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Fabrication of Spinel Ferrite Film by Chemical Method: Its Structural Investigation

KEYWORDS: Ferrite thin film, Chemical method, Spinel ferrite

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ABSTRACT *The nickel zinc ferrite (NZF), $Ni_xZn_{(1-x)}Fe_2O_4$, films were fabricated using modified chemical deposition method (M-CDM) on to glass substrate by optimizing the preparative parameters such as deposition temperature, pH, concentrations of precursor solution, deposition cycles etc. The structural details of the NZF films were evaluated from different characterization techniques. XRD pattern shows that the NZF films were oriented towards the (311) plane confirming the spinel phase. The FTIR shows absorption peaks around 600 cm^{-1} which are typical for cubic spinel structure. The porous morphology is confirmed by SEM study. The TGA was carried out to confirm the stable oxide formation which takes place at 600 °C. The decrease in the static water contact angle indicates the increase in the porosity of the films. Possible applications of the NZF thin film is projected.*

1. Introduction

In the recent years, the synthesis of nanocrystalline nickel zinc ferrite (NZF), $Ni_xZn_{(1-x)}Fe_2O_4$, thin films has become focal point of research and developmental activities in the area of nano materials owing to the quest for their technological applications [1-4]. The NZF thin films acts as an oxide semiconductors. Recently, semiconducting oxides have received significant attention as sensor materials because of their remarkable electrical properties sensitive to oxidative or reductive type of gases [5-9]. The surface of a semiconductor is sensitive to the composition of surrounding atmosphere. Considerable research has been carried out on the development of novel thin films for various applications such as supercapacitor and gas sensors based on semiconducting metal oxides.

At present, bulk NZF components employed in discrete devices at microwave frequencies are not compatible with the rapid developments of electronic applications towards miniaturization, high density, integration and multifunction. Thus, more attention has been attracted to solve these difficulties in performing the required miniaturization for complex devices. The NZF thin films play an important role in facilitating the design and fabrication of devices such as micro-inductors, micro-transformers, and microwave non reciprocal devices [10]. The ferrite thin films incorporated into magnetic integrated circuits are expected to replace the current surface mounting modules in the near future. The NZF thin films have been prepared using various physical as well as chemical deposition methods (CDM).

There are several reports on synthesis of ferrite thin films by chemical deposition method (CDM) [11-13]. But, CDM suffers from the disadvantage that the unnecessary formation of precipitate takes place in the bath and thus the loss of material. In order to avoid such unnecessary precipitation, a CDM is modified and known as modified chemical deposition method (M-CDM). In this modification, thin films are obtained by immersing substrate into separately placed cationic and anionic precursors. The adsorption of ions on the surface of other substances is the fundamental concept of the M-CDM. The growth of thin film in the M-CDM occurred via layer by layer assembly of ions in the precursor solution. Besides the obvious advantage of M-CDM, one another aspect of this method deals with the different morphology. As one of the goal of this research was the preparation of NZF thin films for gas sensing and this applications strongly depends on the morphology. The M-CDM allows the option to prepare NZF thin films with different morphologies than CDM, which is suitable for gas sensing applications. Niesen et al [14] prepared ceramic thin films from aqueous solutions and Pathan et al [15] studied the deposition of metal chalcogenide thin films by the modification of chemical bath deposition (termed as 'SILAR') method. Above two literatures gives the key about the possibility of the deposition of ternary metal oxide ($Ni_xZn_{(1-x)}Fe_2O_4$) using the M-CDM. The M-CDM was adopted for the deposition of binary metal oxides like, CuO [16], ZnO, [17], MnO_2 [18], $FeOOH/Fe_2O_3$ [19], NiO [20], SnO_2 [21] etc.

Among the semiconducting metal oxides the NZF films show high resistivity, high permeability and low loss characteristics. The resistivity of NZF films is in the order of 10^7 to 10^9 Ω/cm and large excitation binding energy. These characteristics leads to the possible application of NZF films for gas sensing.

The present study we report the preparation of $Ni_xZn_{(1-x)}Fe_2O_4$ films by M-CDM. The method is based on using combined aqueous alkaline nickel (II), zinc (II) and iron (II) chlorides as a cationic precursor and double distilled water as a rinsing solution. However, similar to CDM, due to aqueous alkaline nature of the deposition bath, formation of hydroxide is unavoidable, therefore, in present work, we report the annealing of the NZF films to remove hydroxides. Good quality films are obtained from M-CDM by optimizing preparative parameters, such as deposition temperature, concentration of precursor solution, pH of the bath, adsorption and reaction periods, numbers of deposition cycles etc. The films were characterized for their structural, surface morphological and electrical properties using XRD, FTIR, SEM, TGA etc.

2. Experimental work

2.1 Experimental setup of modified chemical deposition method (M-CDM)

Fig. 1 shows the schematic experimental set-up used for the deposition of $Ni_xZn_{(1-x)}Fe_2O_4$ thin films. The M-CDM setup consists of two containers for cationinc and anionic precursors, fixed in a alluminium vessel as water bath equipped with magnetic stirrer and temperature control in order to maintain the desired temperature. The substrates were alternately immersed in beakers containing the precursor solutions.

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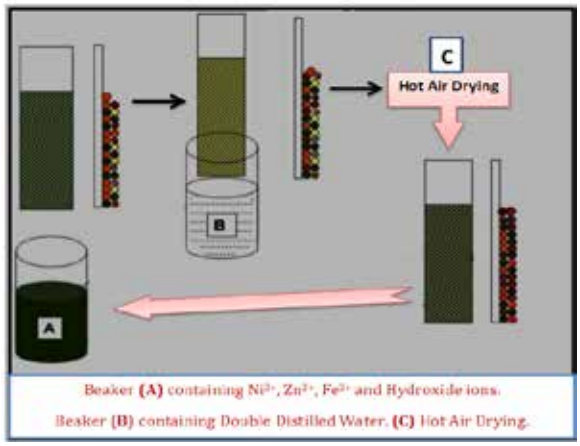

Fig.1 Schematic diagram of M-CDM set-up

The temperature was maintained at 50 - 60 ˚C using the Selec DC-204 temperature controller till the deposition was completed. The reaction vessel of borosilicate glass beaker was used for the deposition of NZF thin films. Substrate cleaning plays an important role in the M-CDM deposition of thin films, because contaminated surface provides nucleation sites facilitating growth resulting into non-uniform films with different orientation and impurities. The glass micro slides used as the substrates were treated with chromic acid followed by washing with double distilled water and then ultrasonically cleaned and lastly rinsed with AR grade acetone.

2.2 Nickel zinc ferrite thin film formation

All the chemicals as $NiCl_2 \cdot 6H_2O$, $ZnCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and NH_3 (29%) used were of sd fine make. The solutions were prepared in double distilled water.

The deposition of NZF thin films was done on micro glass slides. Two-beaker system (Fig.1) was used for the deposition onto the glass substrate by alternate immersion of substrate in cationic precursor and anionic precursor. The cationic precursor contains 0.1 M nickel chloride solution for Ni^{2+}, 0.1 M zinc chloride solution for $Zn^{2+}$and 0.2 M ferrous chloride for Fe^{2+}. The aqueous ammonia solution (29%) was used to adjust the alkaline pH of cationic precursor, it also acts as complexing agent. First, the ultrasonically cleaned glass substrate was immersed in cationic precursor for 30 seconds termed as adsorption period, so as to get nickel, zinc and iron hydroxides adsorbed onto the substrate. Double distilled water was used as anionic precursor maintained at 300 K. Then the substrate was rinsed with cationic precursor for 30 seconds termed as reaction period. These thin films were dried by hot air after each cycle. These thin films were then air annealed at 450 ˚C for 6 hours to form NZF thin film with cubic spinel phase by removing any hydroxide content.

NZF thin films, $Ni_xZn_{(1-x)}Fe_2O_4$ (where x is 0.1, 0.3, 0.5, 0.7 and 0.9), of different composition were prepared, as MCDM-19 ($Ni_{0.1}Zn_{0.9}Fe_2O_4$), MCDM-37 ($Ni_{0.3}Zn_{0.7}Fe_2O_4$), MCDM-55 ($Ni_{0.5}Zn_{0.5}Fe_2O_4$), MCDM-73($Ni_{0.7}Zn_{0.3}Fe_2O_4$), MCDM-91($Ni_{0.9}Zn_{0.1}Fe_2O_4$). All the preparative parameters for the NZF thin films of various compositions are listed in Table 1.

Table 1 Preparative parameters of NZF thin films

Compositions of thin films	pH	Bath temperature (˚C)	Deposition cycles	Adsorption and reaction period (sec)
$Ni_{0.1}Zn_{0.9}Fe_2O_4$	9.70	58	52	30
$Ni_{0.3}Zn_{0.7}Fe_2O_4$	9.60	55	50	30
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	9.45	52	45	30
$Ni_{0.7}Zn_{0.3}Fe_2O_4$	9.15	52	40	30
$Ni_{0.9}Zn_{0.1}Fe_2O_4$	8.90	50	40	30

The formation of NZF films passes through two stages, adsorption and reaction period. First the nickel, zinc and iron hydroxides get adsorbed onto the cleaned stainless steel substrate. During reaction period the oxygen ions reacts with pre-adsorbed hydroxides on the glass substrate and also helps to remove loosely binded hydroxides species. These thin films were dried by hot air after each cycle, which results into oxidation of some of the Fe^{+2} to Fe^{+3} along with that, iron oxyhydroxide (geothite) also formed as required to form NZF [22]. Hot air drying improved adherence of the film. This completes one deposition cycle of NZF thin films by M-CDM. Such types of multiple cycles were carried out. Finally, films were air annealed at 450 ˚C, to form pure NZF thin films with cubic spinel phase by converting hydroxide content [23]. Changing the number of deposition cycles thickness of the film was controlled.

3. Characterization of NZF thin films

The application of the thin film depends upon the various structural features of the material produced. Thus, to understand the structural details the characterization of NZF thin films prepared by M-CDM was carried out using various techniques.

3.1 Thickness measurement

Thickness is third dimension of the thin film, which is negligible as compared to other two dimensions (i.e. length and breadth), which modifies the properties of the films due to surface phenomena. Depending upon deposition cycles, films of thickness typically between 295 to 1610 nm were obtained. The terminal thickness obtained was about 1610 nm. At initial stage the rate of deposition is high up to 50 deposition cycle and then rate of deposition is reduced.

3.2 X-ray diffraction (XRD)

X-ray diffraction technique was used to investigate the structural identification, lattice parameters determination, phase and crystallite orientation of the material.

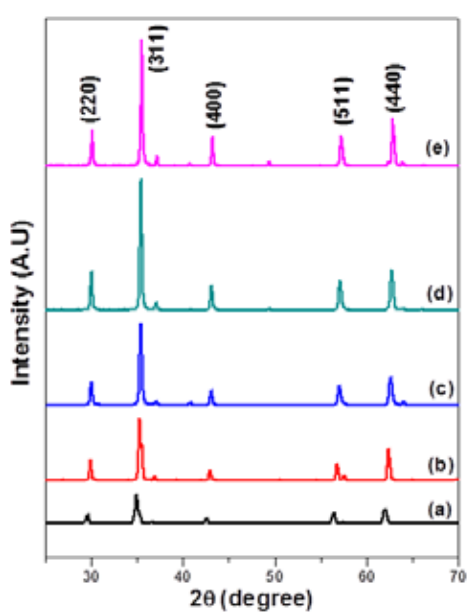

Fig. 2 X-ray diffraction patterns of NZF thin films

The X-ray diffraction pattern of NZF thin films annealed at 450 ⁰C for 6 hours with different composition named as M-CDM19, M-CDM37, M-CDM55, M-CDM73 and M-CDM91 is shown in Fig. 2 (a to e) respectively. The sharp peaks indicate the well crystallized nature of ferrite. All XRD patterns ori-

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ented with high intense (311) plane which is the characteristic peak of the spinel phase of NZF thin films. Other orientations corresponding to (220), (400), (511) and (440) planes present with relatively lower intensities compared to that of (311) plane are in best agreement with the cubic spinel (JCPDS card no: 08-0234). This confirms that nickel zinc ferrite phase has been formed.

Table 2 shows the values of crystallite size evaluated using Debye Scherrer's formula. Film M-CDM37 has 21 nm crystallite size, which is smaller as compared to other composition thin films.

Table 2 Crystallite size of NZF thin films

Sr. No	Thin Film	Crystallite Size (nm)
1	M-CDM19	57
2	M-CDM37	21
3	M-CDM55	45
4	M-CDM73	60
5	M-CDM91	52

The values of lattice parameter of the NZF thin films were also calculated It is observed that the value of the lattice parameter goes on decreasing from 8.4983 to 8.3801 Å as the increase in the nickel content [16, 17].

3.3. FT-IR Spectroscopy

FTIR spectroscopy is used to detect the composition of the solid state reaction and to study metal ion distribution in the material. The FT-IR spectrum of annealed M-CDM19, M-CDM37, M-CDM55, M-CDM73 and M-CDM91 were taken in KBr, with sample to KBr ratio 1:300. In case of ferrite, two bands are observed around 400 cm^{-1} and 600 cm^{-1}. There are reported values of octahedral band at lower frequencies 400 cm^{-1} due to vibration of M-O group and tetrahedral frequencies at around 650 cm^{-1} [18,19]. All composition films shows intense tetrahedral peak and weak octahedral peak. The nitrogen from unconsumed reagent form N-O bond observed nearly at 1630 cm^{-1} in each thin film. During the formation of inverse spinel, octahedral sites are occupied by trivalent Fe^{+3} and divalent Ni^{+2} ions. The presence of Fe^{+3} ions at tetrahedral site is responsible for splitting of absorption band.

3.4. Scanning electron microscope (SEM)

The surface morphology study of annealed NZF thin films was carried out by scanning electron microscope (SEM). The SEM images (Fig 3) of NZF thin films shows large specific surface area useful for gas sensing with high response.

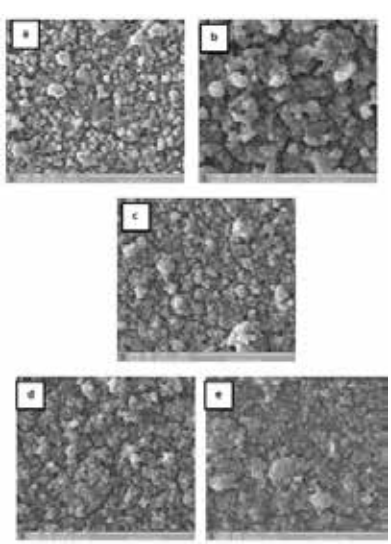

Fig. 3 Scanning electron micrographs a-e of NZF thin films of M-CDM19, M-CDM37, M-CDM55, M-CDM73 and M-CDM91 respectively

Fig 3 (a) has the porous morphology, (b) shows the regular grain like structure and porous morphology. Fig 3 (c) is with disturbed and irregular morphology whereas, M-CDM73 and M-CDM91has agglomerated grains like disturbed morphology and porous morphology respectively. Amongst these films, the M-CDM 37is found to be more suitable for gas sensing application.

3.5. Thermo gravimetric analysis (TGA)

The TGA study shows percentage loss against temperature. There was a continuous weight loss observed up to 600 ˚C of NZF thin film due to removal of the hydroxide/moistures from ferrite. After 600 ˚C there is no weight loss observed, it confirms that, material is thermally stable. However, DTA study shows one exothermic peak at around 150˚C due to the thermal degradation of organic content (reagent) and formed stable metal oxide.

3.6. Contact angle measurement

The surface microstructure plays vital role in the wetting properties of materials [20]. The NZF thin films prepared by modified chemical deposition method are demonstrated by the investigation of static water contact angle measurements. Film M-CDM19 has contact angle 37˚ whereas M-CDM37 has 25˚ due to regular grain like structure and porous morphology. The contact angle of 48˚was observed for M-CDM55 due to disturbed and irregular morphology. M-CDM73 and M-CDM91 shows the contact angle of 41˚and 39˚ respectively due to irregular morphology. Thus the M-CDM with low contact angle finds suitable for the gas sensing.

3.7 Band gap measurement

The UV-VIS data were analyzed from the classical relation (eq. 1) for near edge optical absorption in semiconductors which gives relation between the optical band gap, absorption coefficient and energy (hν) of the incident photon. The estimated band gap is ranging from 1.98 - 2.02 eV. The values of band gap confirms the NZF thin films are semiconductor metal oxide.

$$\alpha = A\frac{(h\nu - E_g)^n}{h\nu} \qquad (1)$$

where, A is a constant independent of hν, E_g is the semiconductor band gap and n is a number.

4. Conclusion

The prepared NZF thin films are of cubic spinel type exhibit nancrystalline nature, porosity and stable after annealing. These properties could be taken an advantage for applications of NZF films as gas sensors.

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REFERENCE

[1] Rongzhou, G., Xiang, S., Zekun, F., Haifeng, L, Xian, W., Huahui, H. 2007, J. Mater. Sci- Mater. Electron., 18, 1045. | [2] Ali, G., Vladimir, S. 2011, J. Magn. Magn. Mater., 323, 1727. | [3] Lakshmikanta, A., Nanda, J., Samajdar, I., Venkataramani, N., Shiva, P., 2009, J. Magn. Magn. Mater., 321, 3373. | [4] Liu, F., Ren, T., Yang, C., Liu, L., Wang, A. Z., Yu, J. 2006, Materials Letters, 60, 1403. | [5] Zhu, L. F., She, J. C., Luo, J. Y., Deng, S. H., Chen., J., Xu, N. S. 2010, J. Phys. Chem. C, 114, 15504. | [6] Wang, L., Teleki, S. E., Pratsinis, S. E., Gouma, P. I. 2008, Chem. Mater., 20, 4794. | [7] Wolcott, A., Kuykendall, T. R., Chen, W., Chen, S., Zhang, J. Z. 2006, J. Phys. Chem. B, 110, 25288. | [8] Li, X., Lou, T. J., Sun, X. M., Li, Y. D. 2004, Inorg. Chem., 43, 5442. | [9] Wang, X., Miura, N., Yamazoe, N. 2000, Sens. Actuators B, 66,74. | [10] Glass, H. L. 1988, Proc. IEEE, 76, 151. | [11] Zi, Z. F., Zhang, S. B., Wang, B., Zhu, X. B., Yang, Z. R., Dai, J. M., Song, W. H., Sun, Y. P., 2010, J. Mag. Mag. Mat. 322, 148. | [12] Singh, V. R., Garg, A., Agrawal, D. C. 2008, Appl. Phys. Lett. 92, 152905/1. | [13] Simoes, A. Z., Gonzalez, A. H. M., Aguiar, E. C., Riccardi, C. S., Longo, E., Varela, J. A. 2008, App. Phys. Lett. 93, 142902/1. | [14] Niesen, T., De Gurire, M., 201, J. Electroceram. 6, 169. | [15] Pathan, H. M., Lokhande, C. D., 2004, Bull. Mater. Sci. 27, 85. | [16] Nair, M. T. S., Guerrero, L., Arenas, O. L., Nair, P. K. 1999, App. Surf. Sci. 150, 143. | [17] Shinde, V. R., Gujar, T. P., Lokhande, C. D., Mane, R. S., Han, S. H. 2007, Sens. Actuat. B, 123, 882. | [18] Tolstoy, V. P., Murin, I. V., Reller, A., 1997, App. Surf. Sci. 122, 255. | [19] Tolstoy, V. P. 1999, Russ. J. Appl. Chem. 69, 856. | [20] Tolstobrov, E. V., Tolstoy, V. P. 1999, Russ. J. Gen. Chem, 69, 856. | [21] Tolstoy, V. P., 1993, Russ. J. Inorg. Chem., 38, 1063. | [22] Olowe, A. A., Genin, J. M. R., 1991, Corros. Sci. 32, 965. | [23] Gunjakar, J. L., More, A. M., Shinde, V. R., Lokhande, C. D. 2008, J. Alloys Compd. 465, 468. |