Role of Cobalt doping on the gas sensing properties of In_2O_3 thick film sensors

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Abstract

Pure and Cobalt doped (Co-doped) In_2O_3 thick film sensors were synthesized via Flux route and doping by dipping technique, respectively. Scanning electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy were used to characterize sensor morphology and structure. Carbon monoxide (CO) sensing performance analysed in the range of temperatures and concentrations showed that Co-doped In_2O_3sensors exhibit significantly enhanced sensitivity and rate of performance with the response and recovery times of 5 s and 10 s, respectively. Combined with excellent selectivity and linearity, these properties make the fabricated sensors a good candidate for practical CO sensing.

Key words: **Co-doped, doping by dipping, sensors, sensitivity, response time, recovery time**

Introduction

Metal oxide semiconductors based gas sensors have attracted considerable attention on account of high gas sensing performances in the detection of toxic, hazardous, flammable and explosive gases. The sensing material, as the heart of a gas sensor, directly influences sensitivity, selectivity, response/recovery rate and working temperature of the gas sensor while the properties of sensing materials are mainly dependent on their morphologies and components [1].Solid-state gas sensors based on the film of metal oxides offer a number of advantages such as simple and low cost production to chemical resistance and suitability for a large number of target gases [2].The structure of the metal oxide semiconductor is easy to change according to the change of the external environment, and the change of the electronic structure affects the resistance. When the resistance of the metal oxide semiconductor changes, it is relatively easy to be detected, so it can be used as gas-sensing material. Semiconductor based sensors with low cost, high response, fast response time, has been widely applied to variousfields [3–6].Among these metal oxides, indium oxide (In_2O_3) is a new n-type semiconductor material with a large band gap (between 3.55 and 3.75eV) and low resistivity, and it has been used widely in fields such as optoelectronics, gas sensing, and catalysis [7].

In semiconductor metal oxide, doping is the considered launch of foreign body into an intrinsic semiconductor for the purpose of modulating its electrical, optical structural and gas sensing properties. Transition metals such as Co, Fe, Ni and Cr are also good catalysts. Research has shown that introduction of transition metals as doping additives, or even as addition phase also allows changing electrophysical properties, structural parameters, catalytic activity and adsorption properties of doped material [8].Among many research dopants in metal oxides, cobalt doped oxide shows potential in various applications. Accordingto reference studies, doping Cobalt in metal oxide creates more vacancies [9].

In this paper, we demonstrate a convenient method to synthesize good sensitive and selective CO sensor. The work was carried out from synthesis to applications of pure and Co-doped In_2O_3 thick film gas sensors. The experimental results indicate that introducing Co ions into the In_2O_3 system facilitate the sensitivity and selectivity variation of CO gas. The synthesis method provided an inexpensive and flexible route toward tailoring the morphology and gas response of pure and doped In_2O_3 thick film sensors.

2. Experimental

2.1 Synthesis of In_2O_3 powder

To obtain In_2O_3 powder, first In_2S_3 was synthesized by flux method. In the synthesis process of In_2S_3, the starting materials were indium sulphate, sulphur and sodium sulphide. The mixture of the starting materials was grinded in a pestle mortar for 3 hours and then taken into a crucible and placed into a furnace. The temperature of the furnace was lifted to 600 ^{0}C with rate of heating as 60 ^{0}C per hour. Surplus sulphur in the mixture got evaporated in the heating process. After this process the mixture was allowed to cool down to room temperature. The product formed was washed out many times in a petri dish with the help of deionised water and finally product was dried.

It could be possible to derive oxides from the respective sulphides by calcinations at higher temperatures in air. Therefore, In_2S_3 was calcineted at 900 ^{0}C for 10 h in air in order to replace sulphur by oxygen so as to get the required In_2O_3 product.

2.2 Formation of Pure In_2O_3 thick films

Screen printing technique was used for obtaining In_2O_3 thick films on glass substrates. Initially the In_2O_3 powder was thoroughly ground in an agate pestle mortar. Fine powder of In_2O_3 was mixed with a temporary binder (ethyl cellulose) and this mixture was combined with the solution of butyl cellosolve, carbitol acetate and terpineol to make a viscous paste. This paste was screen printed or deposited onto the glass substrates. The damp films were dried under IR lamp to remove organic binder and fired at 200 ^{0}C for 30 min.

2.3 Preparation of Sn-doped In_2O_3 thick films

Sn-doped In_2O_3 thick films were prepared by using 'doping by dipping technique'. For this purpose the solution of cobalt chloride,having 0.01 molarity was used. By fluctuating the dipping time (5, 10, 15, 20, 25, and 30 min) the doped films were prepared. For each dipping, a recently made new solution was used. The damp films were dehydrated under IR lamp and then placed into furnace for firing process at 500 ^{0}C for 2 hours. By firing process, cobalt chloride gets converted into cobalt oxide.

2.4 Gas Sensing

Static gas sensing system was used to study the sensing performance of Co-doped In_2O_3 thick films. In static gas sensing system, the electrical connections were provided through the base plate. Dimmerstat was fixed on the base plate to control the heating of the sample upto the expected operating temperature. There was an arrangement of thermocouple connected to the sample plate on which sensor film mounted and to digital temperature metre. The required gas concentration was injected by a syringe into the glass chamber through a gas inlet valve. For the current measurement after injecting gasses of different concentration, the applied voltage of the sensor was kept constant.

3. 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. Scanning electron microscope Hitachi (S-4800, Hitachi, Japan) (SEM) was used to examine the surface morphology of films. Quantitative elemental analysis of the film was carried out by computer controlled energy dispersive X-ray analyser (EDAX) attached to the scanning electron microscope.

4. Results and Discussion

4.1 X-ray Analysis

To elucidate the microstructure of the pure and Co-doped In_2O_3 samples, XRD analysis has been performed and diffraction patterns are reported in Fig. 1 (a) and (b). It was found that thick film microstructure as well orientation was both sensitive to the condition before and after doping.

Fig. 1 (a) shows the XRD patterns of pure In_2O_3 thick films. From this figure, it is clear that the film without doping doesn't shows the preferred oriented (222) peak and different peaks which appeared at 2θ values 22.3, 30.970, 32.59, 37.642, 45.577, 50.171, 60.541 were due to reflections from (211), (104), (110), (113), (024), (116), (125) planes of In_2O_3, respectively. Before doping one can see the increase in peak intensity and narrowing of peak width. The XRD patterns are matching well with JCPDS card no [JCPDS - 01073-1809].

Fig. 2 (b) shows the XRD patterns of Co-doped 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), (4 4 3), (5 4 1), (6 3 3), and (8 0 0) 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.

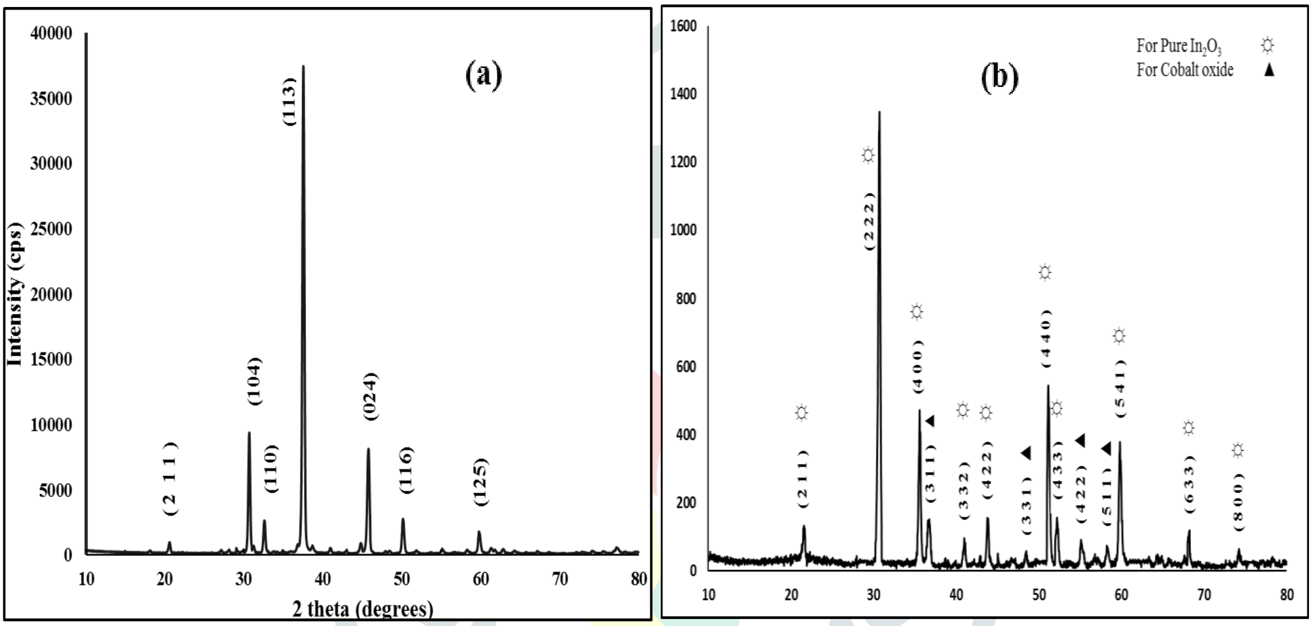

Fig.1XRD patterns of (a) undoped In_2O_3 and (b) Co-doped In_2O_3 thick films

4.2 SEM Analysis

Fig. 2(a) and (b) gives the SEM images of the pure and Co-doped In_2O_3 thick film gas sensors. Fig. 4(a) shows that the pure In_2O_3 thick film is relatively non uniform surface with diameters of 738-876 nm. Fig. 4(b) shows that the surfaces of the Co-doped In_2O_3 thick film is relatively irregular and rough but having small crystallites with diameters ranging within 336-759 nm. Also, the morphology of the doped film has slightly changed with crystallite size and deep cavities. We can see from both figures that the films still maintained their structure before and after doping. The change in the crystallite size and increase in deep cavities/void spaces plays a great role to perform better sensitivity.

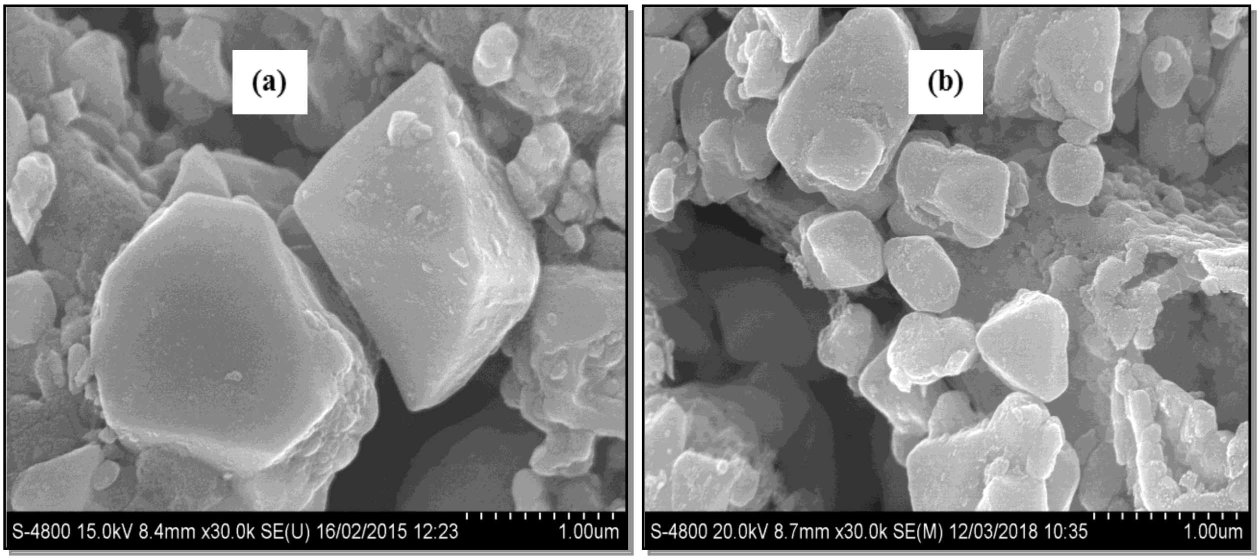

Fig.2SEM micrographs of (a) undoped In_2O_3 and (b) Co-doped In_2O_3 thick films

4.3 EDAX analysis

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 1 that the undoped (pure) In_2O_3 thick films are stoichimetric. 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.

Table 1. Quantitative Elemental Analysis

Element (at%)	Dipping time (min)						
	0 (pure)	5 minute dip	10 minute dip	15 minute dip	20 minute dip	25 minute dip	30 minute 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

4.3 Gas sensing properties

The operating temperature strongly influences response property of a semiconductor oxide sensor. The chemical activity of semiconductor oxide sensors can be fully stimulated out at the operating temperature [10].In Fig. 3(a) and (b) the temperature dependent response to CO (1000ppm) of pure and Co-doped In_2O_3 thick film based sensors is reported. The response of the gas is defined as the quotient $\frac{I_{air}-I_{gas}}{I_{gas}}$where $I_{air}$and I_{gas} are the sample electrical current with constantD.C. voltagein airand gas exposure, respectively. The maximum response of pure and Co-doped In_2O_3 thick film based sensors to COis reached at the same temperature (150 ^{0}C). The response of pure and Co-doped In_2O_3 thick film sensorsdecreases slowly at temperature higher than 200 ^{0}C. One can seethat the maximum responses to COare10.2 and 76.89 at 150 ^{0}Cfor the pure and Co-doped In_2O_3sensors respectively.Gas sensing properties could improve by adjusting crystallite size and the porosity of sensing materials [11,12]. Duringthe process of modification, by doping with Co changes happened to structure and morphology (increase in roughness and cavities) of In_2O_3 thick film sensors. The oxide based semiconductor sensor works on principle of change in conductivity with the interaction of the target gas molecules. It means that a larger surface area provides more adsorption sites for surface reaction. When comparing fig.3 (a) and fig.3 (b), we can conclude that after doping, the selectivity of the sensor is greatly increased.

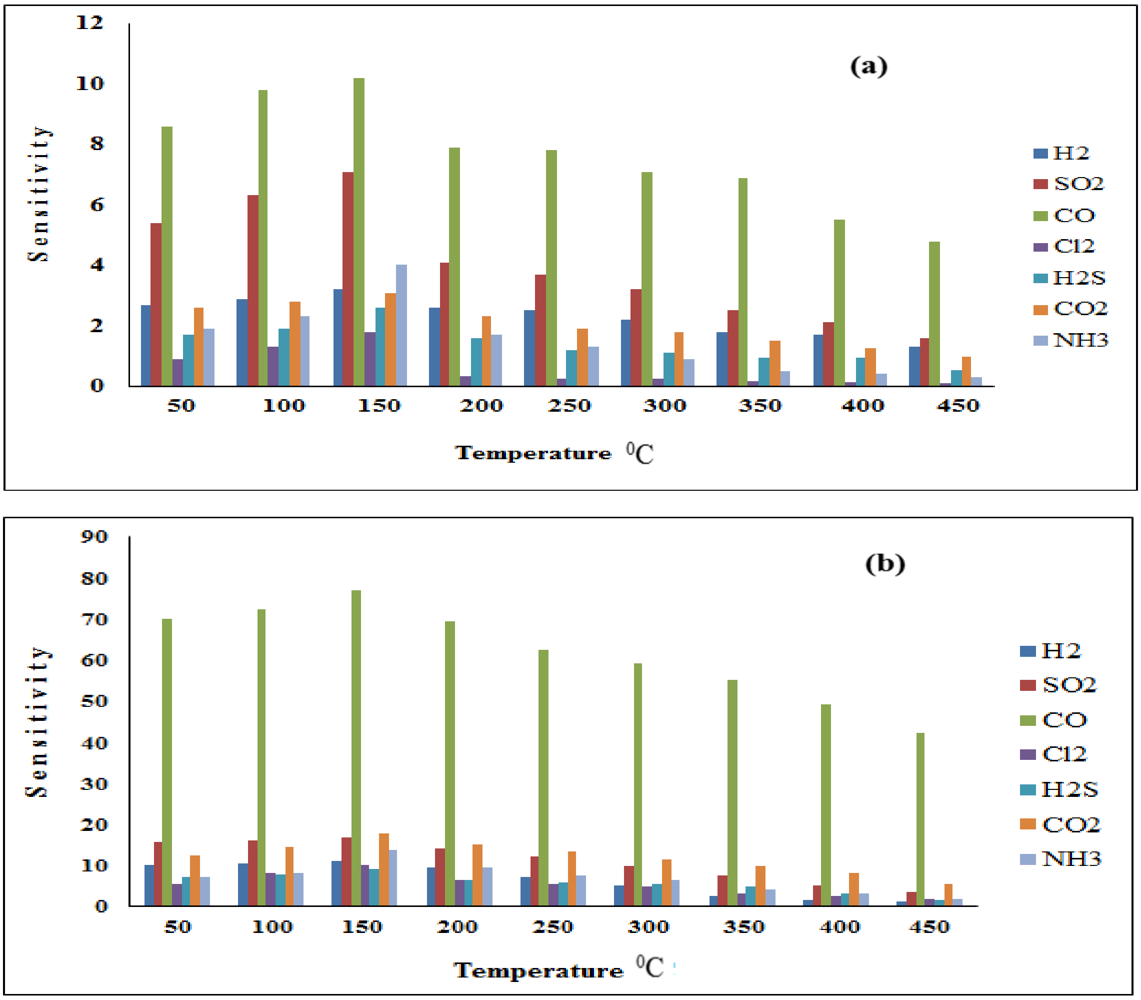

Fig. 3

Sensitivity and Selectivity graph (a) Pure In_2O_3 sensor (b) Co-doped In_2O_3 sensor

4.4 Response and recovery times

Response time is defined as the time taken for the sensor to attain 90% of the maximum increase insensingcurrent on exposure and recovery time means the time taken for the sensor get back to 90% of the maximum decrease in sensing current for unexposed target. The response and recovery times founded at 1000 ppm concentration were 8 and 19 s,respectively for both pure and Co-doped In_2O_3 thick film sensors. The sensor has fast response time which means that the oxygen ions at the film surface may immediately interact and bonded with the CO molecules, this fast interaction provides a large number of charge carriers which caused the sharp rise of the sensing current.

5. Conclusion

In this study, pure and Co-doped In_2O_3 sensors was made using flux route and doping by dipping method respectively. From the results given above, it was demonstrated that Co-doped In_2O_3 sensor could be provide favourable response for CO detection. The XRD pattern confirmed the formation of cubic cobalt oxide. The highest sensitivity measured was 10.2 and 76.89 for pure and Co-doped In_2O_3 sensors respectively. The fabricated sensors have fast response time (8s) and recovery time (19s). Good sensitivity, selectivity and response for 1000 ppmCOgas concentrationhave been obtained.

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