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Structural and Morphological Properties of Mn-Doped Co3O4 ThinFilm Deposited by Spin Coat Method

[1]S. M. Jogade, [1]D. S. Sutrave, [2]V.B. Patil
[1]*D.B. F. Dayanand College of Arts and Science, Solapur, Maharashtra, India-413003*
[2]*Department of Physical Science, Solapur University, Solapur, Maharashtra*

ABSTRACT
In this study, a series of manganese (Mn)-doped Cobalt oxide (Co_3O_4)thin films were deposited on steel substrate by the sol-gel spin coat method and investigated the influence of doping concentrations of Mn in Cobalt ranging from 0.001% to 1% on physical, structural and morphological properties of Co_3O_4 thin films. Cobalt acetate[$(CH_3COO)_2Co.4H_2O$], Mn acetate [$C_4H_6MnO_4.4H_2O$] and Isopropyl alcohol were used as starting material, dopant source and reagent respectively.X-ray diffraction analysis indicated that pureCo_3O_4 thin film iscrystallinein nature andcubic phase with [400] preferential orientation.For Mn doped films, three new peaks corresponding to the planes [310], [320] and [420] of orthorhombic MnO_2 phase were observed.SEM micrographs showed that incorporation of Mn in Co site was found to influence the surface morphology of the films. All the films showed tetragonal shaped grains. TheEDAXanalysis revealedthe amount of Mn element in the sample increased with increasing dopant concentration.
Keywords: Co_3O_4, MnO_2, Doping, XRD, SEM, EDAX, Spin Coat

I INTRODUCTION

Cobalt oxide is an important p-type semiconductor with direct optical band gaps at 1.48 and 2.19 eV[1], Co_3O_4has a stable normal spinel structure, where Co_2^+ ions occupy the tetrahedral 8a sites and Co_3^+occupy the octahedral 16d sites[2]. Cobalt oxides have attracted much attention for their interesting fundamental properties and many technical applications such as promising material in gas-sensing and solar energy absorption and as an effective catalyst in environmental purification and chemical engineering[3,4].In addition, Co_3O_4has been widely studied for its application as lithium ion battery electrodes, ceramic pigments, field-emission materials and magnetic material[5-11]. Co_3O_4hasbeen prepared by a range of methods including sol-gelsynthesis[12], spray pyrolysis[13], electrodeposition[14], chemical vapour deposition(CVD)[15], thermal decomposition [16], pulsed laserdeposition (PLD)[17] and sputtering[18]. According to the literature survey, the systematic investigationson effect of doping on structural, and morphological properties of crystallineCo_3O_4 thin films by sol-gel spin coating methodhas been sparsely studied[19]. Literature study also revealed that, the properties of transition metal oxides can be enhanced by doping, and also attempts are made to modify the physical, chemical and optical properties of thin films by doping with other transition metal oxides. The structural and optical properties have been enhanced by impurity doping and heat treatment[20-23]. Many researchers used Mn as a doping material[24]. So in the present work effect of Mn doping on structural, morphological and compositional properties of cobalt oxide thin films is presented.

II EXPERIMENTAL

2.1 Synthesis

Co_3O_4 was synthesized by using Cobalt acetate tetrahydrate[(CH3COO)$_2$Co.4H$_2$O], isopropyl alcohol as a starting material and reagent respectively. A 0.02 M solution was prepared by mixing 0.249gm cobalt acetate tetrahydrate and 50ml double distilled water and it was stirred well using magnetic stirrer until it became optically transparent, then isopropyl alcohol was added slowly. The prepared solution was stirred again for 6 hours at temperature 50^0 C and then aged for 48.00 hours to get viscous solution in the form of gel. The doped solution was prepared by adding to the precedent solution Manganese acetate [$C_4H_6MnO_4.4H_2O$] as a dopant source. The weight percentages of Mn were 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, 0.5% and 1%. After doping with different concentrations, the above process was repeated to prepare the sol-gel.

1.2 Deposition

For the deposition of thin films, Milman Spin Coat unit was used. Co_3O_4 and Mn doped Co_3O_4thin film electrodes with different doping concentrations of Mnsuch as 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, 0.5% and 1% is done by Sol-gel spin coat technique and the deposition samples were denoted as A1, A2, A3, A4, A5, A6, A7 and A8throughout the paper. In this technique, at first a

drop of 0.1ml of prepared sol was placed on the substrate using a syringe. Which is then rotated at high speed on spin coater unit in order to spread the sol-gel by centrifugal force. The spin coating process can be broken down into the four stages such as deposition, rotating, drying and repeating the same process for multilayers. To dry the film, the film was kept under furnace for 10minutes and temperature of the furnace was set to 900^0C. The steps are repeated to get five layers of the film.

III RESULT AND DISCUSSION

3.1 Physical Properties

The spin coat deposited thin films of Co_3O_4 and Mn doped Co_3O_4 are well adherent to the steel substrate and uniformly distributed throughout the surface area. The pure Co_3O_4 film is dark brown in colour whereas the colour becomes light as Mn doping concentration goes on increased. For maximum Mn doping concentration 1%, light brown colour is observed as compared to 0.001% Mn doping. The thicknesses of the samples were calculated by weight difference method by using the relation,

$$t = \frac{m}{A\rho}$$

Where, 'm' is the mass of the film deposited on area 'A' of the substrate and 'ρ' is the density of the material in the bulk form. The mass 'm' is the difference between weight of the substrate measured before deposition and weight of the substrate measured after deposition. The weight measurements of films have been taken using a single pan microbalance.Figure 1shows the variation of film thickness with different Mn concentrations from 0.001% to 1%.

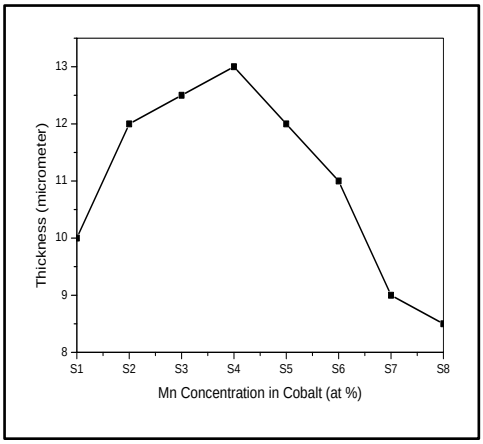

Fig. 1 Variation of film thickness with Mn concentration in cobalt

The density of the deposited material is same as that of the bulk material i.e., ρ = 6.11 g/cm^3 for Co_3O_4 and ρ = 5.026 g/cm^3 for MnO_2. From the figure it is found that increasing percentage of Mn film thickness goes on increase up to 13μm at 0.01 % Mn then after it decreases and for maximum 1% Mn concentration sample shows minimum film thickness of 8.3μm. It may found that at lower Mn% shows easy decomposition and at high Mn % incorporation material shows improper decomposition due to resistive nature and different oxidation states.

3.1 Structural Analysis

The X-ray diffractometer (XRD 6000) with CuKα line radiation (λ = 1.5406 Å) operating at 40KV, 30mA for angles between $2\theta = 10^0$ to 90^0 in steps 0.02 was used for determining the crystallite phase and orientation. The X-ray diffractograms of series of Mn doped Co_3O_4 thin films is shown in figure 2.The characteristic peaks corresponding to the planes [220], [422], [620] and [441] respectively are of Co_3O_4cubic phase. The peak corresponding to plane [400] is dominating in all the samples. These diffraction peaks can be indexed to the crystalline cubic phase Co_3O_4 with lattice constants of a = 8.085 Åand a space group of Fd3 m, which are in good agreement with the reported values in JCPDS card no. 78–1969.In addition, three diffraction peaks corresponding to the planes [310], [320] and [420] observed in all doped XRD patterns, these peaks were matched for MnO_2 phase with orthorhombic structure which were matched with JCPDS card no. 82-2169 which is an indication of secondary phase or clusters, confirming that the samples are of mixed phase. Peaks corresponding to steel substrate are indicated by '*'. In addition, the width of the [400], [620] and [310] peaks increases with increasing doping concentration, which indicates the decrease of the particle size. But for the maximum doping concentration the intensity of peaks corresponding to plane [400] and [320] is less than that observed for minimum doping concentration. This indicates that dopant incorporation deteriorates the crystallinity of films, which may be due to the ion

size difference between Cobalt and Manganese. Crystallite size for different peaks have been calculated by the Scherrer's formula[25] and are represented in figure 3. It can be observed that crystallite size varies with the variation in dopant concentration. The presence of Mn dopant limited the crystal growth, as suggested by the observed difference in crystallite size with respect to increase in Mn concentration in Co_3O_4. As ionic radii of Co is larger than Mn[26,27], $Mn2^+$ ions systematically substituted for the Co^{2+} in the sample reducing the average crystallite size.

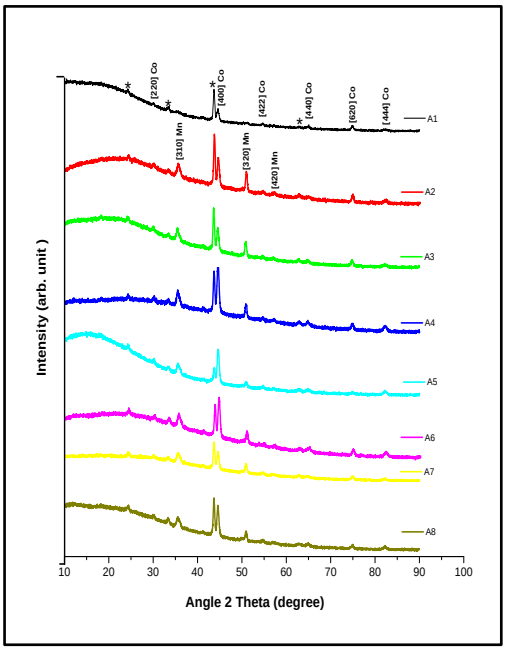

Fig. 2 XRD patterns of Pure Co_3O_4 and Mn doped Co_3O_4 Thin Films

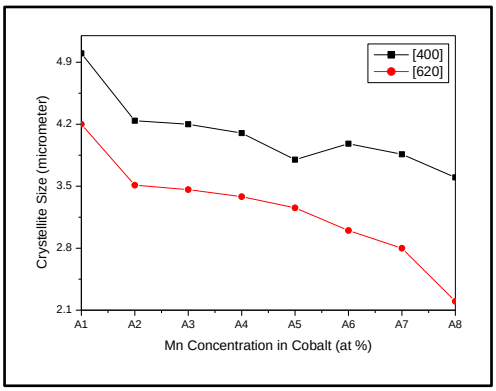

Fig. 3 Variation of Crystallite size with Mn dopant concentration.

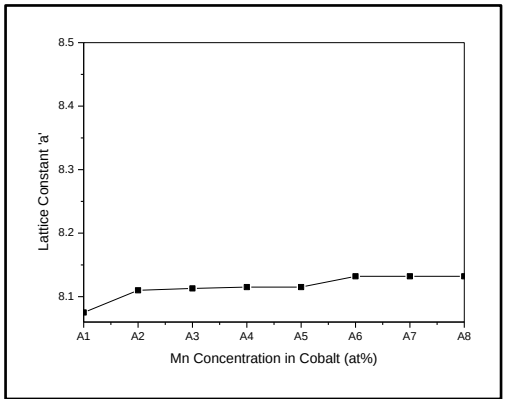

Fig. 4 Variation in Lattice parameter "a" with doping concentration for Co_3O_4 peaks

Lattice constants 'a', 'b' and 'c' are calculated from the XRD data and it shows goodagreement with the standard values (a=8.085 Å)[JCPDS-78-1969] for the different peaks of $Co_3O_4$and (a=9.3229, b=4.4533 and c=2.8482 Å)[JCPDS-82-2169]forMnO_2peaks. Variation in lattice constants with Mn doping are shown in figure 4 and 5 respectively. As observed from the graphs, there is negligible variation in lattice constant 'a' of Co_3O_4. But lattice constants 'a' and 'b' of MnO_2 increases with increase in Mn concentration whereas 'c'is almost constant.

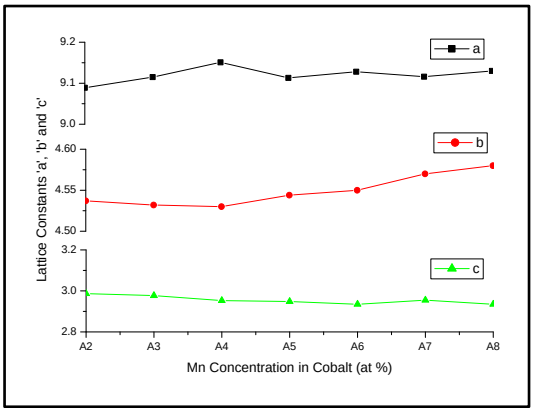

Fig. 5 Variation in Lattice parameter 'a', 'b' and 'c' with doping concentration for MnO_2 peaks peaks

3.2 Surface analysis

The morphological features of the samples were investigated by Scanning Electron Microscopy (SEM) using a JEOL JSM-6360 instrument.The incorporation of Mn at Co site was found to influence the surface morphology of the films. The Mn-doped Co_3O_4film showed the formation of many tetragonal particles all over the surfacewith smooth, well adherent and porous surface morphology. Incorporation of Mn ions changed the surface morphology of films in terms of decreased grain size with more equated grains and continuous grain boundary with increase in Mn concentration as seen from figure 6.Due to the enhancement of the dopant concentration more impurities were included into theCo_3O_4 crystal, resulting in more deviance in the crystal structure so that the crystallinity of the films was affected as seen in the XRD. The graphical analysis of average grain size for all films is shown in figure 7, which sowsat maximum doping concentration 1wt% of Mn there is an increase in grain to surface ratio, which may favourable for accumulation of large number of charges over the surface of electrode .

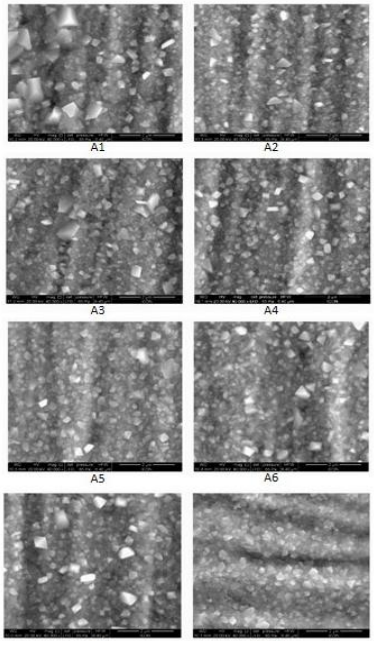

Fig. 6 SEM images of pure Co_3O_4 and Mn doped Co_3O_4Thin Films

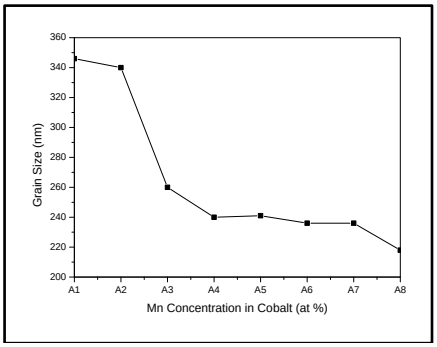

Fig.7 Variation in grain size with Mn Concentration in Cobalt

3.3 Compositional Analysis

The EDAX spectroscopy was used to know the percentage of the element present in the sample. EDAX analysis is carried out using Quanta 200 ESEM instrument. Figure 8 shows the ratio of Co:Mn:O elemental composition. From the obtained data we found that the Co, Mn and O was present in the 33:5:62 percentages. The EDAX spectrum of pure Cobalt Oxide and Mn doped Cobalt Oxide thin films are shown in figure 9. EDAX analysis showed that the atomic percentage of Mn increased in the sample depending on the increasing doping concentration in the solution. As a result Mn incorporation has a strong effect on structural and morphological properties of Co_3O_4thin films.

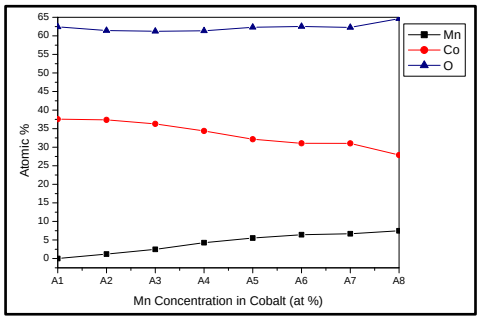

Fig. 8 Variation in atomic % with Mn Concentration in Cobalt

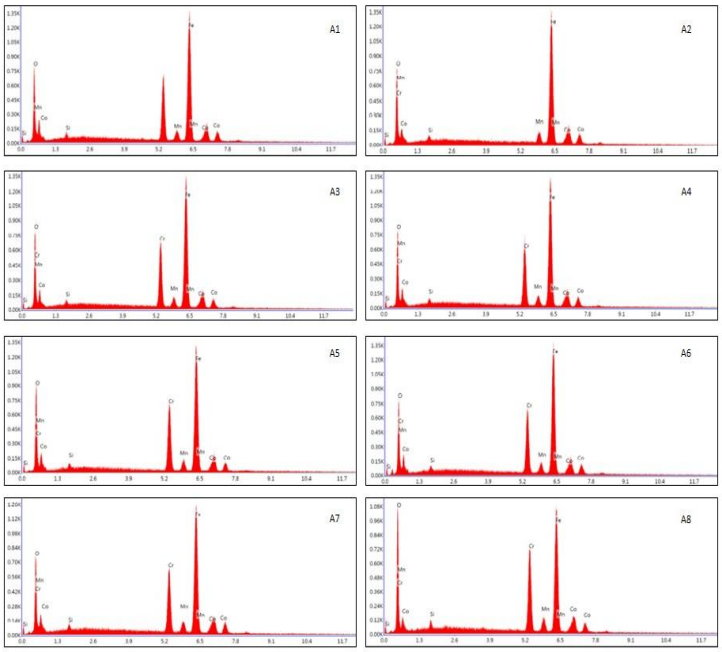

Fig.9 EDAX patterns of pure Co_3O_4 and Mn doped Co_3O_4Thin Films

IV CONCLUSION

Pure and Mn doped Co_3O_4 thin films were prepared with different values of Mn content by the sol-gel spin-coating method. The crystalline structure and morphological properties were investigated.The diffraction patternsreveal a good crystalline behaviour with the cubicphase of cobalt oxide. The doped XRD patterns indicated the secondary phase of MnO_2. The presence of Mn dopant limited the crystal growth as calculated by sherrer's formula.SEM micrographs showed that incorporation of Mn dopants changed the surface morphology of Co_3O_4 and enhanced pore density and grain densityobserved for highest doping concentration (1%).From the EDAX data we found that the Co, Mn and O was present in the sample in 33:5:62 percentages.

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