

Super-Capacitive Properties of Nanocrystalline Copper Ferrite Thin Films Deposited by Environment Friendly Electrodeposition Method

M. R. Kale[†] and N. P. Tendolkar

Abstract: Copper ferrite thin films synthesized at room temperature. Atomic Absorption Spectroscopy (AAS) was used to study stoichiometry as CuFe₂. Alkaline bath and small heat treatment converts this CuFe₂ into CuFe₂O₄. Tetragonal type of crystal structure of copper 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 CuFe₂O₄ as an electrode for Super capacitor. This shows good value of specific and interfacial capacitance.

Keywords: Electro synthesis, Copper ferrite, XRD, SEM, AFM, Super capacitor.

1. Introduction

Copper ferrites have distinctive features such as phase transition from tetragonal to cubic due to the Jahn Teller distortion, electrical switching, change in semiconducting properties etc. [1-4]. Copper ferrites in thin film form, have applications in magnetic cores, optomagnetic devices, bubble memory devices, vertical recording devices [5-9]. Copper ferrites, in thin film form have not been studied intensively. Some reports are available on copper ferrite thin films prepared by physical methods [10-12].

An electrochemical route is a viable method to prepare the films at room temperature.

Sartale et al [13,14] have used electrochemical route for the preparation of copper ferrite thin films. But they have used the anodization step for oxygen incorporation. Instead of anodization, one can deposit oxide materials by cathodic electrodeposition from highly alkaline bath and by applying higher deposition potential to that of metal. Surface precipitation of hydroxides resulting from an increase in pH of solution adjacent to the cathode gives formation of oxides [15]. This electrochemical intercalation carried in air, at room temperature and in alkaline media gives rise to oxide formation [16-19]. Also by cathodic electrodeposition various oxide materials have deposited at room temperature [20-22].

This work presents single-step electrodeposition of copper ferrite (CuFe₂O₄) thin films at room temperature from alkaline solutions. These copper ferrite thin films are used to study structural, morphological and magnetic properties. Also supercapacitive performance is tested by using cyclic voltammetry technique.

2. Experimental

The 0.05 M CuSO₄, 1M FeSO₄ and 0.1 M citric acid solutions were prepared. 1 M NaOH was used to make bath alkaline. Bath composition was optimized [0.05M CuSO₄ (10cm³) + 0.1 M FeSO₄ (10cm³) + 0.1 M citric acid (10cm³)] by varying quantity of 0.1 M FeSO₄ solutions to obtain stoichiometry (CuFe₂) films confirmed from the atomic absorption spec-

troscopy study. The optimized deposition potential and time for copper ferrite thin films were - 0.50 V/s and 25 min, respectively. An d are listed in Table No. 1. Brown colored as-deposited copper 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 copper 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.

Preparative parameters	Range varied for preparative parameters	Optimized preparative parameters
Bath composition	0.1 M FeSO ₄ 2 - 20 cc	0.05 M CuSO ₄ (4 cc) + 0.1 M FeSO ₄ (16 cc) 0.1 M citric acid (15 cc) + 1 N NaOH (5 cc)
Deposition potential (V vs SCE)	-0.2 to -0.6	-0.50
Deposition time (min)	5-30	25

3. Results and discussion

Elemental Stoichiometry:

Fig 1 shows plot of atomic weight percentage of Fe in deposit against quantity of 0.1 M FeSO₄ solutions in bath of fixed quantity (20 cc). From Fig, it is observed that the films deposited by using 4 cc of 0.05 M CuSO₄ and 16 cc 0.1 M FeSO₄ solution contains Cu~ 33% and Fe~ 66% in the deposit.



Fig. 1 A plot of Fe in deposit against quantity of 0.1 M FeSO₄ solution in bath.

Structural and morphological analysis:

Fig. 2 (a, b) shows the XRD patterns of as-deposited and annealed copper ferrite thin film. Well-defined X-ray diffraction peaks were observed for both as deposited and annealed copper ferrite thin films. Observed and standard [23] inter planner spacings were comparable to each other and are listed in Table 2. After heat treatment, preferred orientation along (220) plane was observed and also (400) peak was emerged. The inter planer spacings for annealed copper ferrite thin film were shifted towards lower value than that for as deposited film and intensity of peaks was increased. It also suggested the increase in crystallinity of annealed copper ferrite thin film. Copper ferrite thin film with tetragonal crystal structure was obtained at room temperature and after heat treatment film showed properties comparable to that of bulk material. Tetragonality in copper ferrite thin film was observed due to Jahn Teller distortion of Cu²⁺ ion at octahedral site.

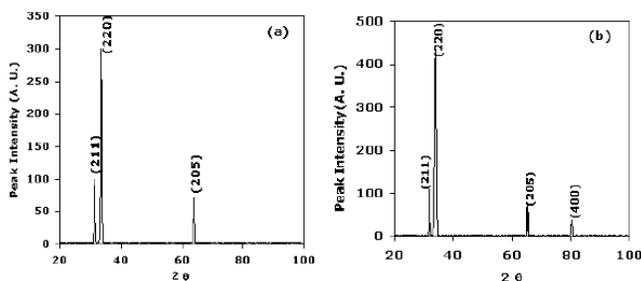


Fig. 2 (a, b) XRD patterns for (a) as deposited and (b) annealed copper ferrite thin films.

The calculated values of axial (c/a) ratios for as deposited and annealed copper ferrite film are listed in Table 2. It was observed that, after heat treatment, c/a ratio was increased, which may be due to the increase in tetragonal distortion and strain in the film. Slow scan of intense peak was recorded as full width at half maxima (for grain size calculation. Using Scherrer's formula, grain size was calculated and were 65 nm and 91 nm for as de-positd and annealed copper ferrite thin film, respectively. Grain size ranges between 60-95 nm, which confirmed the nanocrystalline of copper ferrite thin films. After heat treatment, increase in grain size was observed due to the grain growth.

Film	'd' values		Plane (hkl)	c/a ratio	Grain size (nm)
	Std (Å)	Obs (Å)			
As deposited film	2.50	2.50	(211)	1.432	65
	2.07	2.06	(220)		
	1.65	1.64	(104)		
Annealed film	2.50	2.51	(211)	1.523	91
	2.07	2.06	(220)		
	1.65	1.64	(104)		
	1.46	1.46	(400)		

Fig. 3 (a) and (b) shows scanning electron micrographs for as deposited and annealed. From Fig, it is observed that films are well covered and uniform on the substrate with mud like structure. After heat treatment compact film formation and grains with granular shape connecting with each other were observed. For as deposited films SEM did not show separate grains so calculation of grain size was impossible. But for heat-treated films grain size was estimated to be 80 nm. The SEM confirmed the nanocrystalline film formation.



Fig 3 (a,b) shows SEM Images of as-deposited and annealed

copper ferrite thin films.

Fig 4 (a,b) shows three-dimensional views for as deposited and annealed films. From these AMF images, it is observed that arrangement of grains was in regular manner onto the substrate. Grains were observed with full coverage onto the substrate. For annealed films, size of grains was increased.

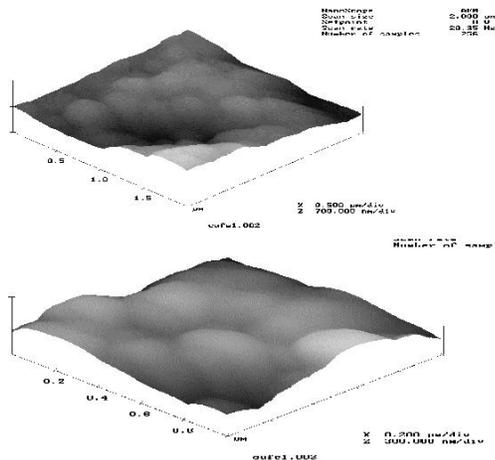


Fig 4 (a,b) shows three dimensional AFM Images of as-deposited and annealed copper ferrite thin films.

Magnetic studies

Fig. 5 (a) and (b) shows plots of magnetization (M) against magnetic field (H) i.e. M-H curve for as deposited and annealed copper ferrite thin films, respectively. The value of saturation magnetization (~280 emu/cc), residual magnetization (~40 emu/cc) and coer-civity (~0.02 Koe) were found to be low as compared to bulk value [24]. Fig (b) shows M-H curve for annealed copper ferrite film. The value of saturation magnetization was 292 emu/cc, which is comparable to the bulk value [24].

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

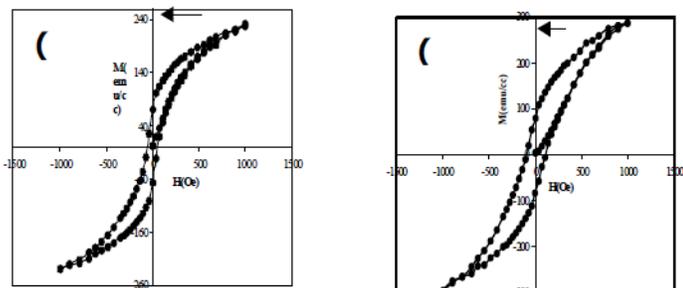


Figure 6 shows cyclic voltametric curves obtained for copper ferrite thin films for (a) 50 (b) 100, (c) 200 and (d) 400 charge discharge cycles.

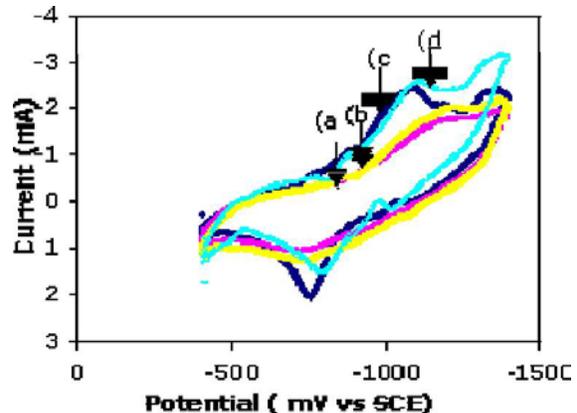


Fig. 6 The CV scanned for copper ferrite thin films at 100 mV^s⁻¹ scan rate in 5 N NaOH solution (a) 50 (b) 100, (c) 200 and (d) 400 cycles.

The curve showed supercapacitive nature with electrochemical redox behaviour. Area un-der the curve 'd' 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 copper ferrite thin film electrode was confirmed. The values of capacitance were calculated and are summarized in Table 3.

Table 3

Value obtained		No of cycles			
		50	100	200	400
Specific capacitance (Fg ⁻¹)		72	63	60	57
Interfacial capacitance (F cm ²) x10 ⁻³		21	25	24	21

Reference

- [1] T. Tanaka, M. Chiba, H. Okimura and Y. Koizumi, J. Phys., IV France 7 (1997) C1 1501
- [2] Ph. Talihadas, C. Villet, A. Ronsset, G. V. Kulkarni, K. R. Kannan, C. N. Rao, and M. Lenglet, J. Solid State Chem., 144 (1988) 56.
- [3] H. A. Jahn and T. Teller, Proc R. Soc., London 161 (1937) 220.
- [4] R. A. Mccurrie, "Ferromagnetic Materials, Structure and Properties" (Academic press, London) (1994).
- [5] F. Zaquine, H. Benz, and T. C. Maye, J. Appl. Phys., 64 (1988) 23
- [6] B. C. Glass, F. S. Sterns, and L. R. Adkins, "Proc. International Conference on Ferrites", Japan, (1980).
- [7] J. L. Dorman (Ed), "Magnetic Properties of Fine Particles", Florani, North Holland, Amstradam (1994).
- [8] F. Bodkar, S. Mourap, and S. Linderorth, Phys. Rev. Lett., 72 (1994) 282.
- [9] C. W. Chen, "Magnetism and Metallurgy of Soft Magnetic Materials", Dover, New York (1963).
- [10] M. Desai, S. Prasad, N. Venkataramani, I. Samjdar, A. K. Ni-

- gam and R. Krishnan, *J. Magn. Magn. Mater.*, 246 (2002) 266.
- [11] M. Desai, S. Prasad, N. Venkataramani, I. Samjdar, A. K. Nigam and R. Krishnan, *J. Appl., Phys.*, 91 (2002) 2220.
- [12] J. Dash, N. Venkataramani, S. Prasad, R. Krishnan, S. N. Shringi, P. Kishnan, N. Kumar, S. D. Kulkarni and S. K. Date, *J. Magn Soc. Jpn.*, 22 (1998) 176.
- [13] S. D. Sartale and C. D. Lokhande, *Mater. Chem. Phys.*, 70 (2001) 274.
- [14] S. D. Sartale, C. D. Lokhande and M. Muller, *Mater. Chem. Phys.*, 80 (2003) 120.
- [15] A. Jacob, D. Bahrut, A. Wattiaux, M. Deville, J. Grenier, M. Pouchard and J. Etourneau, *J. Mater. Chem.*, 10 (2000) 829.

IJSER