films with different temperature is analyzed by using SEM pictures and are shown in fig 1.The electroplated thin films are smooth and uniform. The thin films are bright, crack free and uniform. From SEM analysis we conclude that the formation of thin films on the copper substrate is uniform in nature .

3.3 Structural analysis

X- ray diffraction patterns of electro deposited Ni-Co-S alloy thin films obtained at different temperatures are shown in fig 2.. The crystalline sizes of the coated thin films are calculated by using Scherrer's formula.

$(D=0.954\lambda/\beta\cos\theta)$ ----------(1)

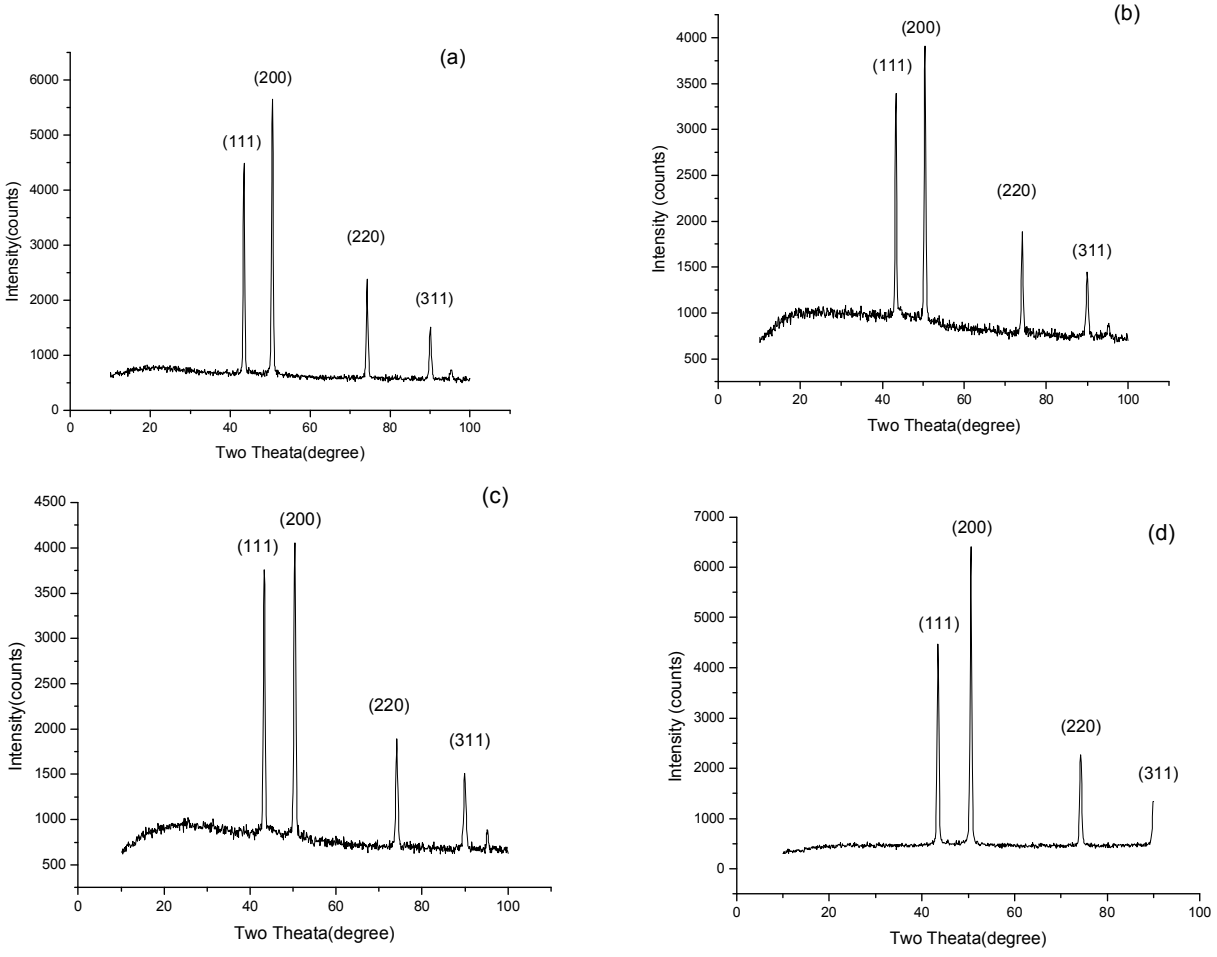


Fig.2 XRD patterns of NiCoS thin films at (a) 30^0C (b) 50^0C (c) 70^0C (d) 90^0C

Where, λ is the X-ray wavelength, β is the full width at half maximum intensity of the diffraction peak located at 2θ and θ is the Bragg's angle. The presence of sharp peaks in XRD pattern reveals that the NiCoS films are crystalline in nature .The obtained data's from XRD analysis are compared with standard JCPDS data and the NiCoS 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 3.The crystalline sizes of the deposits are in the nano scale. When the bath temperature is increased the crystalline size of thin films decrease due to onset orientation of crystals during electrodeposition.

Table.3 : Structural characteristics of NiCoS alloy thin films

S. No	Bath Temperature (^{0}C)	2Ɵ (deg)	d (A^0)	Particle size, D (nm)	Strain (10^{-3})	Dislocation density (10^{14} / m^2)	Thickness (µm)
1	30	50.524	1.8049	20.72	1.7462	23.29	4.3
2	50	50.365	1.8103	19.54	1.8519	26.19	4.8
3	70	50.374	1.8100	18.49	1.9572	29.25	5.4
4	90	50.380	1.8122	18.41	1.9622	29.52	5.9

3.4 Mechanical properties

Hardness of the films was examined by using Vickers hardness tester (the diamond intender method). The results show that the hardness increases with increasing bath temperature.

This may be due to lower stress associated with electrodeposited NiCoS films. The hardness of NiCoS thin films have been shown in table 4.

Table.4: Mechanical Properties of electro deposited Ni-Co-S thin films

S.No	Bath Temperature (˚C)	Vickers Hardness (VHN)	Crystalline size D nm
1	30	39	20.72
2	50	42	19.54
3	70	48	18.49
4	90	56	18.41

3.5 Magnetic properties

The magnetic properties of the electrodeposited NiCoS films have been observed from VSM and are tabulated in Table 5.The magnetic hysteresis loops for NiCoS alloy thin films for different temperatures are shown in Figure 3.The film coated under the temperature of 90℃ exhibits the higher magnetization. It was observed that the magnetization increases from 0.4768 $\times 10^{-3}$ emu/cm^2 to 6.6409 $\times 10^{-3}$ emu/cm^2. From that we concluded the films prepared at higher temperature (90˚C) exhibits a higher value of saturation magnetization .

Table.5 : Soft Magnetic Properties of Ni-Co-S deposits

S.No	Bath Temperature (˚C)	Coercivity H_s (G)	Magnetization M_s (emu/cm^2)	Retentivity M_r (emu/cm^2)	Squareness $S(M_r/ M_s)$
1	30	292.70	0.4768×10^{-3}	0.1495×10^{-3}	0.3135
2	50	273.81	0.7071×10^{-3}	0.2126×10^{-3}	0.3006
3	70	269.31	0.8772×10^{-3}	0.2408×10^{-3}	0.2745
4	90	260.17	6.6409×10^{-3}	3.2170×10^{-3}	0.4844

A low coercivity is an essential needed character for Ni based thin films. Grain size of the film plays an important role to decide the coercivity. If the grain size is large, the ferromagnetic materials properties are decided due to domain wall movement. The magnetic properties may be changed by decreasing the grain size. If the grain size is in the range of nanometers, coercivity of magnetic materials are decreased (grain size is

smaller than the domain wall width). 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. So that NiCoS thin films also have low magnetostriction value which can be used for fabricating devices like magnetic recording heads and sensors.

Coercivity of the films was gradually decreased with increasing Ni content. From VSM results of NiCoS thin films, it is concluded that Ni content increases with increasing bath temperature. The film stress is reduced because of increase in Ni content. Because of low stress and smaller crystalline size the NiCoS thin film obtained at 90˚C bath temperature has 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 nano crystalline films at high temperature

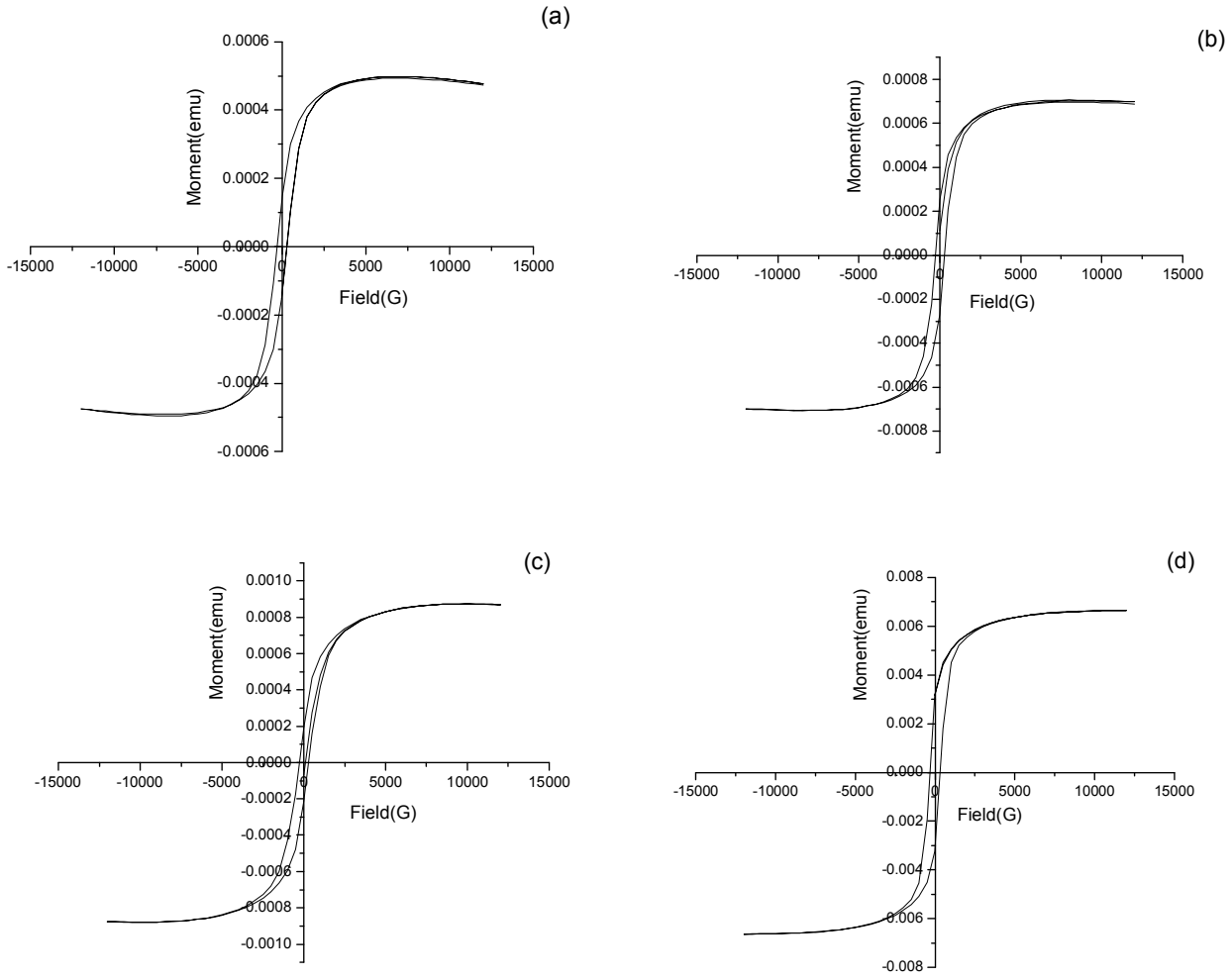


Fig.3 : Magnetic hysteresis loops for Ni-Co-S thin film for different bath temperatures (a) 30˚C (b) 50˚C (c) 70˚C (d) 90˚C

4. Conclusion

The Ni-Co-S magnetic thin films were successfully synthesized by electro deposition at different bath temperatures 30˚C, 50˚, 70˚C and 90˚C .The nano crystalline films obtained at different temperature are crack free, bright and uniform. FCC was the dominant structure of electro deposited Ni-Co-S thin films. The crystalline sizes of the deposits obtained by electro deposition process are in the nano scale.. Hardness is increases with increasing bath temperature. When the bath temperature was increased from 30 ˚C to 90 ˚C, the magnetization values increases from 0.4768 $\times 10^{-3}$ emu/cm^2 to 6.6409 $\times 10^{-3}$ emu/cm^2. The coercivity of the Ni-Co-S thin films reduces from 292.70 to 260.17 Gauss. This is due to nano crystalline microstructure and low

film stress associated with Ni-Co-S.This article summaries the optimized operating condition of electroplated bath. 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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