JES Journal of Engineering Sciences

Vol 11, Issue 4 ,April/2020
ISSN NO:0377-9254

Doping By Dipping Method: Influence of Dipping Time on Selectivity

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Abstract:
Cobalt doped indium oxide thick film sensors were created using doping by dipping method. The dipping time intervals were taken as 5, 10, 15, 20, 25 and 30 minutes. The Co-doped In_2O_3 thick film dipped for 20 minutes in a 0.01 M aqueous solution of cobalt chloride has been shown great sensitivity and selectivity towards carbon monoxide (CO) gas. The structural, morphological and compositional studies were carried out through XRD, SEM and EDAX characterization techniques. The sensitivity versus operating temperature graph of Co-doped In_2O_3 sensors (dipping time 5-30 minutes) for CO gas also has been represented and discussed in this work.

Key words: **Thick film, Co-doped, sensitivity, selectivity, carbon monoxide**

1. INTRODUCTION

The previous few decades have seen instant progress in development of chemical sensors determined by the needs of medical and environmental diagnostics, industrial process monitoring, national security and public safety [1–4]. Sensors established by means of metal-oxide semiconductors involved special attention because of their high sensitivity, good reproducibility, low cost and ease of use [5–7]. In the list of these sensors metal-oxide nanostructures often owned improved sensitivity and quicker response-recovery time, based on their enormous surface area and comfort of absorption of gas molecules on the surface [8–19].

To the extent that chemical sensing is concerned, it has been recognized, from more than five decades, that the electrical conductivity of metal oxides semiconductors fluctuates with the composition of the surrounding gas environment. The sensing qualities of semiconductor metal oxides in configuration of thin or thick films other than SnO_2, like TiO_2, WO_3, ZnO, Fe_2O_3 and In_2O_3, have been investigated as well as the advantages from the addition of dopants in enhancing the selectivity and stability [20].

In_2O_3 semiconductor [band gap of 3.6 eV] have been widely functionalised in areas such as photovoltaic cells, electricity and magnetism. Purposely, the chemical sensors prepared with In_2O_3 nano materials can sense ethanol, formaldehyde, CO, and NO_2. A diversity of In_2O_3 nanostructures, such as nanocubes, nanowires, hexagons and octahedral have therefore been manufactured in latest years. In_2O_3 materials with porous nano structures, for instance, can be produced through annealing $In(OH)_3$ precursors with unusual morphologies [21].

Here in, we would like to report cobalt doped In_2O_3 thick film sensor, which shows excellent performances in detecting carbon monoxide gas. The materials show improved gas sensitivity and selectivity properties.

2. Experimental workout

Synthesis of In_2O_3 powder by flux route

For the synthesis of In_2O_3 powder first In_2S_3 powder was synthesized by flux route. For this purpose, the initial resources used were AR grade powders of sodium sulphide, sulphur and indium sulphate. The all materials were integrated in proper percentage to obtained stoichiometric In_2S_3 product. The mixture was crushed very finely and then transferred into crucible having volume approximately 50 ml. The crucible was lodged in a muffle furnace tolerating temperature regulator of ± 2 ^oC. The furnace temperature was raised to 600 ^0C by a heating rate of 60 $^oC/h$. This temperature was then upheld aimed at 1 hour. Throughout the heating process, excess sulphur would vanish or it may be combines with atmospheric oxygen and water in sodium sulphide to produce SO_2 and H_2S, respectively. The furnace was then turn off to let it to cool down to room temperature all night. The prepared product in the crucible was flow over quite many times with double distilled water. This washing process causes sodium polysulphide to get dissolved in water and separated out easily. Final product was dehydrated by drying process.

It might be feasible to develop oxides from the corresponding sulphides by means of

calcination process at higher range of temperatures in air. For this purpose, the as prepared stoichiometric sample of was calcinated at 1000 ^{o}C for 10 hours in air in demand to exchange sulphur by oxygen so as to obtain the required In_2O_3 products.

Preparation of Thick films of In_2O_3

Screen printing technique was made in use to prepare the thick films of as prepared stoichiometric In_2O_3 powders and therefore, initially, In_2O_3 powder was smoothly ground by using pestle-mortar. For the deposition process the ink was prepared by combining the fine powder of In_2O_3 with the solution of ethyl cellulose in an assortment of organic solvents such as butyl cellosolve, butyl carbitol acetate and terpineol. The ratio of the In_2O_3 powder and the remaining materials was kept as 75:25 in formulating ink. This specific proportion for the ink formulation was promising factor to be thixotropic in nature and contributed a good line sharpness of the prints. The 160 mesh size screen and a flexible squeegee were utilised for the as prepared ink to be screen printed. Back to the deposition process the prepared thick films were dried under IR lamp and after that fired at 200 ^{o}C for the time interval of 30 minutes to vanish the organic binders.

Doping of In_2O_3 thick films

The pure (undoped) In_2O_3 thick films were surface modified by dipping technique and for this cobalt was utilised as a dopant. The thick films of pure In_2O_3 were dipped in 0.01 M aqueous solution of cobalt chloride for different intervals of time, such as 5, 12, 15, 20, 25 and 30 minutes. After the dipping process each film was dried under IR lamp and them fired again at 500 ^{0}C for 2 hour. The cobalt chloride would be converted upon firing into cobalt oxide.

Characterization

The crystalline structure of the films was analysed with Bruker X-ray diffractometer (D8, Advance, Brucker AXS Model) with Cukα radiation (λ = 1.5406 nm) radiation source in the 2θ range 10 - 80^{0}. Surface morphology of the film was studied using scanning electron microscope (S-4800, Hitachi, Japan). For quantitative elemental analysis of the films energy dispersive x-ray analyser which was attached to the scanning electron microscope was used.

3. Results & discussion

EDAX analysis

Co-doped In_2O_3 thick films

The at% of In, O and Co of Co-doped thick films were obtained by EDAX technique at three different locations on the plot of each film and the average of the three is presented in Table.1

The at% of In and O required for the stoichiometric composition of In_2O_3 is 40 and 60 respectively. It is clear from Table.3 that the undoped (pure) In_2O_3 thick films are stoichiometric.

Table.1 Quantitative Elemental Analysis of Co doped In_2O_3 thick films

Element	Dipping time (min)						
	0 pure	5 min dip	10 min dip	15 mi dip	20 min dip	25 min dip	30 min dip
In	41.03	38.35	39.65	36.02	21.93	29.30	31.97
O	58.97	57.97	54.43	51.96	56.97	54.63	59.27
Co	---	3.68	5.92	12.02	21.10	16.07	8.76

The at% of cobalt goes on increasing with dipping time, reaches to a maximum and then decreases with a further increase in dipping time interval. The film dipped for 20 min, consists of the largest at% of cobalt.

Structural analysis by XRD

Fig. 1 shows the XRD patterns of Co-doped (5-30 minutes dipped) In_2O_3 thick films. As can be observed, the XRD patterns indicated well crystalline structure with diffraction peaks corresponding to (2 1 1), (2 2 2), (4 0 0), (3 3 2), (4 2 2), (4 4 0) and (5 4 1) planes, which match with In_2O_3 reference peaks (JCPDS card no. 712194) as cubic form and (3 1 1), (3 3 1), (4 2 2) and (5 1 1) planes, which match with cobalt oxide reference peaks [JCPDS card no. 801544] as cubic form.

Morphological analysis by SEM

Fig.2 (5-30 minutes dipped) depicts SEM images of Co-doped In_2O_3 thick films. It is originate in almost all the Co-doped In_2O_3 thick films that crystalline particles with different sizes and shapes are distributed randomly on the layout of the films. The tiny grains may be because of CoO-species. It is also found that in the film with dipping time 15 minutes, the number of Co-species is reduced. Void spaces are also present in the array of the films.

Response to CO gas

Fig. 3 shows the variation of gas response of Co-doped In_2O_3 thick films of different dipping time intervals to CO gas (1000 ppm) as a function of

operating temperature. It can be seen from the figure that for each of the sample, the response to CO gas increases with increase in operating temperature. The sample with dipping time interval 20 minutes was observed to be most sensitive of all. It shows the response of 76.89 at 150 ^{0}C. The as prepared sensor has fast response time (8s) and recovery time (19s).

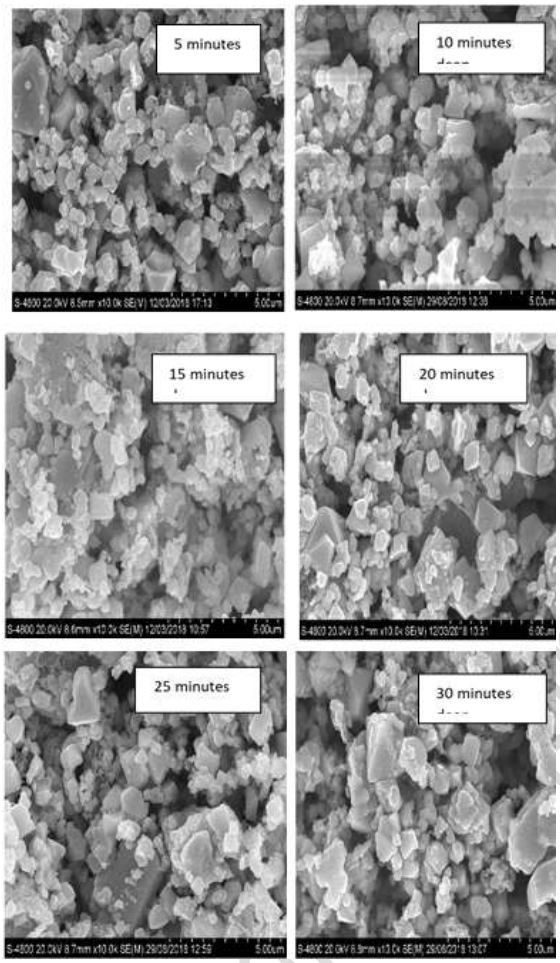

Fig. 1 (a-f) XRD patterns of Co-doped In_2O_3 thick film sensors dipped for 5-30 minute respectively

Selectivity of CO against various gases

Fig.4 illustrates the selectivity profile of Co-doped In_2O_3 thick films to various gases at 150 ^{0}C operating temperature. The film with dipping time of 20 minutes was highly selective to CO (1000 ppm) against H_2S, CO_2, NH_3, H_2, SO_2, LPG, Cl_2 and ethanol.

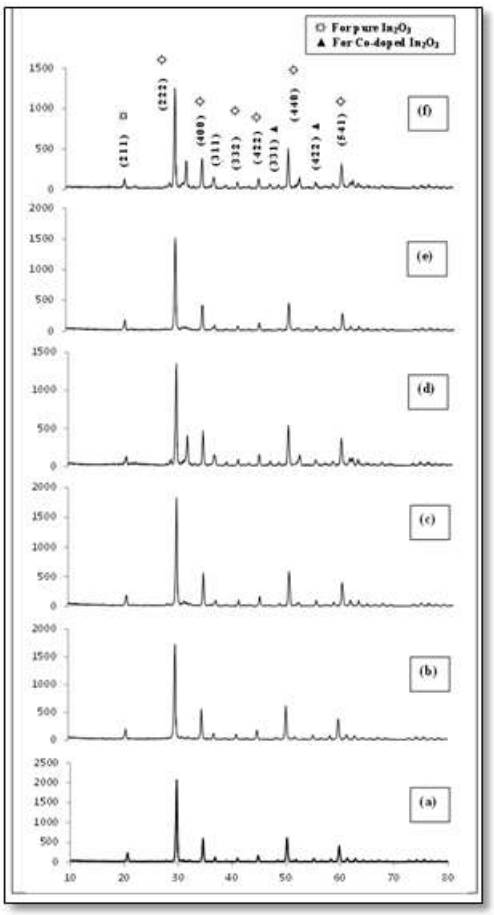

Fig.2 SEM micrographs of Co-doped In_2O_3 thick films

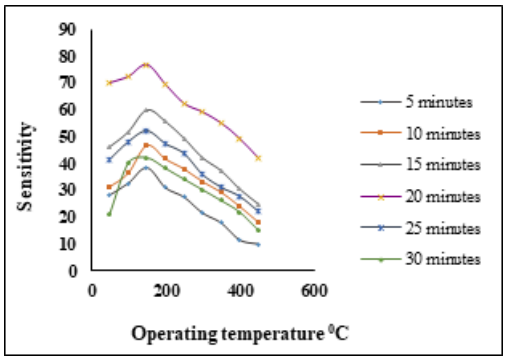

Fig.3 Variation of sensitivity of Co-doped In_2O_3 thick films of different dipping time intervals to CO gas as a function of operating temperature

Table. 2: Selectivity coefficient of Co-doped In_2O_3 thick films

Dipping time	K_{H2}	K_{SO2}	K_{Cl2}	K_{H2S}	K_{CO2}	K_{NH3}	$K_{Ethanol}$	K_{LPG}
5 min	17.4	5.2	8.3	30.7	4	5.8	48	10.3
10 min	9.1	4.3	7.4	12.3	3.6	5.3	30.5	6.1
15 min	7.3	4.6	8.3	10.5	4	5.4	18	6
20 min	6.9	4.5	7.5	8.4	4.3	5.5	10	5.9
25 min	8.3	3.7	6.3	12.7	3.4	4.9	9	6.5
30 min	13.5	6.8	7.9	22.2	3.7	5.9	19.8	13.4

The Table.2 represents the selsctivity coefficients of Co-doped In_2O_3 films to CO gas against the other gases such as H2, SO2, Cl2, H2S, CO2, NH3, ethanol and LPG.

Conclusion

In this study, Co-doped In_2O_3 thick film gas sensors were prepared via doping by dipping method. According to XRD results the as-prepared sample had a cubic structure. The morphology of the films shows that the film grains tend to agglomerate and irregular shaped particles when doped with Co for dipping time intervals 5-30 minutes. Elemental analysis shows that the pure sample is stoichiometric. We investigated the gas-sensing properties of the Co-doped In_2O_3 (5, 10, 15, 20, 25 and 30 minutes dipped) for different 9 gases. We found that the Co-doped In_2O_3 sensors excellent sensitivity and selectivity to CO gas. Thus, the Co-doped In_2O_3 sensor has potential applications in gas sensing.

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