Pyrolytic Spray Deposition and Characterization of Nanocrystalline Cobalt Ferrite Thin Film

Gajanan L. Jadhav[1*], S. D. More[2], M. K. Babrekar[3], C. M. Kale[3]
[1]Dept of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India (MS)
[2]Department of Physics, Deogiri College, Aurangabad (M.S.) India
[3]Department of Physics, Indraraj Art, Commerce and Science College Sillod (M.S.) India

Abstract: Cobalt ferrite thin film has been deposited by chemical spray pyrolysis method on a glass substrate at a temperature of 350°C. The deposited film was annealed at 550°C for 3 h. X-ray diffraction technique was employed to confirm the formation of single phase nanocrystalline thin film. The crystallite size of the present thin film is of the order of 12 nm confirming the nanocrystalline nature of the film. The thickness of the film was measured using surface profiler and found to be 260 nm. The band gap of 2.75 eV and 2.02 eV for allowed direct and indirect electronic transition was observed through UV-vis studies.

Index Terms - Cobalt ferrite nanoparticles, X-ray diffraction, M-H plot.

I. INTRODUCTION

Ferrites are the most important magnetic material due to their combined electrical and magnetic properties, which can be modified for the desired application [1]. Now day's ferrite thin films are used in a lot of applications, such as magnetic recording media, sensors, and microwave device [2, 3]. The ferrite films are effectively utilized as magnetic core materials with the low iron loss, opto-magnetic devices, and vertical recording magnetic material in surface magnetism study [4-6]. The $CoFe_2O_4$ has an inverse spinel structure in which the octahedral [B] sites are occupied by eight Co^{2+} and eight Fe^{3+} cations, while the tetrahedral (A) site are occupied the remaining eight Fe^{3+}. The spinel cobalt ferrite thin film has been a great deal of attention for its application such as high density magnetic, including in magneto-optic recording technique, excellent chemical stability, and high corrosion resistivity [7-9]. The film can be prepared by several methods, such as a method is physical and chemical. The physical method includes sputtering [10], pulsed laser deposition [11] etc. while chemical method includes spin coating [8], chemical bath deposition [12], spray pyrolysis etc. Spray pyrolysis technique can be used for depositing a wide variety of thin films, which are used in devices like solar cells [13], sensors, solid oxide fuel cells etc. It has evolved into an important thin film deposition technique and is classified under chemical methods of deposition. The spray pyrolysis method is widely used due to its low cost and simple method and also useful for the production of ferrite film with large areas**.** Amongst the different spinel ferrites, $CoFe_2O_4$ (CFO) is unique and most promising magnetic material for various applications. Cobalt ferrite possesses high permeability, high saturation magnetization (M_S), high electrical resistivity, high coercivity (H_C), and high magnetocrystalline anisotropy. Depending on the distribution of cobalt and ferric ions over the tetrahedral (A) and octahedral [B] sites, CFO is considered as an inverse spinel ferrite. The inversion parameter can vary in between 0.80 to 0.95 depending upon the various parameters like synthesis method, synthesis conditions, annealing temperature, annealing condition, annealing time etc.

In the present work, cobalt ferrite thin film was prepared by spray pyrolysis technique by optimizing all the necessary parameters. The structural and optical properties were systematically studied and the results are presented in this work.

II. EXPERIMENTAL METHOD

The cobalt ferrite ($CoFe_2O_4$) thin film was deposited on to preheated glass substrate (350 ºC) by using spray pyrolysis technique. The solutions are prepared by using a mixture of Co $(No_3)_2.6H_2O$ (cobalt nitrate hexahydrate) of 0.08 M and Fe $(No_3)_3.9H_2O$ (ferric nitrate nonahydrate) of 0.08 M in separately dissolving in double distilled water. The final solutions are prepared by mixing two initial solutions in 1:2 volumetric proportions.

The $CoFe_2O_4$ thin film was prepared by spraying solution on to glass substrate. The glass substrate was pre-heated with an ultrasonication for 30 min in distilling water before film deposition. Then after cleaning glass substrate was mounted on to a surface hot plate and set the substrate temperature to 300 °C. The temperature controller was used to control the temperature within ± 10 °C through a thermal couple connected to the surface of a hot plate. The other preparative parameter such as spray rate 5ml/min. the solution of total quantity 75ml. the parameters of the nozzle to substrate distance 28.5 cm was kept constant and the freshly prepared solution was atomized in air 0.30 M pa. Compressed air was used as a carrier gas to atomize the spray. The atomized droplets were transferred on to the heated glass substrate for 10s intermittently. Further, the as prepared thin film sample was annealed at 550°C for 4 h and used for the characterizations. In order to investigate structural and optical properties of cobalt ferrite thin film, different standard characterization techniques were used. X-ray diffractometer (Bruker D8 Advance) was employed for the structure and phase analysis. UV-Vis spectrophotometer (Perkin Elmer) was used to study the optical properties of the prepared cobalt ferrite thin film..

III. RESULTS AND DISCUSSION

X-Ray diffraction studies

The Fig. 1 shows that X-ray diffraction pattern of the $CoFe_2O_4$ thin film deposited on glass substrate at 350°C temperature and annealed 550 °C for 4 h. The X-ray diffraction shows that some lower intensity peaks appeared in the cobalt ferrite thin film due to the lower peaks as (220), (311), (400), (422), (511), (440) and (533) also the spinel cubic crystal structure of the deposited film. Average crystallite size of nanoparticles was calculated from the Debye-Scherrer's equation [12].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where, D is the crystalline size, λ is the wavelength of x-ray (1.5406 A), β the full-width of the diffraction line at half–maximum intensity and θ is the Bragg's angle. The crystalline size of the cobalt ferrite was estimated to 12 nm.

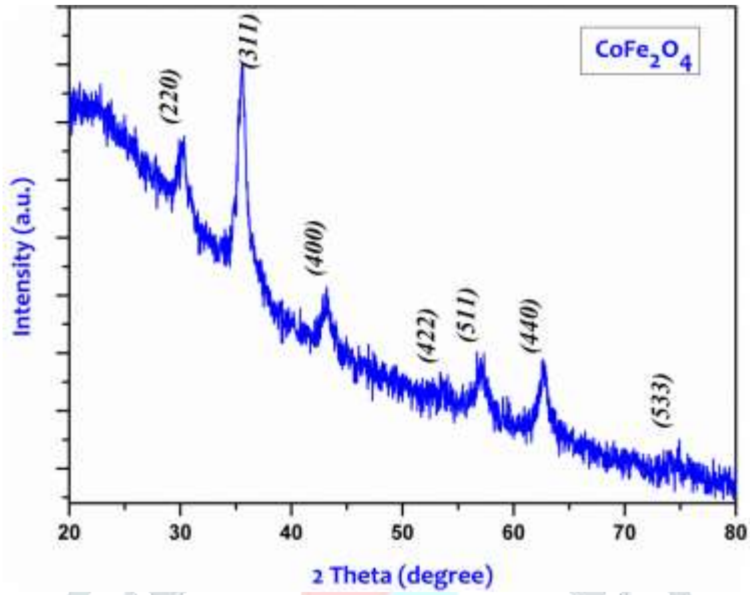

Fig. 1 X-ray diffraction pattern of CoF_2O_4 thin film at annealed 550 °C

The film thickness is one of the important physical parameters, its most of the properties depend upon a film thickness [14]. The grain size of film changes with thickness. The thickness of the film was measured using surface profiler and found to be 260 nm.

UV-Vis spectroscopy

The optical properties of cobalt ferrite thin film were carried out to investigate the band gap energy of the film. The optical absorbance of cobalt ferrite thin film was studied in the range 300-800 nm, using UV-Vis spectrophotometer, which has been further used for the energy band gap calculation. Fig.2 (a) shows the optical absorption verses wavelength. The following relation can be used for calculating the absorption coefficient (α) [15].

$$\alpha = \frac{2.303\, A}{t} \qquad (2)$$

Where, (A) is the absorbance and t are the film thickness. Fig 3 shows the absorption coefficient as a function of the photon energy of the $CoFe_2O_4$ thin film. The result shows that the absorption coefficient increases with increasing the photon energy.

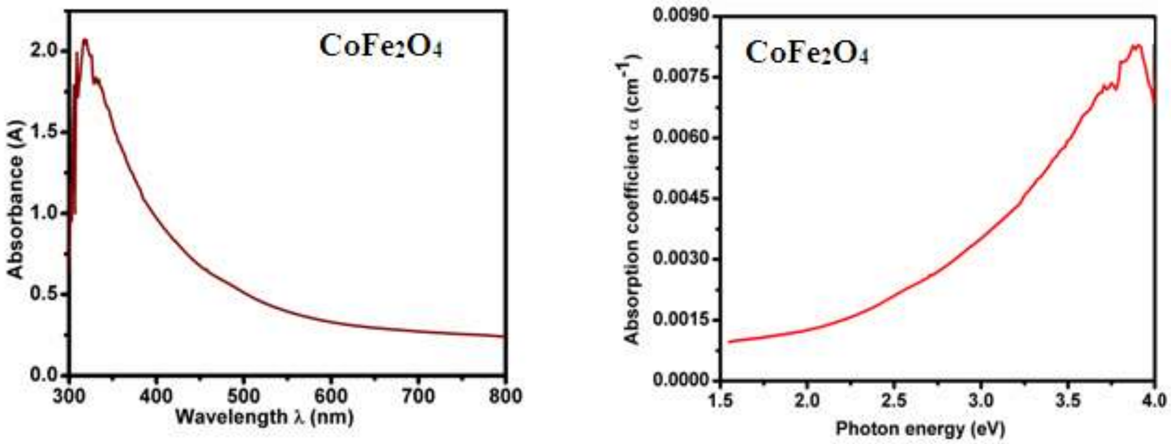

Fig. 2 (a-b) Absorption spectra (a) and Absorption coefficient (b) of $CoFe_2O_4$ thin film at annealed 550 °C

Also, we note that the absorption coefficient values are greater than at high photonic energies suggesting the occurrence of the direct electronic transition. $CoFe_2O_4$ thin film is annealed at 550°C for 4 h, The annealing process helps the atoms to arrange themselves in the right direction, leading to increases in the grain size and the improvement in the crystal structure as well as that the annealing process leads to the removal of synthetic defect and works to reduce the dislocation density. The optical energy gap (E_g) is given by the classical relation [16].

$$\alpha = \frac{A(h\nu - E_g)^{n/2}}{h\nu} \qquad (3)$$

Where, A is a parameter independent of hν, Eg the optical band gap energy and n is a number equal to 1 for the direct gap and 2 for indirect gap compound. The direct and indirect band gap energy of $CoFe_2O_4$ thin films has been determined by Tauc plot based on the above formula as shown in fig.3.The value of optical band gap is calculated by extrapolating the straight line portion of the graph on 'hν' axis. The obtained band gap value for cobalt ferrite thin film is 2.57 eV for direct and 2.02 eV for indirect. The extinction coefficient (k_o) can be determined by using the relation [12].

$$k_o = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Where, λ is the wavelength of the incident photon. Fig 4.shows the extinction coefficient as a function of the photon energy of the $CoFe_2O_4$ thin film at annealed 550˚C. It can be noted that the extinction coefficient gradually increases with increasing the photon energy and then followed by rapid increases at high photonic energies for the film. This can be attributed to the decrease in the absorption coefficient of the film.

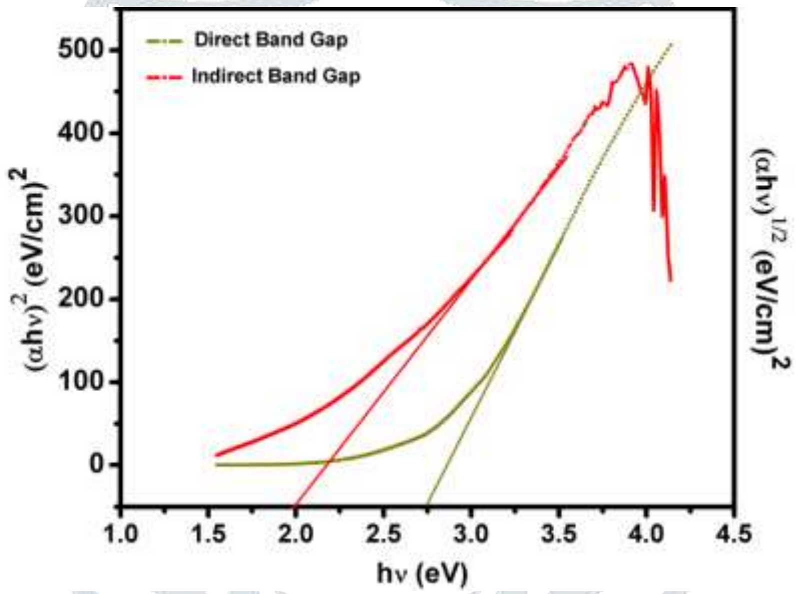

Fig 3 Direct and indirect band gap CoF_2O_4 thin film at annealed 550ºC

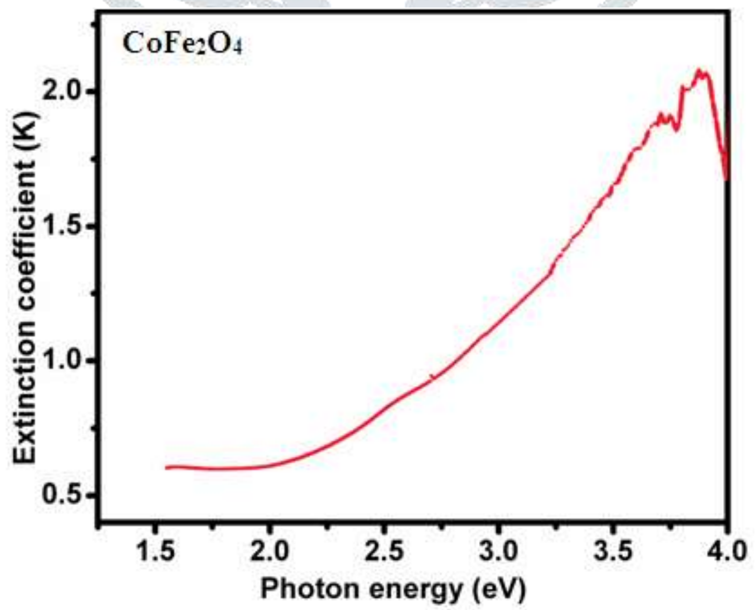

Fig. 4 Extinction coefficient of CoF_2O_4 thin film at annealed 550ºC

IV. CONCLUSION

In this work, cobalt ferrite thin film was successfully prepared by spray pyrolysis technique using a glass substrate. The X-ray analysis reveals the nanocrystalline cobalt ferrite thin film with spinel cubic structure. The Tauc's plot gives the band gap energy of $CoFe_2O_4$ thin film 2.37 eV. The optical properties have shown that the optical constants such as absorption coefficient and extinction coefficient have been affected by the $CoFe_2O_4$ thin film. Spray pyrolysis method becomes a convenient method for preparation of $CoFe_2O_4$ thin film.

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