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Magnetic studies on one-step chemically synthesized nickel ferrite thin films

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Abstract

Nickel ferrite thin films were synthesized at room temperature using one-step electrodeposition solution processing. Reaction kinetics was also proposed. An effect of air baking on the structural, surface morphological and magnetic properties was investigated. As-deposited nickel ferrite thin films were cubic in crystal structure. Calculated grain size after annealing was increased from 30 to 48 nm in addition to formation of rough surface morphology. Due to decrease in defect levels after air baking the annealed nickel ferrite thin film showed saturation magnetization of 268 emu/cc, higher than non-annealed (230 emu/cc), when used in magnetic studies.

Keywords: C. Magnetic properties; Electrosynthesis; Nickel ferrite; Thin films; Structural elucidation

1. Introduction

Ferrite thin films with spinel structure are potentially interesting and scientifically promising for high frequency devices, where low conductivity and high saturation magnetization are important aspects [1]. The physical properties of spinel cubic metal iron oxide are of great interest due to its wide implication in magnetic recording media, microwave devices, computer hard disc read/write heads and micro-electromechanical systems and sensors [2,3]. Among all the ferrites, nickel ferrite ($NiFe_2O_4$) is a ferromagnetic material used in thin film form efficiently for magnetic cores, opto-magnetic devices, bubble memory devices and vertical recording magnetic materials applications [4]. Apart from technological importance in electronic and magnetic industries, nickel ferrite has been used as highly reproducible material for humidity and gas sensors [5].

Several methods have already been used for the deposition of nickel ferrite thin films, which include pulse laser deposition [6], sputtering [7], dip coating process [8], non-aqueous sol–gel [9] etc. However, these methods prefer sophisticated instrumentations in addition to substrate heating during and/or after deposition etc.

Among all these methods, previously our group [10,11] has reported simple electrochemical route for the preparation of $NiFe_2O_4$ thin films from aqueous and non-aqueous mediums in two-steps, i.e., the formation of alloy film with appropriate composition onto conducting substrates followed by its oxidization at high temperature. In continuation of our research on nickel ferrite thin films [10,11], in this paper, we synthesized nickel ferrite thin films at room temperature using one-step electrodeposition method from an aqueous bath by optimizing various preparative parameters including the bath composition, deposition potential and deposition time to achieve desired properties. Films were baked in air at 773 K for 4 h. Further, structural, surface morphological and magnetic properties of as-deposited and annealed nickel ferrite thin films were studied using various techniques.

2. Experimental details

For the deposition of nickel ferrite thin films, standard three-electrode electrodeposition method was used. Nickel sulphate ($NiSO_4$) and iron sulphate ($FeSO_4$) precursors were used as nickel and iron metal ion sources, respectively. The 0.1 M citric acid was used as complexing agent and 1 M NaOH was used for increasing the pH of resultant solution. Preparation of nickel

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ferrite thin films was carried out at room temperature from unstirred electrolyte bath. Solutions of nickel and iron sulphates were mixed in various proportions and the bath composition of 0.1 M $NiSO_4$ (7 cc) + 0.1 M $FeSO_4$ (13 cc) + 0.1 M citric acid (10 cc) + 1 M NaOH (8 cc) was optimized. In presence of standard calomel electrode (SCE) reference electrode, the deposition potential of −0.68 V/SCE was chronopotentiometrically applied between the working and the counter electrodes. A deposition was carried out for 25 min to obtain uniform and adherent nickel ferrite thin films onto stainless steel substrate.

As-deposited and annealed nickel ferrite thin films were characterized for their structural elucidation using X-ray diffractometer (Reguka). Films were scanned in-between 20° and 100°. For surface morphological study, scanning electron microscope (SEM) was used. Vibrating sample magnetometer (VSM) technique was used for knowing magnetic behavior by applying magnetic field in the plane of films.

3. Results and discussion

3.1. Optimization of bath composition, one-step film formation and growth mechanism

Nickel ferrite thin films were deposited onto pre-electroformed stainless steel substrate from the bath of mixture 0.1 M $NiSO_4$ and 0.1 M $FeSO_4$ in various volume ratios with a total quantity of 20 cc solution. In Fig. 1 the variation of iron content obtained using atomic absorption spectroscopy in deposited film against quantity of 0.1 M $FeSO_4$ is presented. The nickel ferrite film so deposited from 0.1 M $NiSO_4$ (7 cc) and 0.1 M $FeSO_4$ (13 cc) showed ∼33% and ∼66% nickel and iron contents, respectively. Thus, for further deposition of nickel ferrite thin films this optimized bath composition was considered.

The current transient obtained during the nickel ferrite thin film deposition under applied potential of –0.68 V vs. SCE was presented in Fig. 2. Presence of three different regions in current transient confirmed the growth mechanism of nickel ferrite film. The rapid surge and exponential decay of the current observed in region I is due to double-layer charging. A continuous decay current observed in region II, corresponds to formation of nickel iron oxide clusters [12] and after that, the longer current decrease in region III is the characteristic of diffusive controlled growth [10]. Thus, (a) cluster formation after double layer charging, (b) critical nuclei formation, and (c) further diffusive controlled growth of the oxide nuclei, could be the responsible steps for the nucleation formation and subsequent growth of nickel ferrite thin film. In short, reaction mechanism of one-step electrodeposited nickel ferrite thin films can be presented as;

$$Ni^{2+} + 2Fe^{3+} + 8OH^- + 8e^- \rightarrow NiFe_2O_4 + 4H_2O \quad (1)$$

Nickel ferrite thin films were deposited from the optimized bath composition by applying –0.68 V vs. SCE deposition potential for various time periods. The variation of nickel ferrite film thickness with deposition time was plotted in Fig. 3. For the deposition time of 25 m in, maximum film thickness of 0.72 μm was observed and after that decrease in film thickness is due to porous film formation.

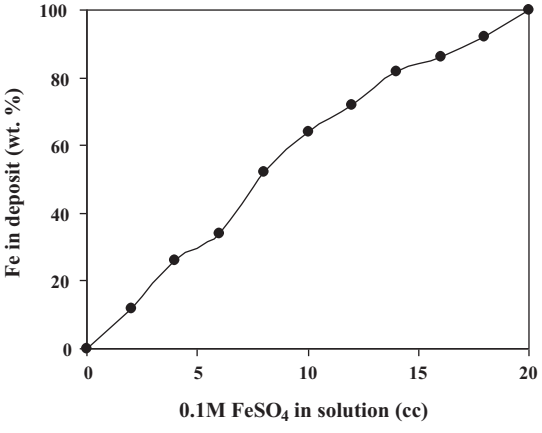

Fig. 1. The variation of Fe content in deposit with the quantity of 0.1 M $FeSO_4$ solution.

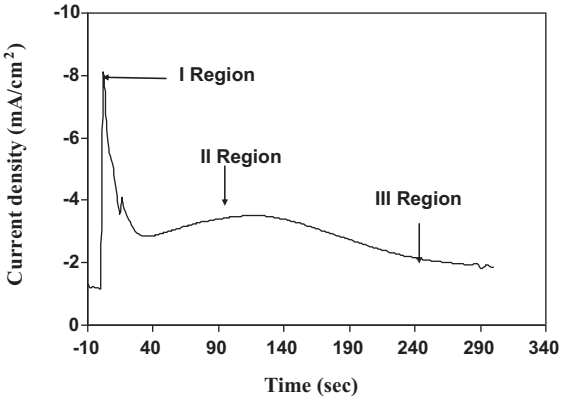

Fig. 2. The variation of deposition current as a function of deposition time during the deposition of nickel ferrite film onto stainless steel substrate.

3.2. Structural elucidation and surface morphological studies

For the structural elucidation of nickel ferrite, X-ray diffraction pattern was considered. The X-ray diffraction

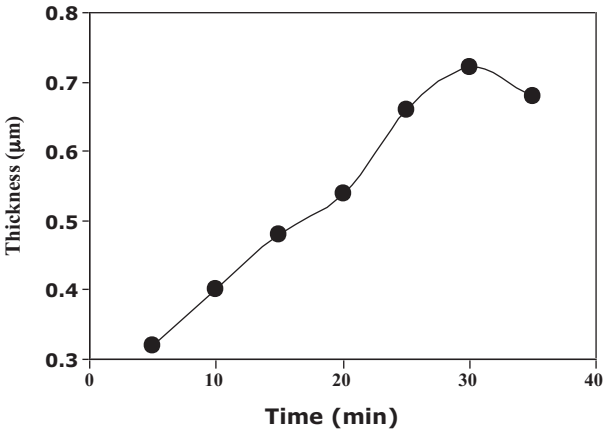

Fig. 3. A plot of nickel ferrite film thickness vs. deposition time.

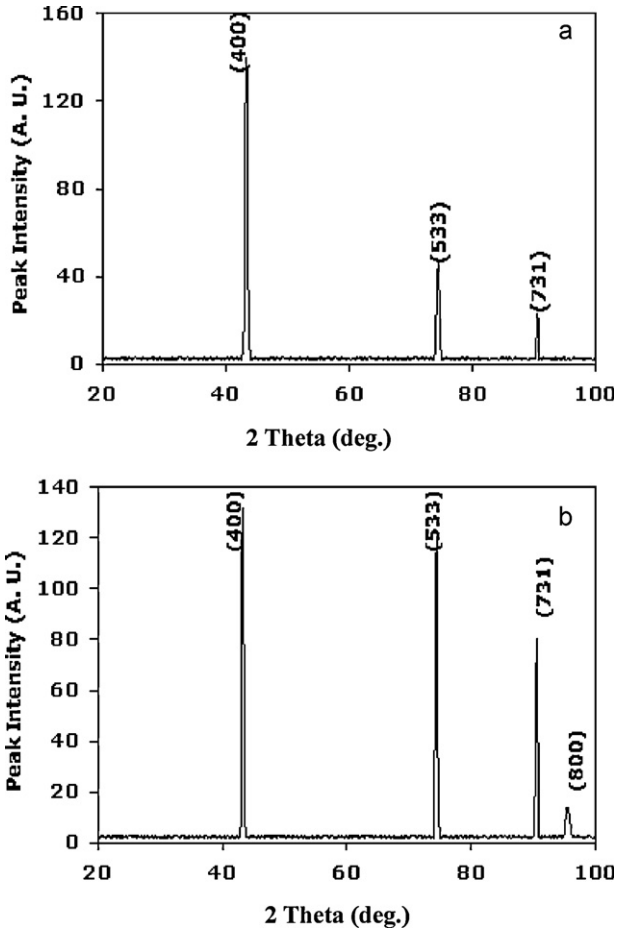

Fig. 4. The XRD patterns of (a) as-deposited and (b) annealed nickel ferrite thin films.

patterns of as-deposited (a) and annealed (b) nickel ferrite thin films were presented in Fig. 4. The interplanar spacing (d) values observed from the patterns were comparable to the standard [JCPDS card file No. 74-2081] confirming the formation of cubic nickel ferrite. Due to annealing, the peak intensities of (5 3 3) and (7 3 1) planes were increased with newly emerged (8 0 0) plane. This observation led to make conclusion that metallic Ni and Fe would have completely been oxidized at room temperature as mentioned in the reaction mechanism one-step formation of nickel ferrite structure. For bulk nickel ferrite (3 1 1) reflection plane is the most intense peak, but due to nanocrystallinity of present film, preferred orientation along (4 0 0) reflection plane was observed, which also has been previously reported [13].

The lattice constant (a) of as-deposited and annealed nickel ferrite films was calculated by using cubic crystal structure relation,

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \tag{2}$$

Values of lattice parameter 'a' were 8.324 and 8.341 Å for as-deposited and annealed nickel ferrite thin films, respectively. Increase in the strain in the film after annealing, in general, is responsible for lattice parameter change. The 30 nm grain size of as-deposited nickel ferrite was increased to 48 nm after air baking, consistent to lattice parameter change.

In Fig. 5(a and b) the SEM images of as-deposited and annealed nickel ferrite thin films deposited onto stainless steel substrate were placed. Randomly grown, dissimilar oval-shaped crystallites were observed onto the surface substrate. Under a close view, spherically grown nanoparticles were also noticed. After annealing there was no significant change in surface appearance except surface overgrowth.

3.3. M–H curves

Nanocrystalline thin films are usually characterized by a lack of long range atomic order, similar to that of the liquid state. The lack of crystallinity causes nanocrystalline thin films to have a very low magnetic anisotropy. The magnetization against magnetic field (M–H) hysteresis measurements were carried out at room temperature for nickel ferrite thin films for knowing induced magnetization. To study the magnetic properties of magnetic material, VSM is the most convenient technique. The plots of M–H for as-deposited and annealed nickel ferrite thin films are presented in Fig. 6(a and b). The M–H curve for as-deposited nickel ferrite film was not well saturated. The 230 emu/cc value of saturation magnetization

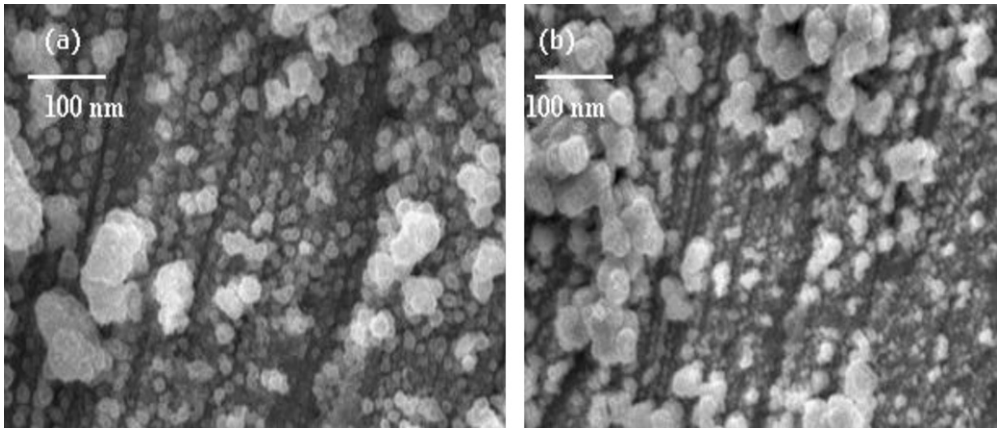

Fig. 5. The SEM images of (a) as-deposited and (b) annealed nickel ferrite thin films.

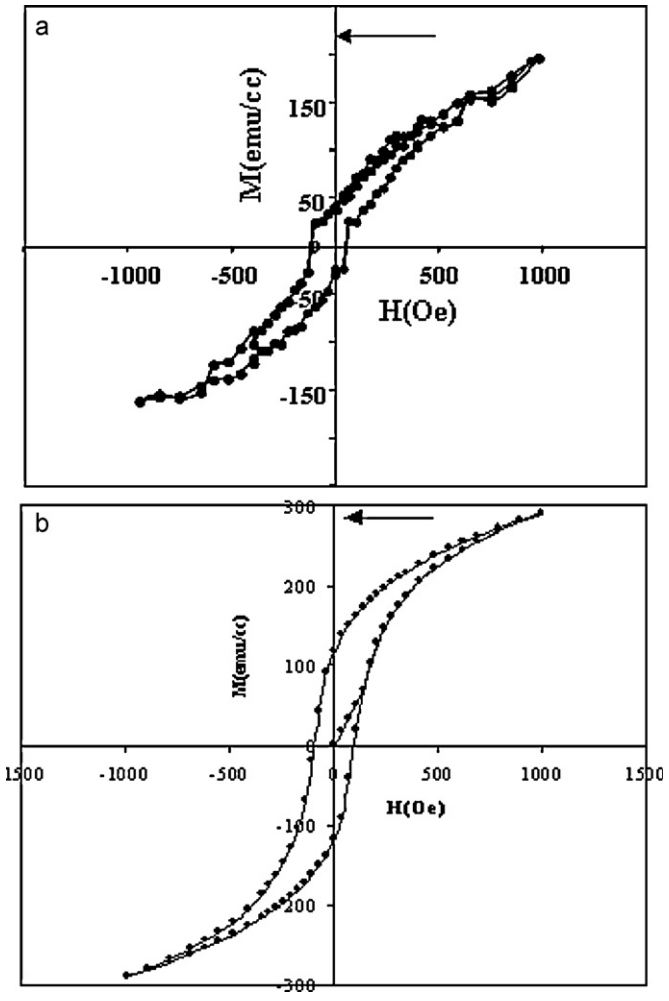

Fig. 6. The *M–H* curves of (a) as-deposited and (b) annealed nickel ferrite thin films.

was increased to 268 emu/cc after annealing. It is commonly accepted that with increase in grain size after annealing defect and impurity levels decreases significantly which, indirectly, changes the cation distribution and lead to an increase the saturation magnetization [14].

4. Conclusions

We here have reported direct one-step nickel ferrite thin film synthesis using a single-step electrodeposition method at room temperature and studied the effect of annealing on structural, surface morphological and magnetic properties. Increase in grain size from 30 to 48 nm with rough surface was confirmed after annealing. Increase in saturation magnetization to 268 emu/cc from 230 emu/cc is due to the decrease in defect and impurity levels.

Acknowledgements

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References

[1] S.H. Yu, M. Yoshimura, Direct fabrication of ferrite MFe_2O_4/Fe (M=Zn, Mg) composite thin films by soft solution-processing, Chem. Mater. 12 (2000) 3805–13805.
[2] F. Bodker, S. Morup, S. Linderoth, Surface effects in metallic iron nanoparticles, Phys. Rev. Lett. 72 (1994) 282–285.
[3] C.V. Gopal Reddy, S.V. Manorama, V.J. Rao, Semiconducting gas sensor for chlorine based on inverse spinel nickel ferrite, Sens. Actuators B55 (1999) 90–95.
[4] W.A. Roshen, Effect of finite thickness of magnetic substrate on planar inductors, IEEE Trans. Magn. 26 (1990) 270–275.
[5] N. Rezlescu, N. Iftimie, E. Rezlescu, C. Doroftei, P.D. Popa, Semiconducting gas sensor for acetone based on the fine grained nickel ferrite, Sens. Actuators B: Chem. 114 (2006) 427–432.
[6] N. Keller, M. Guyot, A. Das, M. Porte, R. Krishnan, Study of the interdiffusion at the interfaces of NiO/αFe_2O_3 multilayers prepared by pulsed laser deposition, Solid State Commun. 105 (1998) 333–337.
[7] A.J. Stirling, W.D. Westwood, Reactive sputtering of nickel, iron, and nickel ferrite, Thin Solid Films 8 (1971) 199–205.
[8] S.D. Sathaye, K.R. Patil, S.D. Kulkarni, P.P. Bakre, S.D. Pradhan, B.D. Sarwade, S.N. Shintre, Modification of spin coating method and its application to grow thin films of cobalt ferrite, J. Mater. Sci. 38 (2003) 29–33.
[9] D.M. Scheich, Y. Zhung, Preparation of some metal ferrite MFe_2O_4 thin films through a nonaqueous sol method, Mater. Res. Bull. 30 (1995) 447–452.
[10] S.D. Sartale, C.D. Lokhande, Room temperature preparation of $NiFe_2O_4$ thin films by electrochemical route, Ind. J. Eng. Mater. Sci. 7 (2000) 404–410.
[11] S.D. Sartale, C.D. Lokhande, M. Gersig, V. Ganesan, Novel electrochemical process for the deposition of nanocrystalline $NiFe_2O_4$ thin films, J. Phys. Condens. Mater. 15 (2004) 773–784.
[12] G. Oskam, P.M. Vereecken, P.C. Searson, Electrochemical deposition of copper on n-Si/TiN, J. Electrochem. Soc. 146 (1999) 1436–1441.
[13] N. Gupta, S.C. Kashyap, D.C. Dube, Dielectric and magnetic properties of citrate-route-processed Li–Co spinel ferrites, Phys. Status Solidi A 204 (2007) 2441–2452.
[14] T. Tsuchiya, H. Yamashiro, T. Sei, T. Inamura, Preparation of spinel-type ferrite thin films by the dip-coating process and their magnetic properties, Chem. Mater. Sci. Eng. 27 (1992) 3645–3650.