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Contents

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CdO Doped Indium Oxide Thick Film as a Low Temperature H_2S Gas Sensor

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Abstract: The thick films of AR grade In_2O_3 were prepared by standard screen-printing technique. The gas sensing performance of thick film was tested for various gases. It showed maximum gas response to ethanol vapor at 350 ^oC for 80 ppm. To improve the gas response and selectivity of the film towards a particular gas, In_2O_3 thick films were modified by dipping them in an aqueous solution of 0.1 M $CdCl_2$ for different intervals of time. The surface modified (10 min) In_2O_3 thick film showed maximum response to H_2S gas (10 ppm) than pure In_2O_3 thick film at 150 ^oC. Cadmium oxide on the surface of the film shifts the gas response from ethanol vapor to H_2S gas. A systematic study of sensing performance of the thick films indicates the key role played by cadmium oxide on the surface of thick films. The selectivity, gas response and recovery time of the thick films were measured and presented. *Copyright © 2011 IFSA.*

Keywords: Thick film, Ethanol vapor, CdO, H_2S gas sensor, Gas response, Selectivity.

1. Introduction

Now-a- days the vast growing industries, various machines and an increasing large number of vehicles are responsible for spoiling the healthy life of human beings and all living organisms. Air pollution is found to be very dangerous as it is related to the respiratory systems. Some gases like CO, CO_2, H_2S and Cl_2 evolved are found to be very toxic and create allergic and respiratory diseases like asthma, allergic bronchial asthma and rhinitis [1-4].

The need for a novel gas sensor capable of providing reliable operation in harsh environments is now greater than ever. Such sensors find a range of applications, including the monitoring of traffic pollutants or food quality with specially designed electronic noses [5, 6]. Gas sensors based on metal oxides are commonly used in the monitoring of toxic pollutants and can provide the necessary sensitivity, selectivity and stability required by such systems [7]. Gas sensing at room temperature is of great interest; most of the currently available sensors, expect a few types of polymer-based gas sensor operate at elevated temperature [8, 9]. Thick film technology is often used to fabricate such sensors and possesses many advantages; for example, low cost, simple construction, small size and good sensing properties [10]. In addition, this approach provides reproducible films consisting of a well-defined microstructure with grains and grain boundaries that can be studied easily [11].

Hydrogen sulphide (H_2S) is a toxic gas with a peculiar foul smell. It is corrosive and is naturally occurring due to decomposition of some organic matter in wastewater, volcanic gases, hot springs with smells like rotten eggs, coking ovens, craft paper mills, food processing, coal mines, oil and natural gas industries. It is used in large amounts in various chemical industries, research laboratories and as a process gas in the production of heavy water.

Gas sensors have been used for industrial process controls, for the detection of toxic environmental pollutants, in human health and for the prevention of hazardous gas leaks, which comes from the manufacturing processes [12-14]. Though these are different types of gas sensors that have been used to detect several inflammable, toxic and odorless gases, the gas sensors based on metal- oxide are playing an important role in the detection of toxic pollutants and the control of industrial processes. Hydrogen sulphide (H_2S) detection is nowadays a very important target for different processes, such as coal or natural gas manufacturing. This gas can be very dangerous for human bodies when its concentration is greater than 250 ppm. Monitoring and controlling of H_2S is crucial in laboratories and industrial areas. Semiconductor gas sensor in the form of thin or thick films, based on metal-oxide like SnO_2, WO_3 and p-n heterojunctions, have been reported in the literature for H_2S detection [15-21].

Gas sensitivity, selectivity and durability are the most important sensor properties. In order to attain high response and excellent selectivity, different approaches such as microstructure control, additives, physical or chemical filters, operating temperature etc. have been adopted to modify the sensing properties of semiconductor metal oxide gas sensors. It is well known that sensing mechanism is based on the surface reaction of the particles with the exposed gas (adsorption and desorption of the test gas). Semiconductor metal oxide has attracted great attention in the past few years [22, 23]. It is well known that the semiconductor metal oxide such as ZnO, SnO_2, Fe_2O_3, Ga_2O_3, Sb_2O_3, In_2O_3 etc. are sensitive to toxic and inflammable gases [24].

Indium oxide (In_2O_3) belongs to the class of wide – band gap metal oxide, which has a wide application in preparing transparent conducting windows [25]. Moreover, this oxide has been shown to be a promising material for semiconductor gas sensor [26, 27]. As a gas sensing material In_2O_3 has been extensively applied to detect O_3, NO_2 and CO etc. [28, 29]. But, up till now, there are very few reports on the H_2S sensing properties of In_2O_3.

In this work, In_2O_3 thick films were prepared by screen printing on to glass substrates .The films surface were modified by dipping them into the aqueous solution of 0.1 M $CdCl_2$. The sensing performance of the films were tested by static gas sensing system for different gases such as H_2S, CO, CO_2, H_2, LPG, NH_3, Cl_2, O_2 and ethanol vapor etc.

2. Operating Principle of Gas Sensor

Since long it has been known that adsorption of reducing gas molecules results in decrease in electrical resistance of oxide material [30]. The In_2O_3 materials are characteristically n-type semiconductor due to non-stoichiometry associated with oxygen vacancy and/or metal excess which acts as donor states thus providing conduction electrons. However, the overall surface resistance of such films is generally influenced by chemisorptions (chemical adsorption) of oxygen from air on the surface and at the grain boundaries. The chemisorbed oxygen traps conduction electrons and remains as negatively charged species (O_2^-, O^- or O^{2-} depending on temperature.) on the surface [31]. The process results in an increase of surface resistance. In presence of reducing gases the trapped electrons are released due to the reaction between the gas molecules and negatively charged chemisorbed oxygen species resulting in decreasing in resistance of the materials. When the gas is removed from the sensor environment, the resistance again increases and the material recovered to original resistance.

3. Experimental

3.1. Preparation of Pure In_2O_3 Thick Films

The AR grade powder of In_2O_3 was calcined at 1000 ^oC for 6 h. Then In_2O_3 powder was milled for 2 hrs using planetary ball mill to obtain fine-grained powder. The thixotropic paste was formulated by mixing the fine powder of In_2O_3 with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbital acetate and terpineol etc. The weight ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen printed on a glass substrate in a desired pattern [32, 33]. The sensitivity increases with the porosity as well as with thickness of the thick film [34]. The thick films were fired at 550^oC for 30 min. Silver contacts are made for electrical measurements.

3.2. Preparation of Surface Modified In_2O_3 Thick Films

The pure In_2O_3 thick films were surface modified by dipping them into 0.1 M aqueous $CdCl_2$ solution for different intervals of time: 5, 10, and 20 min. [35]. These thick films were dried under IR lamp at 80 ^oC for 1h and followed by firing at 550 ^oC for 30 minutes. During firing process, at higher temperature $CdCl_2$ would be converted into CdO.

3.3. Thickness Measurements

The thickness of the thick films was measured by using the Taylor-Hobson (Talystep, UK) system and was observed in the range from 60 to 65 µm. The reproducibility of the thickness was achieved by maintaining the proper rheology and thixotropy of the paste

3.4. Details of Gas Sensing Unit

The sensing performance of the thick films was examined using a 'static gas sensing system'. There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the thick film. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the thick film sensor, and the current was measured by a digital Pico ammeter. The air was allowed to pass into the glass chamber after every gas exposure cycle.

4. Characterizations

4.1. Structural Analysis

The purity and crystallinity of the calcined powder structure was examined using X-ray diffractogram (XRD) with CuKα radiation (wavelength 1.5418 Å). The average grain size was calculated according to Debye- Scherrer's equation, it was observed to be 51 nm, provided in Eq. (1).

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

where β is the full width at half-maximum intensity (in radians) of a peak at an angle θ; K is a constant, depending on the line shape profile; λ is the wavelength of the X-ray source.

Fig. 1 depicts that the XRD patterns are indexed with pure In_2O_3 with cubic structure. The observed peaks in figure are matched well with (JCPDS Card No. 01-071-2194) reported data of In_2O_3 [36].

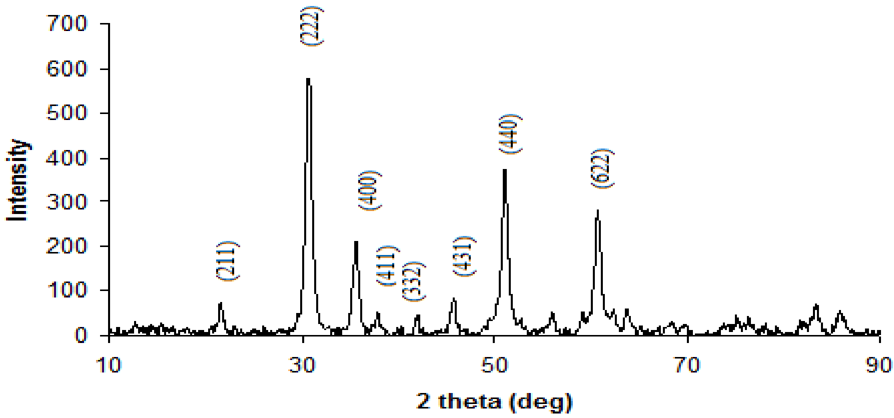
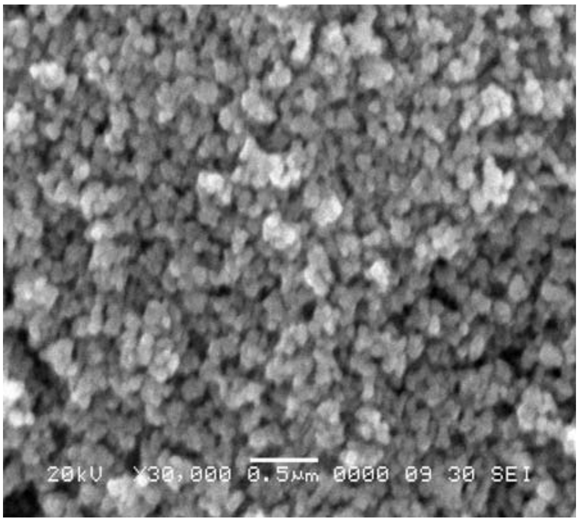


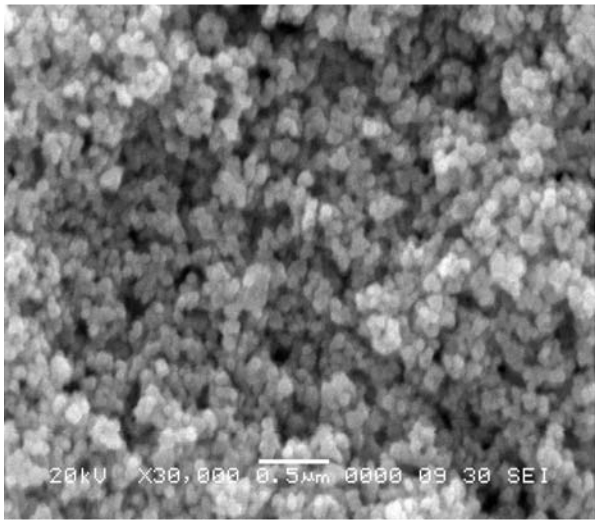
Fig. 1. X-ray diffractogram of pure In_2O_3.

4.2. Microstructural Analysis

Fig. 2 shows the micrographs of pure In_2O_3 and surface modified In_2O_3 thick films. The comparison of these micrographs shows the interesting changes in morphology. Scanning electron microscopic (SEM) studies were carried out by using JEOL JSM 6360 (LA) Japan. Fig. 2(a) depicts the SEM image of pure In_2O_3 thick film fired at 550 ^oC. The thick film consists of voids and a wide range of grains with size distribution ranging from 0.25 μm to 0.5 μm, distributed non-uniformly. Fig. 2 (b) represents the SEM image of surface modified In_2O_3 (10 min.) thick film fired at 550 ^oC. It shows a number of small particles distributed uniformly between the larger grains around the In_2O_3, which may be attributed to the presence of CdO. The grain size range was observed to be from 0.22μm to 0.5μm. The presence of CdO particles on the surface of the thick films alters the adsorption-desorption ability of the thick films. The altered surface morphology of the thick films shifts the affinity and reactivity of thick films towards the H_2S gas**.** EDAX analysis of CdO surface modified thick films shows the presence of CdO and the appearance from the thick films indicates that the CdO particles are present at the surface of the In_2O_3 thick films.



(a)



(b)

Fig. 2. SEM images of (a) pure In_2O_3 and (b) CdO surface modified In_2O_3 (10 min.) thick films.

4.3. Quantitative Elemental Analysis by EDAX

The quantitative elemental analysis of the pure and CdO surface modified In_2O_3 thick films was carried out by using an energy dispersive spectrophotometer (EDS) JEOL – JED– 2300 LA Japan. The constituent elements such as In, O and Cd associated with various thick films are presented in Table 1.

It is clear from the Table 1 that the weight percentage of cadmium is increased with dipping time and reached to a maximum. The thick film with the dipping time of 10 min. as observed to be more oxygen deficient (55.03wt.%). This oxygen deficiency may make the sample possible to adsorb a large amount of oxygen species.

Table 1. Quantitative elemental analysis of pure and CdO surface modified In_2O_3 thick films.

Film	In (wt%)	O (wt%)	Cd (wt%)
Pure In_2O_3	41.33	58.67	-
CdO Surface Modified, Dipping time: 5 min.	37.90	61.17	0.94
Dipping time: 10 min.	41.73	57.05	1.22
Dipping time: 20 min.	41.30	58.10	1.98

5. Electrical Properties

5.1. I-V Characteristics

Fig. 3 shows the I-V characteristics of pure In_2O_3 and surface modified CdO thick films at room temperature. I-V Characteristics are observed to be symmetrical in nature, indicating the ohmic nature of silver contact.

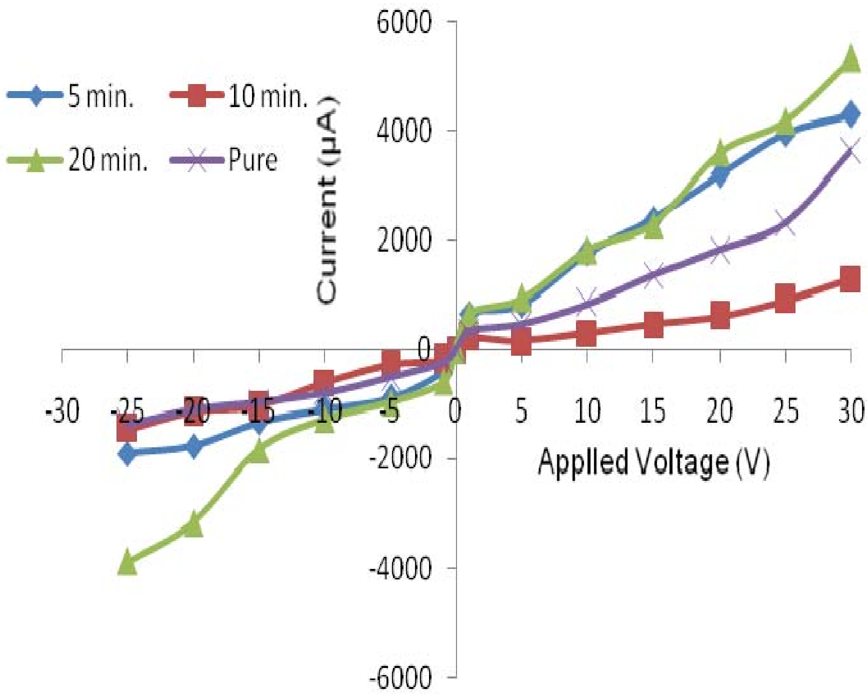


Fig. 3. I-V Characteristics of pure In_2O_3 and surface modified CdO thick films.

5.2. Dependence of Electrical Conductivity with Temperature

Fig. 4 shows the dependence of electrical conductivity of pure In_2O_3 and surface modified by CdO In_2O_3 thick films in air ambience. The electrical conductivity of these thick films goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semi conducting nature of the thick films.

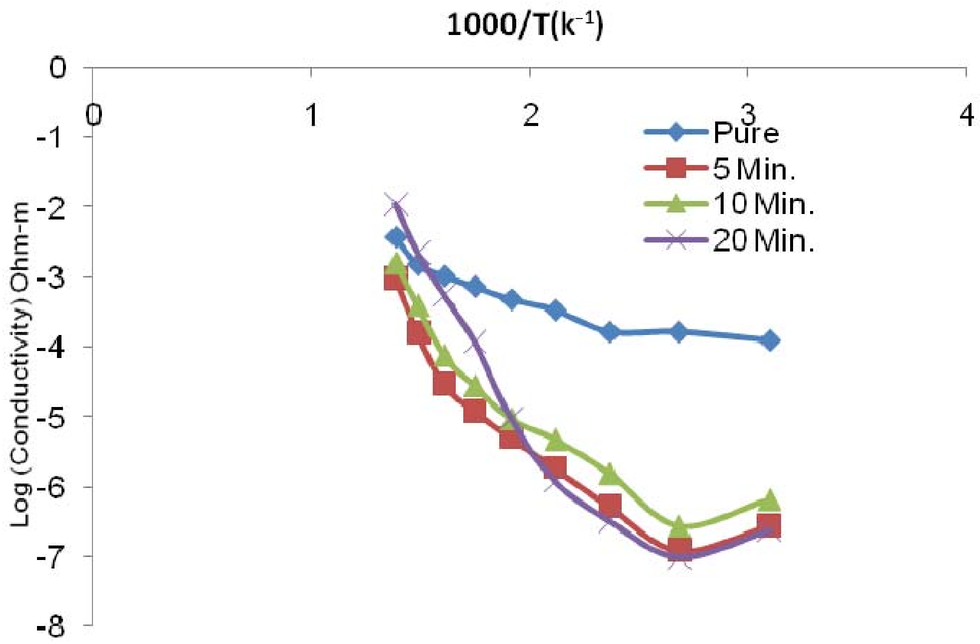


Fig. 4. Variation of electrical conductivity with temperature.

6. Gas Sensing Performance

6.1. Gas Response of Pure In_2O_3 Thick Film

Gas response of thick films was defined as the ratio of the change in conductance of a sample on exposure to the test gas to the conductance in air [37].

$$\text{Gas response} = \left|\frac{Gg - Ga}{Ga}\right| = \left|\frac{\Delta G}{Ga}\right|, \quad (2)$$

where Ga= conductance of sensor in air, Gg = Conductance of sensor in gas. & ΔG is the change in conductance.

Fig. 5 shows the variation in the gas response of ethanol vapour (100 ppm) with operating temperatures ranging from 50 °C. to 450 °C. It is noted from the graph that response increases with increasing temperature, and attains a maximum at 350°C, and decreases with further increase in operating temperature.

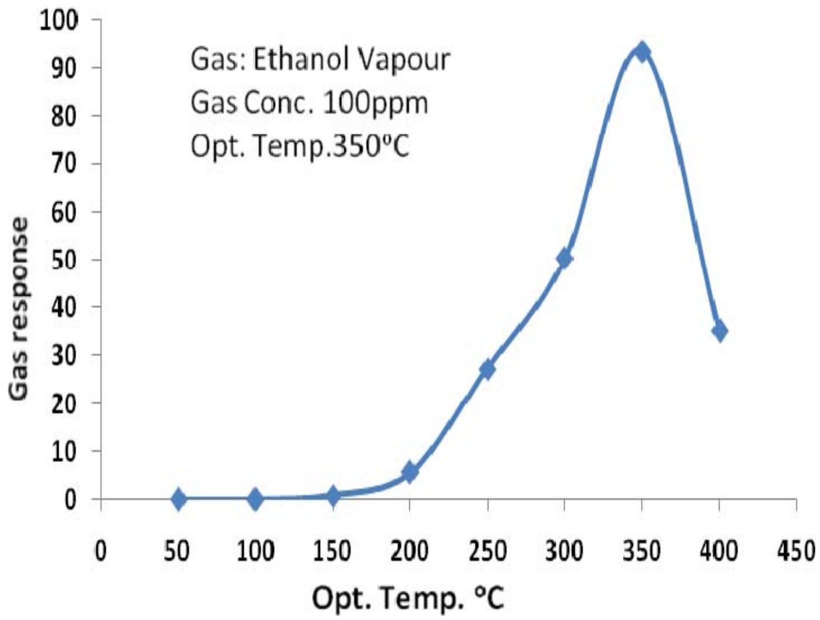


Fig. 5. Variations of ethanol vapor response of pure In_2O_3 thick film with operating temperature.

6.2. Selectivity of Pure In_2O_3 Thick Film

Selectivity is defined as the ability of sensor to respond to a certain gas in the presence of other gases. Selectivity is another important parameter of a gas sensor .The sensor must have rather high selectivity for its application. Pure In_2O_3 thick film is examined for different gases at different operating temperatures and the results are shown in Fig. 6. The bar diagram indicating selectivity of pure In_2O_3 thick film at 350°C to ethanol vapour against the other gases. The thick film is the most selective to ethanol vapor against the other gases.

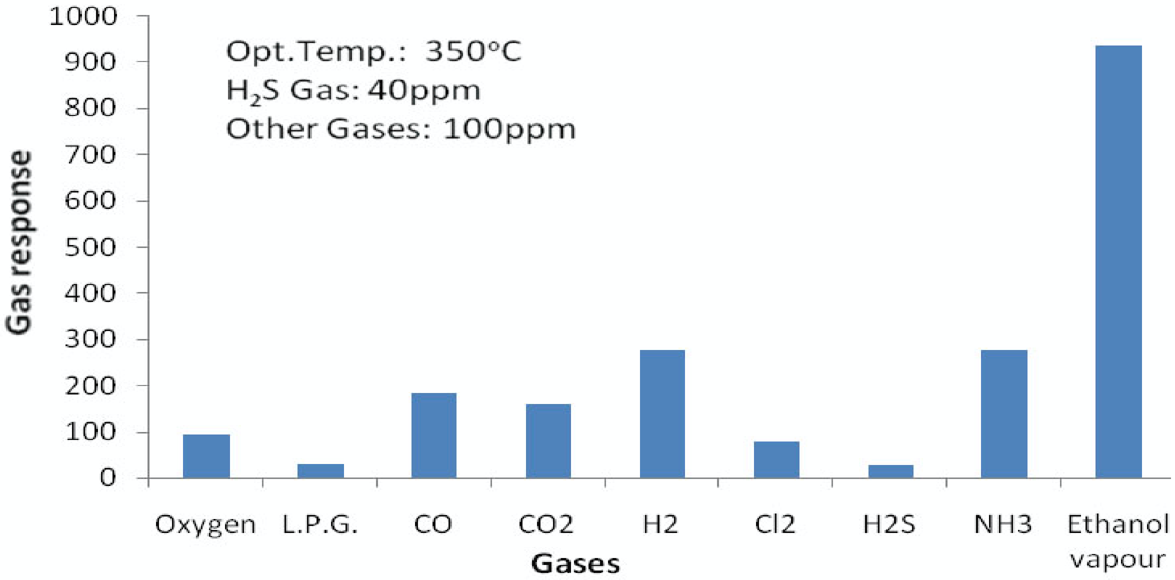


Fig. 6. Selectivity of pure In_2O_3 thick film.

6.3. Gas Response with Operating Temperature

Fig. 7 shows the variation in the gas response of pure and CdO surface modified In_2O_3 thick films to H_2S gas with operating temperature ranging from 50 °C to 450 °C. The H_2S gas response of pure In_2O_3 thick film fired at 550 °C was 5.3 at 150 °C while that of CdO surface modified (10 min.) In_2O_3 thick film was 8971 at the same operating temperature. The CdO surface modified of In_2O_3 thick films was observed to be good response for H_2S gas sensing than the pure In_2O_3 thick film. The CdO surface modified (10 min.) In_2O_3 thick film showed maximum gas response to H_2S gas. The amount of CdO incorporated onto the In_2O_3 thick film surface would be optimum to cover the surface uniformly, leading to the enhanced adsorption mechanism.

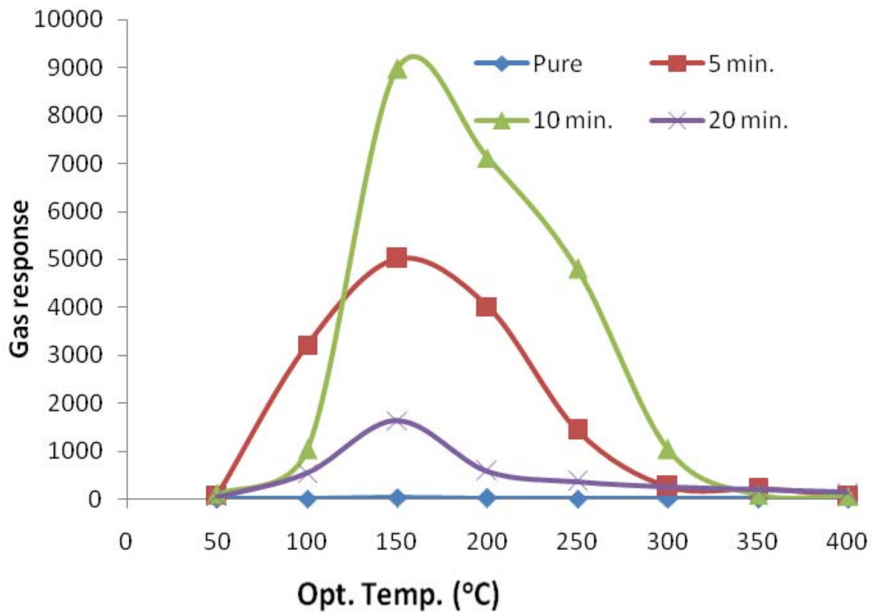
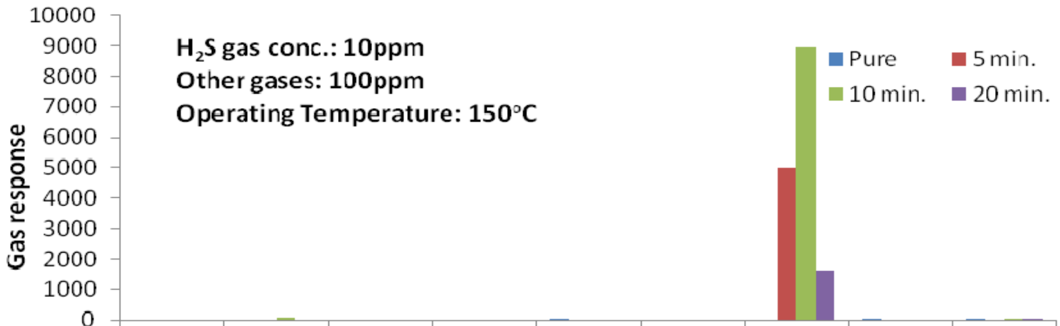


Fig. 7. Variation of H_2S gas response with operating temperature.

The gas response to H_2S gas goes on increasing with increasing the amount of CdO up to a certain limit attains maximum gas response and decreases with increasing the amount of CdO. The largest gas response in case of the sample (10 min.) may be because of more available sites (misfits). The surface of CdO misfit regions enhances the oxygen adsorption on the surface. Thus the number of oxygen species adsorbed on the activated surface would be larger. The larger the number of oxygen species adsorbed, the faster would be oxidation of H_2S gas. The pure In_2O_3 thick film showed highest response to ethanol vapor, while CdO surface modified thick film shows highest response to H_2S gas. The alteration in nature of gas sensing response from ethanol vapor to H_2S gas for the CdO surface modified In_2O_3 thick film could be largely due to possibility of formation of cadmium sulphide more easily. This would increase the conductance of the thick film crucially, enhancing gas response. The abrupt decrease of response for the thick film doped with more amount of Cd is probably due to the reduction of active sites correlated with the agglomeration of Cd grains. At higher concentrations, the Cd would mask the entire base material and would resist the gas to reach to the surface active sites, so gas response would decrease further [38].

6.4. Selectivity of CdO Surface Modified In_2O_3 Thick Films

It is well known that the gas sensitivity is greatly influenced by the operating temperature and the amounts of additives. In order to determine the optimum operating temperature and additive amount, the gas response of CdO thick films with different CdO content to 10 ppm H_2S gas were measured at different operating temperatures. The gas response of pure In_2O_3 thick film to H_2S gas was also measured for comparison. The results are shown in fig. 8 It can be seen obviously from Fig. 8 that the pure In_2O_3 thick film has a poor response to H_2S gas, while the CdO surface modified thick films with different amounts of Cd, all exhibit much higher gas responses than the pure one. Among all the CdO surface modified In_2O_3 thick films, the one with dipping time 10 min. (0.38 wt.%) shows the largest gas response to H_2S gas. Whilst, the gas sensing property change trend is similar to the specific surface area change trend of the samples. The lower operating temperature could lead to lower energy consumption, while is one of current pursuits in solid-state gas sensors. Based on the above results, we can see that the CdO/In_2O_3 thick films exhibit much better gas response and lower operating temperature. Fig. 8 represents the bar diagram indicating selectivity of CdO surface modified In_2O_3 thick film dipped for 10 min. and the operating temperature was 150 °C to H_2S gas against the other gases. The CdO surface modified In_2O_3 thick film dipped for 10 min. was the best selective to H_2S gas.



	Oxygen	L.P.G.	CO	CO2	H2	Cl2	H2S	NH3	Ethanol Vapour
Pure	9.3	6	12.4	16	27.6	7.7	5.3	43	63
5 min.	0.9	8.13	0.4	0.14	0.9	0.28	5014	2.1	14.17
10 min.	0.13	67.4	0.99	0.9	0.11	0.23	8971	3.1	45.5
20 min.	0.09	9.5	0.97	0.55	0.18	0.11	1632.33	4.9	33.2

Fig. 8. Selectivity of pure and CdO surface modified In_2O_3 thick films at operating temp. 150 °C.

7. Discussion

7.1. Pure In_2O_3 Thick Film as an Ethanol Vapor Sensor

Indium Oxide is a basic oxide. Interaction of ethanol vapor with the oxide surfaces is quite complicated and sensor signal depends both on the density and nature of surface centers. There are two general ways of ethanol vapor conversion [39]: dehydration and oxidative dehydrogenation. The first one takes place mainly over the surface with Bronsted acidity and gives a low sensor response. On the contrary, dehydrogenation process needs Lewis acid-base pairs [40] and leads to high response due to reaction with chemisorbed oxygen O_s^- :

$$C_2H_5OH + O_s^- \rightarrow CH_3CHO + H_2O + e^- \tag{3}$$

In metal oxide surface oxygen species with a negative charge and metal cations play a role of Lewis basic and acidic centers, respectively. Therefore, in the case of similar adsorptive ability of samples the selectivity of ethanol vapor conversion into acetaldehyde and the sensor signal value depend on the ratio between strong (Lewis) and weak (Bronsted) acid centers. It means that over the surfaces showing mainly Bronsted acidity, ethanol vapor undergoes conversion via C_2H_4 (dehydration) and such materials have poor sensitivity towards ethanol vapor. On the contrary, samples with a dominant Lewis acidity show high response towards C_2H_5OH vapor because of dehydrogenation conversion

7.2. CdO Surface Modified In_2O_3 Thick Film as a H_2S Gas Sensor

The In_2O_3 sensors were surface modified by dipping it into a 0.1 M $CdCl_2$ solution. The CdO species would be distributed uniformly throughout the surface of In_2O_3 thick film. Due to this not only the initial resistance of the sensor is high but this amount is sufficient to promote the catalytic reaction effectively, and the overall change in the resistance on exposure of reducing gas (H_2S) leading to high sensitivity.

As generally mentioned earlier, the gas-sensing mechanism 0f In_2O_3-based thick films belong to the surface controlled type, which is based on the change in conductance of the semiconductor. The oxygen adsorbed on the surface directly influences the conductance of the In_2O_3-based sensors. The amount of oxygen adsorbed on thick film surface depends on the operating temperature, particle size and specific surface area of sensor. The state of oxygen on the surface of CdO/In_2O_3 thick film undergoes the following reaction,

$$O_2(gas) \rightarrow O_{2(ads)} \tag{4}$$

$$O_{2(ads)} + e^- \rightarrow O^-_{2(ads)} \tag{5}$$

$$O^-_{2(ads)} + e^- \rightarrow 2\ O^-_{(ads)} \tag{6}$$

$$O^-_{(ads)} + e^- \rightarrow O^{2-}_{(ads)} \tag{7}$$

The oxygen species capture electrons from the material, which results in the concentration changes of holes or electrons in the CdO/In_2O_3 semiconductor. When the CdO/In_2O_3 thick film is exposed to H_2S gas, the reductive gas reacts with the oxygen adsorbed on the thick film surface. Then the electrons are released back in to the semiconductor, resulting in the change in the electrical conductance of CdO surface modified In_2O_3 thick films. It can be expressed in the following reaction:

$$H_2S + 3O^{2-} \rightarrow H_2O + SO_2 + 6e^- \quad (8)$$

$$CdO + H_2S \rightarrow H_2O + CdS \quad (9)$$

CdO surface modified In_2O_3 thick film when exposed to H_2S gas, cadmium oxide is converted into cadmium sulphide and cadmium sulphide shows metallic in nature, so conductivity would be very low in air and very high on exposure of H_2S gas and therefore, the gas response would be highest for modified thick film. For the CdO/In_2O_3 thick film, the low gas response at low operating temperature can be attributed to the low thermal energy of the gas molecules, which is not enough to react with the surface adsorbed oxygen species. As a result, the reaction rate between them is essentially low [41, 42] and low gas response is observed. On the other hand, the reduction in response after the optimum operating temperature may be due to the difficulty in exothermic gas adsorption at higher temperature [43]. Therefore the maximum gas response can just be observed at the right operating temperature. Figure10 illustrates the effect of dispersion of surface additive on the film conductivity. When amount of CdO on the surface of the sensor is less than the optimum, the surface dispersion, may be poor and the sensitivity of the sensor is observed to be decreased. Since the amount may not be sufficient to promote the reaction more effectively. On the other hand, as the amount of CdO on the surface is more than optimum, the CdO atoms would be distributed more densely on the surface of sensor. As a result, the initial resistance of the thick film would be decreases and the overall change in resistance on the exposure to gas would be smaller leading to lower response to the target gas. Uniform and optimum dispersion of an additive dominates the depletion of electrons from semiconductor. Oxygen adsorbing on additive (misfits) removes electrons from the additive and additive in turn removes the electron from the nearby surface region of the semiconductor and could control the conductivity.

7.3. Response and Recovery Time

Response and recovery time are the basic parameters of the gas sensors. Which are defined as the time taken for the sensor to attain 90 % of maximum change in resistance on exposure to gas is the response time. The time taken by the sensor to get back 90 % of the original resistance is the recovery time [44]. The 90 % response and recovery time were attained within 6s and 128 s respectively. The very short response time is the important features of the CdO surface modified (10 min.) In_2O_3 thick film. The large recovery time would be due to lower operating temperature. At lower temperature O_2^- species is more prominently adsorbed on the surface and thus it is less reactive as compared to other species of oxygen, O^- and O^{--}.

8. Summary

Following conclusions can be drawn from the experimental results:

1. The In_2O_3 thick film was found to be non stoichiometric and oxygen deficient material. It showed negative temperature coefficient in nature.
2. The pure In_2O_3 thick film showed highest response to ethanol vapor (100 ppm) at 350 ^oC.
3. The pure In_2O_3 thick films were modified by $CdCl_2$ aqueous solution by dipping technique. The surface modified (10 min.) thick film showed best response to H_2S gas (10 ppm) at 150 ^oC.
4. The surface modification shifts the gas response of the thick film from ethanol vapor to H_2S gas.
5. Due to introduction of CdO on the surface of In_2O_3 thick film, would alter the adsorption-desorption relationship of the sensor. The optimum dipping time was found to be 10 min.
6. The surface modification alters only the surface morphology of the thick film not the bulk properties.
7. The surface modification facilitated adsorption of larger number of oxygen ions on the surface, could immediately oxidize the exposed H_2S gas leading to faster response time of the sensor.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
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- Signal processing;
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