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Super-Capacitive Properties of Electro-Synthesized Nanocrystalline Nickel Ferrite Thin Films Deposited from Non-Aqueous Bath

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Abstract: Nickel ferrite thin films synthesized at room temperature. Atomic Absorption Spectroscopy (AAS), was used to study stoichiometry as $NiFe_2$. Alkaline bath and small heat treatment converts this $NiFe_2$ into $NiFe_2O_4$. Cubic type of crystal structure of Nickel ferrite thin films was confirmed from XRD. SEM and AFM images confirm smooth and well adhered morphology. Magnetic properties show comparable results as that of bulk material We have tested $NiFe_2O_4$ as an electrode for Supercapacitor. This shows good value of specific and interfacial capacitance.

Keywords: Electrosynthesis, Nickel ferrite, XRD, SEM, AFM, Supercapacitor.

1. INTRODUCTION

Nickel ferrite is a ferromagnetic material, which is having potential applications in magnetic cores, opto-magnetic devices, bubble memory devices and vertical recording magnetic materials in thin film form [1-3]. Apart from technological importance in electronic and magnetic industries, $NiFe_2O_4$ has been used as highly reproducible material for humidity and gas sensors [4]. Oxide film based thin film supercapacitors have been the subject of considerable attention as energy storage systems, particularly for applications which involve a micro power sources for microelectronic mechanical systems (MEMS) and for back up sources for computer memory chips [5-8] Some reports are available on the iron-based compound in electrochemical devices such as Li-ion batteries [9].

Several methods have already been used for the deposition of nickel ferrite thin films, which include ferrite plating, pulse laser deposition technique [10,11], arc plasma method [12] chemical transport, chemical vapour deposition [13-15] sputtering [16] etc. but all these methods require sophisticated instrumentation, substrate heating during and/or after deposition etc. Among the all these methods for preparation of thin films electrochemical deposition is one of the less expensive and room temperature operated technique.

This work presents single-step electrodeposition of nickel ferrite ($NiFe_2O_4$) thin films at room temperature from non aqueous alkaline solutions. These nickel ferrite thin films are used to study structural, morphological and magnetic properties. Also supercapacitive performance is tested by using cyclic voltammetry technique.

2. MATERIALS AND METHODS

Ethylene glycol was used as an organic solvent for synthesis of nickel ferrite thin film. The 0.1 M $NiSO_4$, 1M $FeSO_4$ and 0.1 M citric acid solutions were prepared in ethylene glycol. 1 M NaOH was used to make bath alkaline. Bath composition was optimized [0.1M $NiSO_4$ ($10cm^3$) + 0.1 M $FeSO_4$ ($10cm^3$) + 0.1 M citric acid ($10cm^3$)] by varying quantity of 0.1 M $FeSO_4$ solutions to obtain stiochiometry ($NiFe_2$) films confirmed from the atomic absorption spectroscopy study. The optimized deposition potential and time for nickel ferrite thin films were – 0.80 V/s and 20 min, respectively. And are listed in Table No. 1. Blackish colored as-deposited nickel ferrite thin films were annealed for 1h at 773K temperature and furnace cooled. X-ray diffraction patterns carried out with Philips PW-3710 X-ray diffractometers. Morphological studies were carried out by using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques. Magnetic properties of as-deposited and annealed nickel ferrite thin films were measured with fully automated vibrating sample magnetometer (VSM) unit. Further cyclic voltametric curves (CV), which provide a means to measure of supercapacitor charge response with regards to a charging voltage, were used to evaluate the capacitance. The electro analytical measurements were carried out at room temperature in voltage of 0.5 to -0.5 V vs SCE. The number of charge-discharge cycles was tested for the stability of electrodes in the electrolyte.

3. RESULTS AND DISCUSSION

Elemental Stoichiometry

Fig 1 shows plot of atomic weight percentage of Fe in deposit against quantity of 0.1 M $FeSo_4$ solutions in bath of fixed quantity (20 cc). From Fig. 1, it is observed that for a mixture

of 10 cc 0.1 M $NiSo_4$ and 10 cc 0.1 M $FeSo_4$ solutions, stoichiometry in the film was $NiFe_2$. For this stoichiometry, the Ni and Fe contents in the deposited film were ~ 32% and ~63%, respectively.

Table 1

Preparative parameters	Varied range	Optimized parameters
Bath composition	0.1 M $FeSO_4$ 2 to 20 cc	0.1 M $NiSO_4$ (10cc) + 0.1 M $FeSO_4$ (10cc)+M citric acid (5cc) (Prepared in ethylene glycol) + 1 N NaOH (8 cc) prepared in water.
Deposition potential (V vs SCE)	-0.6 to –0.9	-0.8
Deposition time (min)	5 to 25	20

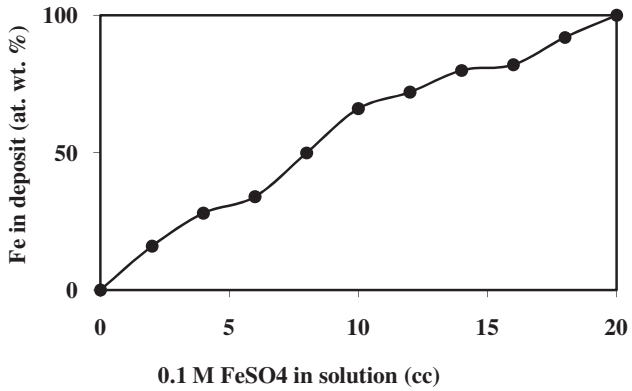

Fig. 1 A plot of Fe in deposit against quantity of 0.1 M $FeSO_4$ solution in bath.

4. STRUCTURAL AND MORPHOLOGICAL ANALYSIS

Fig. 2 (a, b) shows the XRD patterns of as- deposited and annealed nickel ferrite thin film. Observed and standard interplaner spacing,'d' values confirmed formation of cubic structure of spinal nickel ferrite film formation. The XRD pattern of as deposited nickel ferrite film exhibited three peaks as (400), (311) , (422) and annealed films shows five diffraction peaks such as (111), (220), (400), (422) and (511), which confirmed after annealing crystallinity increases.

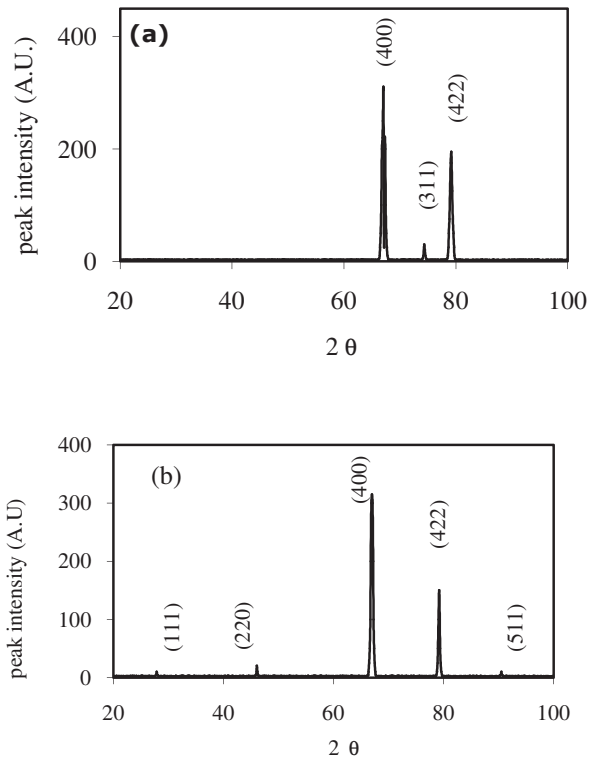

Fig. 2 (a, b) XRD patterns for (a) as deposited and (b) annealed nickel ferrite thin films.

Also the value of the grain size (calculated by well known Scherrer's formula) was increased from 34 nm to 48 nm after annealing. Observed and standard'd' values are comparable and are listed in table no. 2.

Table 2

Film	Std 'd' values Å	Obs 'd' values Å	Plane (hkl)
As deposited	2.078	2.074	400
	1.8	1.89	331
	1.78	1.795	422
	4.72	4.749	111
Annealed	2.923	2.92	220
	2.078	2.076	400
	1.78	1.798	422
	1.63	1.614	511

From SEM images [Fig. 3 (a, b)] it is observed that films shows good surface coverage, smooth morphology. Fig. 4(a, b) shows AFM images from these images it is clearly observed that the films are consisting of island like grains, which is the most considerable characteristics feature of nanocrystalline materials.

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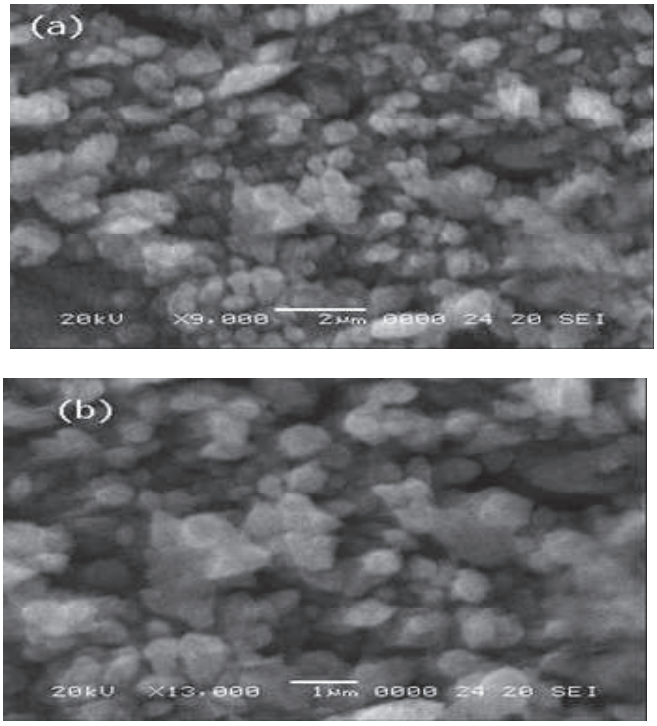

Fig. 3 (a, b) SEM images of (a) as deposited and (b) annealed nickel ferrite thin films.

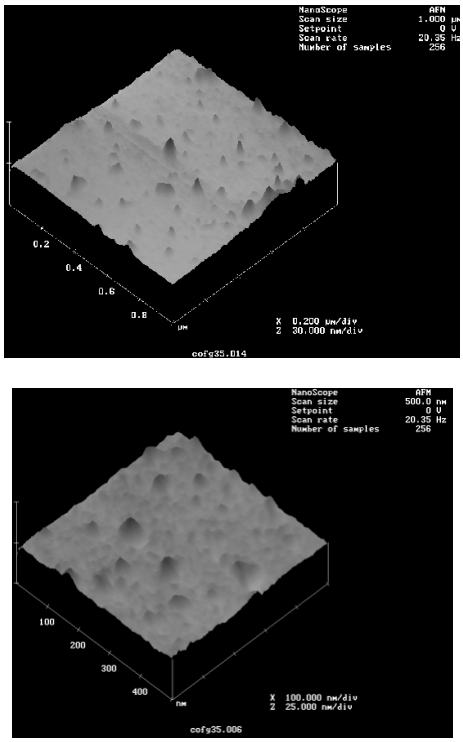

Fig. 4 (a, b) AFM images for as (a) deposited and (b) annealed nickel ferrite thin films.

5. MAGNETIC STUDIES

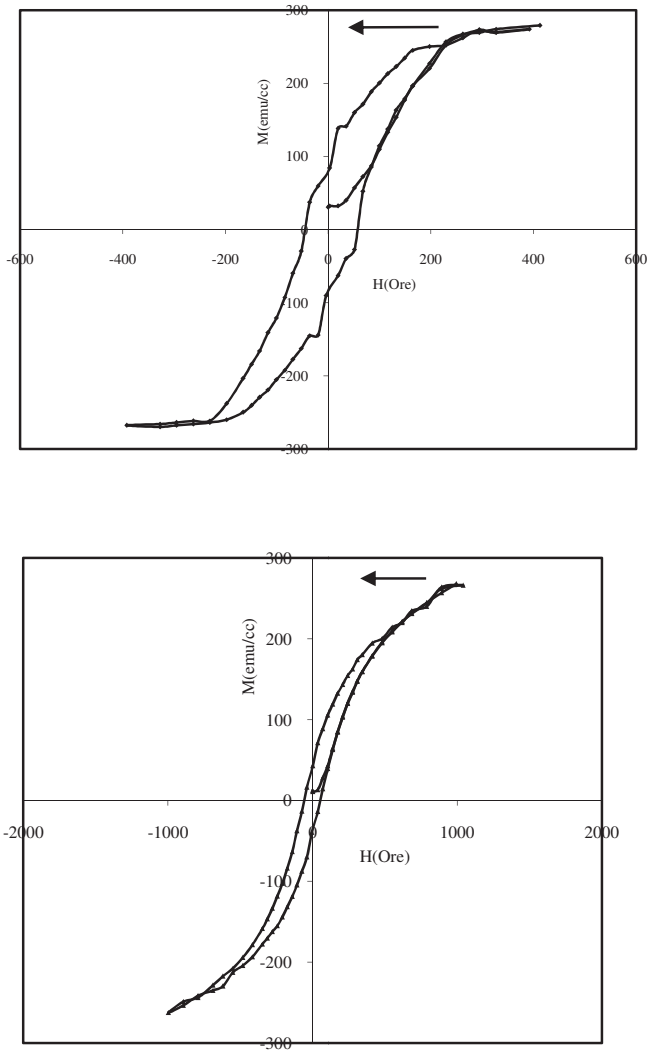

Fig. 5 (a, b) show M-H curve for nickel ferrite films.

The observed values of saturation magnetization and coercivity were 285 emu/cc and 0.08 KOe for annealed nickel ferrite films. The smaller value of saturation magnetization than that of bulk was due to nanocrystalline nature of nickel ferrite thin films.

6. ELECTROCHEMICAL PERFORMANCE: NICKEL FERRITE THIN FILMS

Figure 6 shows cyclic voltametric curves obtained for nickel ferrite thin films for (a) 50 and (b) 400 charge discharge cycles.

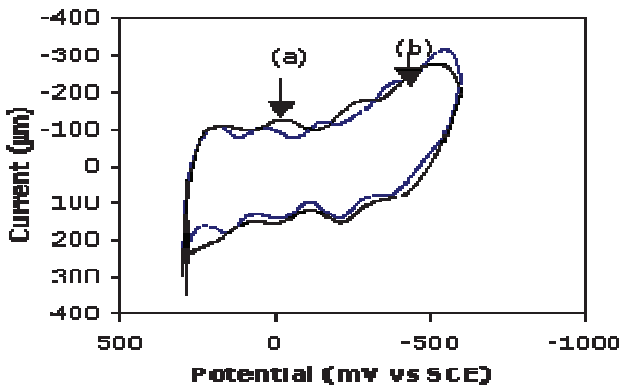

Fig. 6. (a,b)The CV scanned for nickel ferrite thin films at 100 mVS^{-1} scan rate in 5 N NaOH solution (a) 50 (b) 400 cycles.

The curve showed supercapacitive nature with electrochemical redox behaviour. Area under the curve 'b' is ~ 1.82 mC, which shows charge storing capacity of these electrodes. The current was decreased slightly with increase in number of cycles and was stable after 500 cycles. Thus stability of nickel ferrite thin film electrode was confirmed. The values of capacitance were calculated and are summarized in Table 3.

Table 3

Values observed	**Nickel ferrite**	
Number of cycles	50	400
Specific capacitance (Fg^{-1})	110	82.4
Interfacial capacitance (Fcm^2)	0.4	0.32

7. CONCLUSIONS

In a single step electrodeposition, nanocrystalline nickel ferrite thin film formation was made possible at room temperature. Non-aqueous bath avoided the problem of hydrogen evolution. Due to an alkaline bath, incorporation of oxygen in solid film was possible resulted into ferrite thin film formation. In conclusion, nickel ferrite thin film deposition at room temperature from alkaline non-aqueous bath resulted into good quality of deposits. Nickel ferrite thin films were cubic in crystal structure and uniformly distributed over the substrate surface with additional random porous particles. Due to nanocrystalline nature of film, smaller value of saturation magnetization (285 emu/cc) was observed than that of bulk nickel ferrite. Nickel ferrite thin films are promising material as an electrode for Supercapacitor. These films showed significant values of capacitance.

8. REFERENCES

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