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Authored by

Kardile H. J,
Postgraduate Department of Physics, Arts, commerce and science College, Sonai, Tal- Newasa, Ahmednagar - 414105. Affiliated by SavitribaiPhule Pune University Pune.(M.S.) India.

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INFLUENCE OF Ni^{2+} IONS ON THE STRUCTURAL AND WETTABILITY PROPERTIES OF $Co_{1-x}Ni_xFe_2O_4$SPINEL FERRITE THIN FILMS DEPOSITED BY SPRAY PYROLYSIS METHOD

Kardile H. J, Postgraduate Department of Physics, Arts, commerce and science College, Sonai, Tal- Newasa, Ahmednagar - 414105. Affiliated by SavitribaiPhule Pune University Pune.(M.S.) India.Corresponding Author Email id :drkardile2019@gmail.com

Abstract:
In the current study, cobalt nickel ferrite (CO_{1-X} $Ni_XFe_2O_4$) is used. The structural, optical, and wettability features of the produced cobalt ferrite thin film were studied and optimized before being placed on glass substrate by spray pyrolysis, investigations with the aid of UV-VIS spectroscopy and X-ray diffraction (XRD). At room temperature, the XRD pattern was measured in the 2ɵ range of 20 to 80 degree. The cubic spinel structure is represented by all of the reflections in the XRD pattern. The structural characteristics that were computed from the XRD data, such as the lattice parameter and X-ray density, matched the conventional JCPDS data quite well. The generated cobalt ferrite thin film's nanocrystalline nature was confirmed by the crystallite size, which Scherer's formula determined to be 28 nm. The near edge band emission was visible in the PL spectra between 690 and 740 nm in wavelength. With increasing the Ni^{2+} content x, it was discovered that the optical band gap computed using the Tauc plot was in the range of 2.43 eV to 2.61 eV. It was discovered that the contact angle ranged from 55.99^0 to 87.50^0, indicating the hydrophilic nature of all the samples.

INTRODUCTION:

In recent years, a nanocrystalline spinel cobalt ferrite thin film has been used for gassensing and supercapacitors applications. The crystal structure of cobalt ferritepossesses inverse spinel structure with one-half of Fe3+ ions on (A) site and resttogether with Co2+ ions at [B] site at room temperature. A variety of physical as wellas chemical methods have been applied for the deposition of cobalt ferrite thin films [5,9-11]. On the other hand, Nickel ferrite (NiFe2O4) is one of the versatile andtechnologically important soft ferrite (low anisotropy field) materials with spinelstructure because of its typical ferromagnetic properties, low electrical conductivityand thus lower eddy current losses, high electrochemical stability, catalytic behaviorand abundance in nature [12, 13]. Cobalt ferrite is a well-known hard magneticmaterial with relatively high coercivity and saturation magnetization while nickelferrite is a soft material with low coercivity and saturation magnetization. Many ofthese (hard and soft magnetic) properties make them very promising candidates for avariety of applications in biomedical, electronic as well recording technologies [14-16].From the application point of view, the magnetic character of the nanoparticlesdepends crucially on the size, shape, purity, and magnetic stability of these nanoparticles.CoFe2O4 and NiFe2O4 are room-temperature insulating ferrimagnetism with high
Curie temperature and large saturation magnetization make them promisingcandidates for applications in spin-filter devices or as building blocks of artificialmultiferroicsheterostructures. For all these possible applications the spinel ferriteshave to be grown on suitable substrates, which usually incorporate strain into the thinfilm material. This strain can have a strong influence on the structural and magneticproperties of the grown structures. It has been shown experimentally for CoFe2O4that, depending on growth conditions and substrate treatment. Furthermore, a strongenhancement of magnetization and conductivity has been reported in NiFe2O4. Fromthe experimental point of view, it is not clear whether the observed deviations frombulk behavior are determined solely by the strain incorporated in the thin films.
Physical methods include pulsed laser deposition, sputtering, etc. Physical methodshave many drawbacks such as small area of deposition, the requirement of sophisticatedinstruments, high working cost of the system, wastage of depositing material, cleaningafter each deposition, etc. Keeping drawbacks of physical methods in mind, recently,several chemical methods are used for the preparation of ferrite thin films. On theother hand, chemical methods are simple, economical, and

convenient for thedeposition of metallic thin films. The different preparative parameters are easilycontrollable. Chemical methods including sol-gel route, low-pressure chemical vapordeposition, electrodeposition, and so on are considered for the synthesis of spinelferrite thin films of fascinating magnetic properties. Out of all these chemicalmethods, the spray pyrolysis method is the most convenient and suitable for the preparationof spinel ferrite thin films. This can be done either by varying the sizes of thesenanoparticles or by adjusting the concentrations of soft (e.g. nickel ferrite) and hard(e.g. cobalt ferrite) magnetic phases in these materials. For this purpose nickelsubstituted cobalt ferrite nanoparticles have been synthesized by spray pyrolysistechnique. In the present work, we report the structural and wettability properties of Ni2+ substituted CoFe2O4 thin films in detail.

Experimental

Analytical reagent (AR) grade nickel nitrate (Ni (NO3)2.6H2O), cobalt nitrate (Co(NO3)3.6H2O), and ferric nitrate (Fe (NO3)3.9H2O) were used as starting materialwithout any purification. The glass substrates were carefully cleaned by sequentialtreatment with chromic acid, ethanol, and acetone followed by dipping with deionizedwater in an ultrasonic bath for 30 min, and the same glass plates were used for thedeposition.The glass substrate cleaning plays an important role in the deposition of thin films.The extreme cleanliness of the glass substrate is required for the chemical deposition.The contaminated surface provides nucleation sites facilitating growth resulting innon-homogeneous films with different orientations and impurities. The glass microslides supplied by 'Blue Star' of dimension 75 x 25 x 1.45 mm have been used as thesubstrates for the deposition of cobalt-nickel ferrite thin films. The glass slides werewashed with chromic acid and distilled water. The substrates were washed withdouble distilled water. The substrates were ultrasonically cleaned for 30 minutes byusing an ultrasonic bath. Finally, the substrates were dried, degreased in AR-gradeacetone, and were used for deposition.The Ni^{2+} substituted $CoFe_2O_4$ thin film was prepared by spray pyrolysis technique.Analytic reagent grade chemicals Co (NO_3)2.6H2O and Fe (NO_3)3.9H_2O were used asstarting materials. The two metal nitrate solutions were dissolved separately in deionizedwater at the concentration of 0.1 M for $CO^{2+,}Fe^{3+,}$ and Ni^{2+} solutions. Finalsolutions were prepared by mixing these two solutions in 1:2 volumetric proportions.Ni^{2+} substitution $COFe_2O_4$ thin films were prepared by spraying the solution ontoa previously cleaned glass substrate. Glass substrates mounted on a holder were placedon the surface of a hot plate. A temperature controller was used to hold the presettemperature of 350^{oC} with an accuracy of ± 500^{oC} through a channel-alumethermocouple connected to the glass substrate. A prepared solution was atomized inthe air via a pneumatic spray system under an air pressure of 0.25 MPa. The atomizeddroplets were transformed onto the heated glass substrate for 0.5 sec intermittently. The substrate temperature could be reduced under the effect of spray and requiresseveral seconds to recover the preset temperature. The solution spray rate was 5ml / min,and the distance between nozzle 28 cm and substrate temperature 350^{oC} were keptconstant. When an aqueous solution of cobalt, nickel, and ferric nitrate is sprayed over thehot substrates, fine droplets of solution thermally decompose after falling over the hotsurface of substrates, resulting in the formation of well adherent and homogeneous Ni $^{2+}$substitution $CoFe_2O_4$ thin films. The prepared thin films were annealed at $500^{0c}$for 4 h.

RESULT AND DISCUSSION:

X-ray diffraction

The X-ray diffraction patterns of Ni2+ substitution CoFe2O4 thin films annealed at500□C for 4 h show the crystallinity of the final product as given in **Fig. 1**. All thepeaks in the XRD pattern correspond to the cubic CoFe2O4 and NiFe2O4 phasesaccording to the standard JCPDS cards (742081 for NiFe2O4 and 791744 forCoFe2O4). The **Fig:1**shows XRD patterns of nanocrystalline Co1-xNixFe2O4 (x=0.0,0.2, 0.4, 0.6, 0.8 and 1.0) thin films. The reflections (111), (220), (311), (222), (400),(422) (511), and (440) belonging to single phase cubic spinel structure, are present inthe XRD pattern. The lattice constant was calculated using the interplanar spacingdistance (d) and the respective (hkl) parameters using the following relation.

$$a = \frac{\lambda[h^2+k^2+l^2]^{1/2}}{2\,Sin\,\theta}A^0 \text{ ---------- } (1)$$

All prepared samples could be refined using the Fd3m space groupand have a single-phase spinel cubic structure. The lattice parameters of prepared ferritesamples are listed in **Table:1.** The values of the lattice parameters of Ni^{2+}substitution $CoFe_2O_4$ are in agreement with that reported by Ashok

Kumar *et al.*,[17].It has been found that the lattice parameter decreases from 8.382 Å to 8.332 Å withthe increase in Ni^{2+} concentration. The decrease in lattice parameter with the increasein Ni^{2+} ion concentration is due to the replacement of large ionic radii Co^{2+}ions (0.78 Å)by smaller ionic radii Ni 2+ ions (0.63 Å) in the host lattice of cobalt ferrite thin film.

The X-ray density of all the thin film samples was calculated using the volume of theunit cell and molecular weight using the following formula.

$$d_X = \frac{8M}{N_A \ a^3} (gm/cm^3) \ .... (2)$$

where$M$ is molecular weight, N is Avogadro's number, and 'a' is the latticeparameter. The values of X-ray density with Ni^{2+} content are presented in **Table :1**.The X-ray density is found to increase with increasing Ni^{2+} content x. As the volumeof the thin films on the substitution of Ni^{2+} content x increases the X-ray densitydecreases. The crystallite size of the deposited thin films has been estimated from themost intense peak (311). The crystallite size calculated for all the thin films as afunction of Ni2+ content x using Debye-Scherrer's formula is tabulated in **Table :1**

$$t = \frac{0.94\lambda}{\beta \cos\theta} \qquad (nm) \ .... (3)$$

where λ is the wavelength of the X-ray radiation, β is the full-width half maximumand 2θ is the diffraction angle. The crystallite size of $Cu_{1-x}Zn_xFe_2O_4$ was found to bein the range of 17- 33 nm. Thus, the nanocrystalline nature of the deposited Ni_{2+}substitution cobalt ferrite thin films was confirmed.

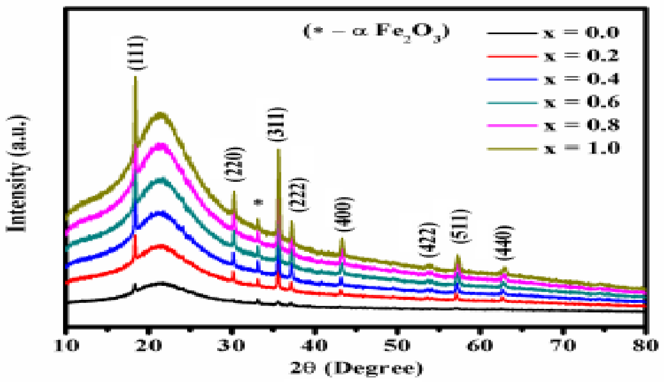

Figure 1. X- ray diffraction patterns of $Co_{1-X}Ni_XFe_2O_4$ thin films

Lattice parameter (a), X-ray density and Crystallite size (t) of $Co_{1-x}Ni_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) thin films

Composition 'x'	a (Å)	d_x (gm/cm^3)	(t) (nm)
0.00	8.382	5.293	17
0.20	8.379	5.312	21
0. 40	8.372	5.352	23
0.60	8.365	5.355	27
0.80	8.351	5.357	31
1.00	8.332	5.381	33

Wettability Properties

The surface wettability of many nanomaterials is almost driven by the tendency toreduce the total Gibbs free energy of the structure via reducing the surface energy. Itdepends on the composition, morphology, surface roughness, local homogeneity, etc.The aperture on the film surface could induce the air pocket forming and it will let thewater drop and easily stand on the surface of as-deposited ferrite thin films. Theaperture size and the roughness effect of Ni_{2+} substitution cobalt ferrite thin filmswithout and with a post-annealing process. The topography of the thin films wasfurther supported by the contact angle measurement. The wettability of Ni_{2+}substitution cobalt spinel ferrite thin films was evaluated by measuring the contactangle of a water droplet placed on the surface of the thin film using a contact angle meter.The contact angle recorded for Co1-xNixFe2O4 (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) is inthe range of 55.99^o - 87.50^o which indicates the hydrophilic nature in **Fig :2.** Thevalues of contact angle for each thin film are given in **Table :2.**

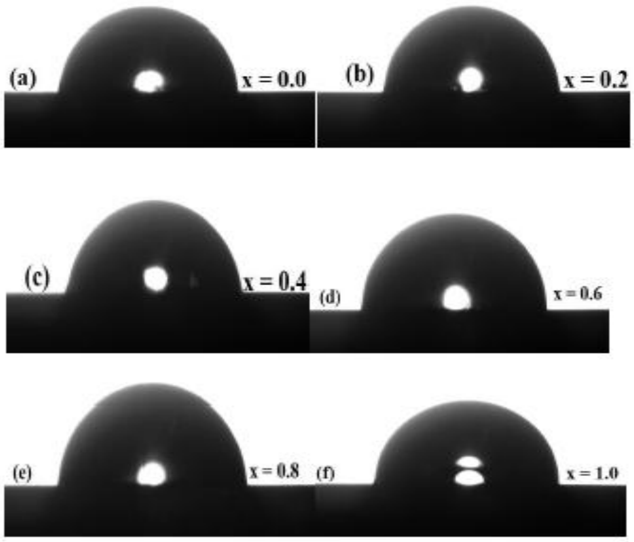

Figure 2Contact angle of Co1-XBiXFe2O4(X=0.0, 0.2,0.4,0.6, .08 and 1.0) thin films.

Contact angle (C.A.), surface energy (S.E.), Energy Band gap (E_g) and thickness of $Co_{1-x}Ni_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) thin films

Composition 'x'	C. A. θ	S.E. (m J/m^2)	E_g (eV)	Thickness of thin film (nm)
0.0	65.47	44.49	2.61	249
0.2	55.99	50.24	2.60	253
0.4	84.28	32.80	2.57	274
0.6	80.90	34.92	2.51	254
0.8	88.28	30.46	2.49	265
1.0	87.50	30.50	2.43	267

CONCLUSION

The nickel substituted cobalt ferrite thin films of various compositions weresuccessfully grown on preheated glass substrates using the spray pyrolysis technique. Allthe films show uniform thickness ranging between 249 nm - 274 nm. Structuralstudies carried out by the X-ray diffraction method confirm the formation of a single-phasecubic spinel structure. Lattice constant was found to be decreased with an increase in nickelcontent x. Crystallite size was found to be increased with an increase in nickel content x.The contact angle was found to be in the range of 55.99^o - 87.50^o which indicates thehydrophilic nature of all the samples.

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