Sn Doped In_2O_3 Thick Films: Doping by Dipping, Characterizations and Gas Sensitive Properties

Fahemeeda Bano Khursheed Ahmed[1], M.D. Mahanubhav[2]

[1,2]*Dept. of Physics, JET's Z.B. Patil College, Dhule-424002, Maharashtra, India*

[1]*faim_dhule@rediffmail.com,*[2]*mahanubhav@rediffmail.com*

Abstract

This study aimed at the preparation of Sn doped In_2O_3thick film gas sensor with a doping by dipping method and tested its gas-sensing properties to LPG gas at room temperature. The sensors were characterized through scanning electron microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), and X-ray diffraction (XRD). The sensing results demonstrate that Sn-doped In_2O_3sensor shows an excellent gas sensing properties as compare to undoped (pure) In_2O_3 sensors. The response to 1000 ppm LPG was 51.64. The response and recovery times were 4 and 11s respectively for both pure and Sn-doped In_2O_3 sensors.

Keywords: *In_2O_3, thick film, doping, XRD, SEM, EDAX*

1. Introduction

In the recent years, noticeable advancement has been achieved in gas sensors. The driving approach includes house hold dangerous gas, detection of noxious gasses in industrial area, food quality level, prominent applications in medical diagnostic field and atmosphere quality [1]. Indium oxide (In_2O_3), is a wide-band gap n-type semiconductor (~ 3.7 eV), is inclusively used to sense harmful dangerous gasses with particular response in consideration of their electrical conductivity could differ with a great extent as the enclose gas atmosphere changes [2].Still, there are some downsides which limit their applications such as poor selectivity and low sensitivity [3]. Hence, to improve the sensing quality of these materials various methods have been introduced including doping, hetrostructure formation and decorating with noble metals [4].For much improvement in the gas sensing properties of In_2O_3 sensors, establishment of dopant in the host In_2O_3 is one of the successful and implicit methods [5].

Sn-doped In_2O_3, oftenly specified as indium tin oxide (ITO), possessing the properties of transparent conductive materials. It has a wide band gap (~3.8 eV). Two fundamental properties of ITO are: electron conductivity because of high electron degeneracy and high transmittance near IR region [6].From the last few decades, ITO has been broadly used as elegant windows, LED'S and solar cells [7].

To upgrade the utilities and assembling new applications, modern and modified methods of film preparation have been introduced. There are assorted methods such as sol gel method, dc sputtering, pulsed laser deposition and surface modification [8]. These are the various methods used by different researchers; instead of these methods we used dipping method for doping, which was a simple

and easy technique. Here in we would like to report tin doped In_2O_3 thick film sensor, which shows excellent performances in detecting LPG. The materials show improved gas sensing properties, after doping with tin.

2. Experimental

2.1 Synthesis of In_2O_3 powder

To synthesize the In_2O_3 powder, first In_2S_3 was prepared by flux method using sodium sulphide as a flux. In the synthesis process of In_2O_3, the starting materials wereindium sulphate, sulphur and sodium sulphide. The starting materials were taken in a proper proportion to get In_2S_3 compound. The mixture of the starting materials was grinded in a pestle mortar for 3 hours and then poured into crucible and placed into a furnace. The temperature of the furnace was raised to 600 ^{0}C with rate of heating as 60 ^{0}C per hour. Excess 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. To compose the paste of appropriate viscosity, 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. This paste was screen printed onto the glass substrates. The damp films were dehydrated under IR lamp and to remove organic binder,fired at 200 ^{0}C for the time span of 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 tin chloride with 0.01 molarity was used. By varying 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, tin chloride gets converted into tin oxide.

2.4 Gas Sensing

Static gas sensing system was used to study the sensing performance of Sn-doped In_2O_3 thick films. In static gas sensing system, the electrical connections were provided through the base plate. Dimmer stat 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.

2.5 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 and Discussion

3.1 Elemental Composition

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 Indium deficient and oxygen rich and hence nonstoichiometric. The at% of tin goes on increasing with dipping time, reaches to a maximum and then decreases with a further increase in dipping time interval. The film with dipping time 20 min was observed to be most Indium deficient. The film dipped for 20 min, consists of the largest at% of Sn.

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	32.54	27.73	25.13	19.91	12.49	15.51	21.62
O	67.46	67.89	68.13	68.47	68.28	68.62	67.58
Sn	---	4.38	6.74	11.62	19.23	15.87	10.8

3.2 XRD analysis

Fig. 1 shows the XRD patterns of the (a) pure In_2O_3 and (b) Sn-doped In_2O_3 thick film gas sensor. It is clear that the crystalline peaks in the XRD pattern in Fig. 1 (a) and (b) are in a good agreement with the diffraction data of cubic indium oxide and indium tin oxide from the respective JCPDS cards. Both patterns show (211), (222), (411), (440) and (145) peaks whichassign In_2O_3 (JCPDS No. 89-4595). Fig. 1(b) reveals additional peaks such as (123) and (411) which assign SnO_2 (JCPDS No. 89-4598).

Since the amount of In_2O_3 is much higher than that of SnO_2, the peak intensity of In_2O_3 is relatively high compared to that of SnO_2. The intensity of diffraction peak corresponding to the (222) orientation is lower in case of pure In_2O_3 thick film sensor but after doping it becomes prominent as compare to other peaks.

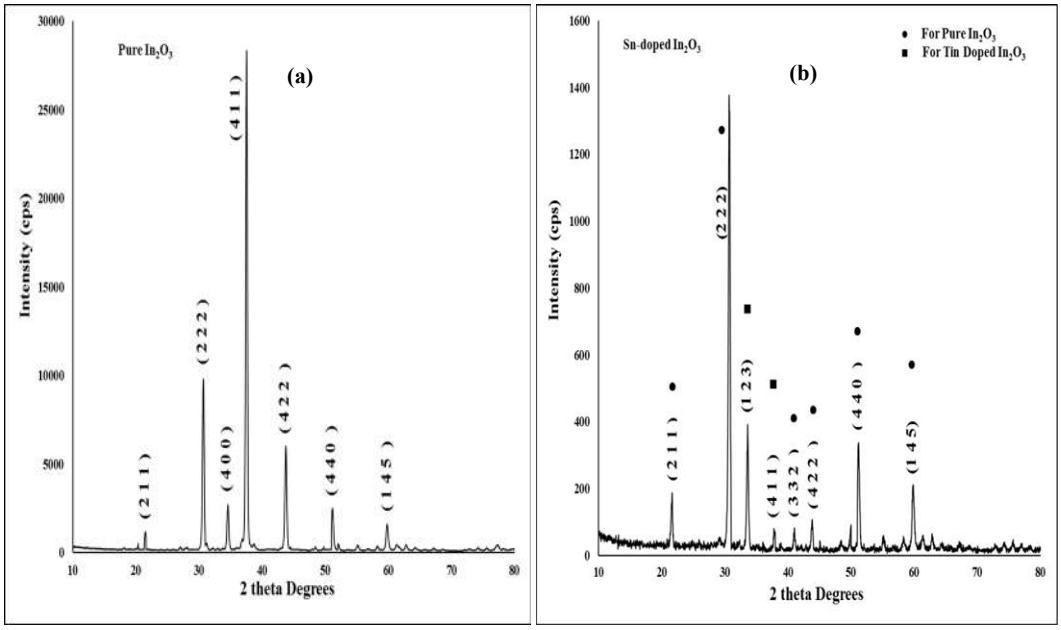

Figure. 1 XRD patterns of (a) pure In_2O_3 and (b) Sn-doped In_2O_3 thick film gas sensor.

3.3 SEM analysis

Fig.2 (a) and (b) shows typical SEM images of samples before and after doping respectively. It can be observed pure In_2O_3 thick film gas sensor contains large grains and more void spaces as compare to Sn-doped In_2O_3 thick film gas sensor.

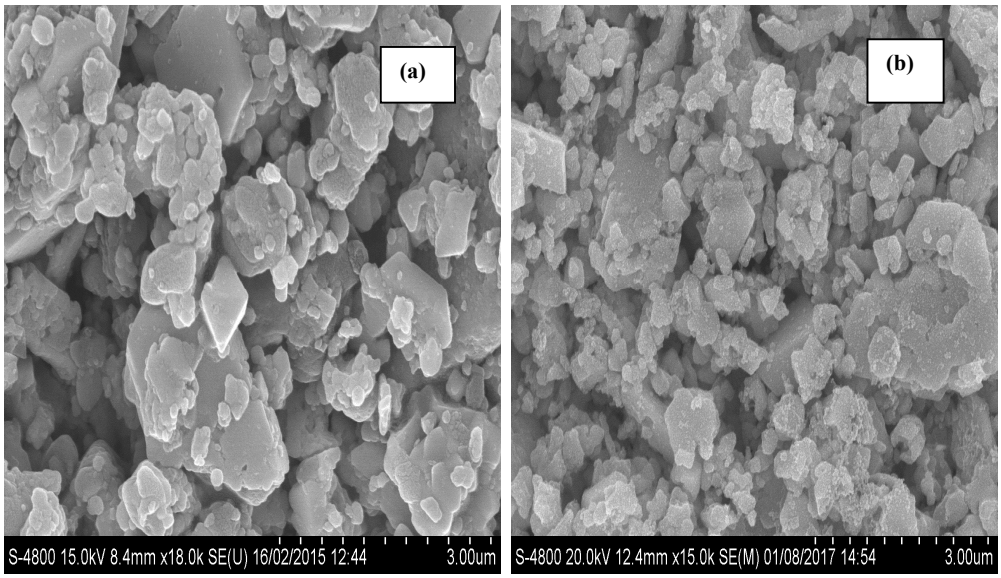

Fig.2SEM micrographs of (a) undoped In_2O_3 and (b) Sn-doped In_2O_3 thick films

3.3 Gas sensing properties for LPG

Gas sensing mechanism is a chemical process between objective gas in the surrounding and metal oxide surface [9]. The response of the pure In_2O_3sensor to 1000 ppm of various testing gases at 250 ^{0}C is described infig.3. (a) In_2O_3 sensor shows good selectivity to LPG gas in comparison with H_2, SO_2, CO, Cl_2, H_2S, CO_2, Ethanol and NH_3 gasses. The sensitivity is found to be 16.89 at 250 ^{0}C. The response and recovery time was 4 and 11 seconds, respectively. Fig.3. (b) shows the response of Sn-doped In_2O_3 sensor. From fig.3.(b) one can clearly observe that Sn-doped In_2O_3 sensor shows an excellent response to LPG gas as compare to pure In_2O_3. The gas sensitivity is 51.64 at 250 ^{0}C for 1000 ppm LPG gas and the response and recovery time was 4and 11 seconds, respectively.

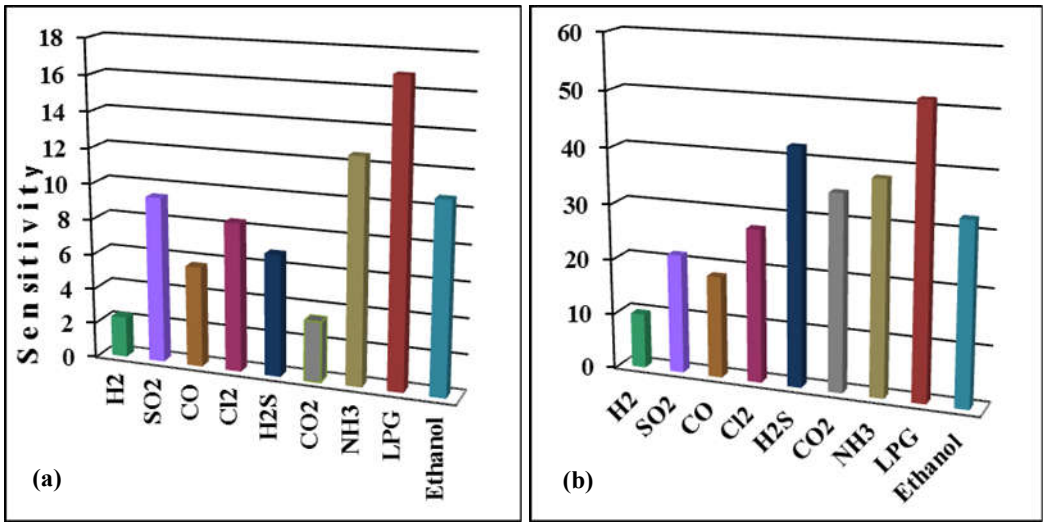

Fig.3 The selectivity of the In_2O_3 sensor to 1000 ppm for LPG gas among different gases at 250 °C. (a) for undoped (pure) In_2O_3 and (b) for Sn-doped In_2O_3

4. Conclusions

The gas sensing properties of In_2O_3 thick films have been investigated. First, In_2S_3powder was prepared by flux route and after calcination of In_2S_3 powder In_2O_3 was obtained. Morphologies and microstructures of the sample were characterized by means of XRD and SEM. The gas sensing results shows that the response to LPG gas was 16.89 and 51.64 at 250 ^{0}C for pure and Sn-doped In_2O_3 respectively..

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