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Review Of Research

STUDY OF GAS SENSING PROPERTIES OF NANO In_2O_3: PREPARED BY SPRAY PYROLYSIS METHOD

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ABSTRACT:
We report preparation of nano-In_2O_3 thin films by a simple, inexpensive spray pyrolysis (SP) method and their gas sensing application. Nano-In_2O_3 thin films were prepared by using Indium trichloride in de-ionized water as a precursor at substrate temperature 350 ^oC. As-prepared In_2O_3 thin films were used for further characterization after annealing at temperature 550 ^oC for 30 min. The structural and surface morphological properties of the films were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. These films were tested to various gases at different operating temperature ranging from 50^{o}C to 450^{o}C. A high value of sensitivity is obtained for ethanol at operating temperature of 350^{o}C for 80 ppm. The mechanism of ethanol sensing by the In_2O_3 thin film is explained on the basis of adsorbed oxygen on the sensor surface. The In_2O_3 thin films exhibited good sensitivity and rapid response–recovery characteristics to ethanol.

KEYWORDS: *Spray pyrolysis, In_2O_3 thin films, Ethanol vapor sensor.*

1. INTRODUCTION

Hydrocarbon gases, widely used as industrial and domestic fuels, have often proved to be hazardous because of explosions caused by leaks. It is therefore of vital importance to develop good sensors for hydrocarbon gases. Due to the advantages of small size, low cost, simple operation and good reversibility, the semiconductor sensors have become the most promising devices among the sold-state chemical sensors. Hence, the metal oxide gas sensing materials are widely investigated. Many semi conductor oxides such as SnO_2, Fe_2O_3, In_2O_3, WO_3, and CuO have been explored to detect the polluting, toxic and inflammable gases, such as CO, CO_2 NO_x, H_2S and ethanol (Maekawa 1992, Korotcenkov 2000, Chu 2006, Aifan 2008, Vomiero 2007, Neri 2008, Jain 2006). In this area, In_2O_3 sensor material has been widely applied as a basic material in gas sensors primarily due to its high sensitivity and low cost (Patil 2009). In In_2O_3 sensors, the gas sensing mechanism can be described in terms of an adsorption/desorption process of oxygen at the surface of a sensing element. Thus, for the complete description of sensor response, the interactions between the sensor element and the target gas should be clarified. The reaction mechanism of alcohol detection by tin oxide films was extensively investigated to understand the nature of alcohol gas detection.

Spray pyrolysis technique (SPT) is useful alternative to the traditional methods for obtaining thin films (Patil 1999). It is of particular interest because of its simplicity, low cost and minimal waste production. In this technique, a solution consisting of the ions of required compound is sprayed on a heated substrate and

The aim of the present work is to develop sensor based on the In_2O_3 thin films prepared by spray pyrolysis technique, which could be able to detect the ethanol vapors.

2. EXPERIMENTAL

(a) Thin film technique: Preparation of Thin Films by Spray Pyrolysis

The schematic experimental set up of the spray pyrolysis system which is built in our lab as shown in figure 1. It consists of spray gun with nozzle, substrate heater, automatic temperature control unit, air compressor, pressure regulator, thermocouple, stepper motor with controller and power supply. The heater is a stainless steel block furnace electrically controlled by an automatic temperature controller unit to attain the required substrate temperature to an accuracy of $\pm$ 2^{o}C. The resulting temperature on the surface of the substrate is measured with a chromel-alumel thermocouple. Hazardous fumes evolved during the thermal decomposition of the precursor are given out an exhaust system attached to the spray pyrolysis unit. The spray nozzle is made up of borocil glass having a different bore diameter (viz. 0.1mm, 0.3mm, 0.5mm). Due to the air pressure of the carrier gas, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts. The spray nozzle is fixed at an appropriate distance from the substrate. The precursor solution was sprayed on to the substrate in the air as small drops and around a high temperature zone where thermal decomposition and possible reaction between solutions occur, through compressed air, which is used as carrier gas with a flow rate controlled through air compressor regulator.

To achieve uniform deposition the moving arrangement has been used. For this substrate is kept stationary, while the nozzle is free for to and fro motion with mechanical moving arrangement as stepper motor has been advantageous, so we don't have to spend energy moving the table with the hot plate and all electrical connections. The nozzle system is very lightweight with easy slider trolley attached. The spraying system and heater are kept inside a metallic chamber of size 60x60x60 cm^3. The inner surface of the box is painted by epoxy liquid, to reduce the heat loss through the surface.

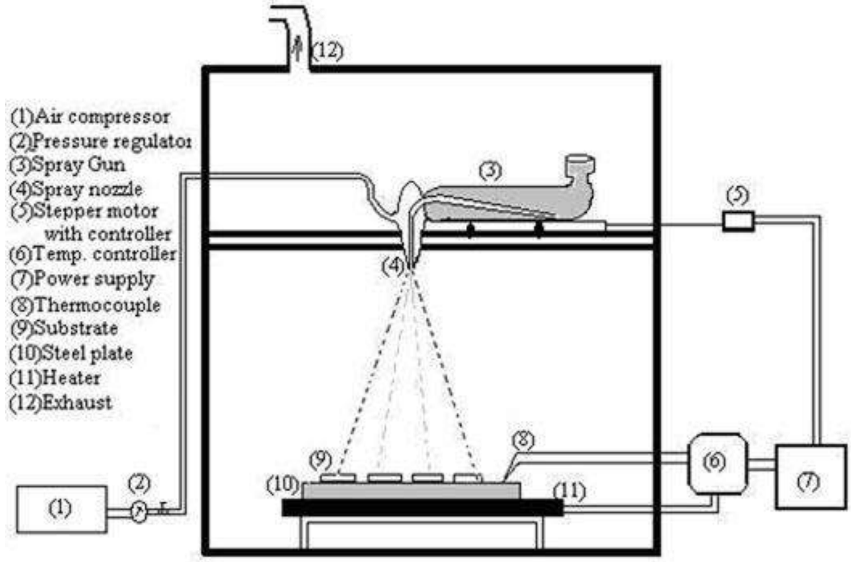


Figure 1. Schematic representation of the spray system

KINETICS IN THIN FILM DEPOSITION

The deposition process needs fine droplets to react on the heated substrate, owing to the pyrolytic decomposition of the solution. The hot substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species. In many cases large droplets of the solution do not vaporize before reacting to deposit on the substrate. They hit the surface and form a powdery deposit. If it strikes at a high enough velocity, the droplet will splatter and form a dispersed powdery layer. As mentioned above, the droplet cannot be completely vaporized before it hits the surface and for this reason, film growth cannot occur. Sears et al 1998 investigated the mechanism of SnO_2 film growth. The influence of forces which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed. Figure 2 shows the types of trajectories that are expected to occur in the spraying of a solution on hot glass substrate.

It is reported that the behavior of precursor drops that undergo three major steps during the course of spray pyrolysis: (12) drop size shrinkage due to evaporation, conversion of precursor into oxides, and (13) solid particle formation. The particle formation may involve two mechanisms: intraparticle reaction (conventional one-particle-per-drop mechanism) and gas-to-particle conversion (Kodas et al 1999). In the oneparticle- per-drop mechanism, each droplet is regarded as a micro reactor and converts into one solid particle when it travels towards substrate. In contrast, gas-to-particle conversion occurs when the precursor is volatile and is transported across the particle-gas interface. He was also measured precursor drop size precisely. He found that bimodal particle size distributions were produced, suggesting that both one-particle-per-drop and gas-to-particle conversion mechanisms were involved in spray pyrolysis.

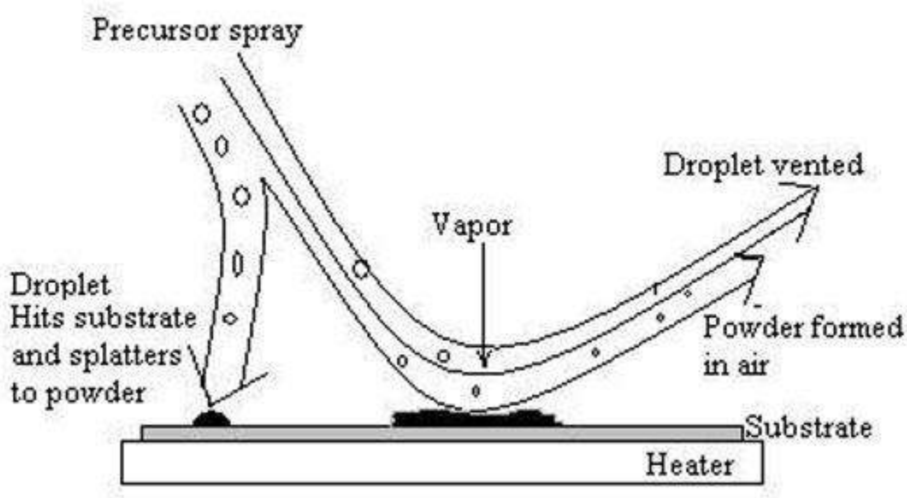


Figure 2. Kinetics in thin film deposition.

(b) Experimental Procedure: Preparation of Thin Films by Spray Pyrolysis

In_2O_3 thin film was deposited by spray pyrolysis technique (SPT) onto ultrasonically cleaned glass substrate using Indium trichloride as precursor solution. The solution of $InCl_3$ (0.05M) was prepared in de-ionized water and methanol in a volume ratio of 1:1. The solution was sprayed continuously through a glass nozzle of 0.1 mm inner diameter onto substrate kept at 350 ^oC. The deposition parameters like spray rate 5 ml/min. was adjusted using air as a carrier gas, nozzle to substrate distance (25 cm) were kept constant, and to and fro frequency of the nozzle (18 cycles min^{-1}) were kept constant at the optimized values indicated in brackets. Due to the air pressure of the carrier gas, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts. The precursor solution was sprayed on to the substrate in the air as small drops and around a high temperature zone where thermal decomposition and possible reaction between solutions occur, through compressed air, which is used as carrier gas with a flow rate controlled through air compressor regulator. To achieve uniform deposition the moving arrangement has been used. For this substrate is kept stationary, while the nozzle is free for to and fro motion with microcontroller based moving arrangement as stepper motor has been advantageous, so we don't have to spend energy moving the table with the hot plate and all electrical connections. As prepared In_2O_3 thin film was annealed at 550 ^oC for 30 min.

3. CHARACTERIZATION

3.1 Phase Identification

X-ray diffraction pattern was recorded on diffractometer (Miniflex Model, Rigaku, Japan) using CuK_α radiation with a wavelength λ =1.5418 A^o at 2 ϑ values between 20^o and 80^o. The average crystallite size (D) was estimated using the Scherrer equation (Cullity, 1956) as follows:

$$D = \frac{0.9\lambda}{\beta \, cos\theta} \quad (1)$$

where λ, β and ϑ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Braggs diffraction angle, respectively.

3.2 Surface Morphology

A JEOL 2300 model (Japan) was used to examine the surface morphology of the sample by scanning electron microscopy (SEM) and the percentage of constituent elements was evaluated by the energy dispersive X-rays analysis (EDAX) technique.

3.2 Gas Sensing Characterization

Sensitivity (S) is defined as the ratio of change in resistance of the sample on exposure to a test gas to the resistance in air (Gaikwad, 2009).

$$\text{S} = \frac{(Ra - Rg)}{Ra} = \frac{\Delta R}{Ra} \quad (2)$$

where *Ra* and *Rg* are the resistance of a sensor in air and the test gas, respectively. The sensor was examined under different gases such as LPG, H_2, CO, CO_2, NH_3, O_2, Cl_2 and ethanol.

4. RESULT AND DISCUSSION

4.1 Structural Analysis

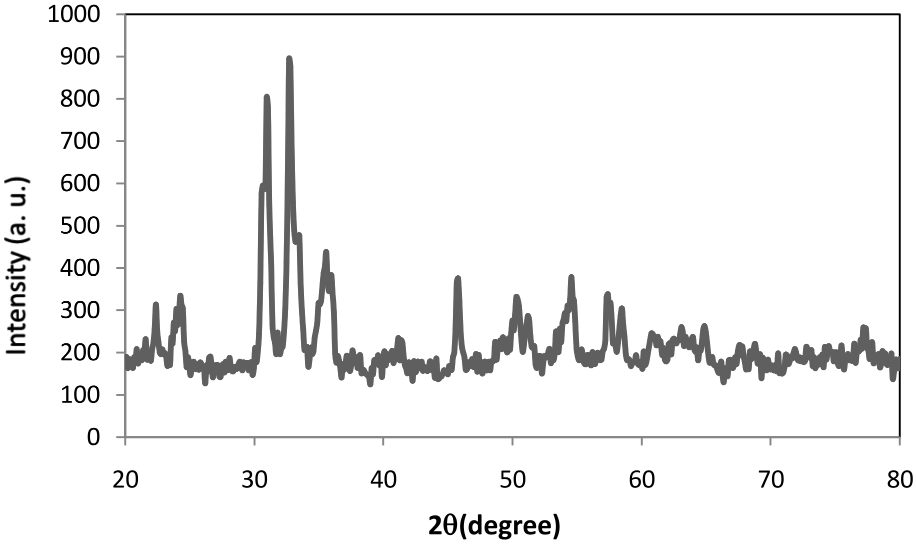
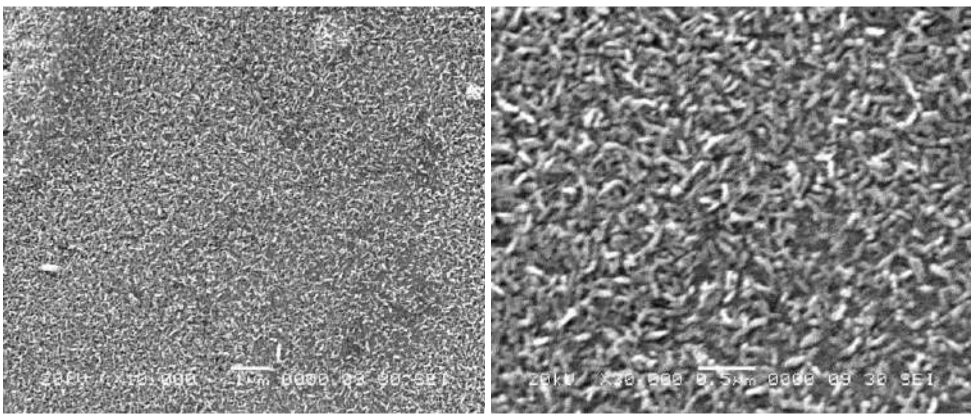


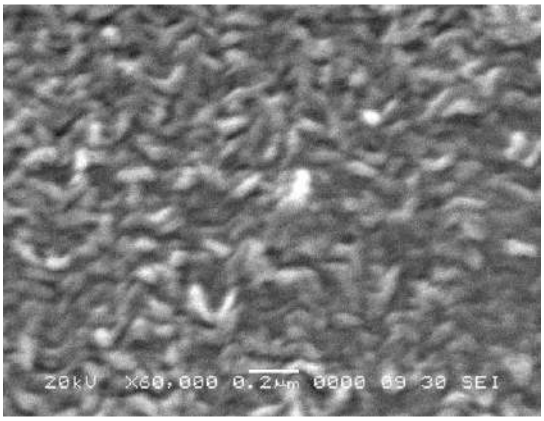
Figure 3. X-ray diffraction pattern of In_2O_3 thin film.

The X-ray diffraction pattern of the In_2O_3 thin film is shown in figure 3. It shows well defined diffraction peaks, indicating formation of nanocrystalline phases. The diffraction peak indexing, done by matching with the Joint Committee on Powder Diffraction Standard (no.72-1147), clearly revealed formation of the In_2O_3 phases with tetragonal structure. The average crystallite size was determined using Scherrer equation which was observed to be 84 nm.

4.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-rays Analysis (EDAX)



(a) (b)



(c)

Figure 4. SEM image of In_2O_3 thin film at three different magnifications of (a) 10,000×, (b) 30,000× and (c) 60,000×.

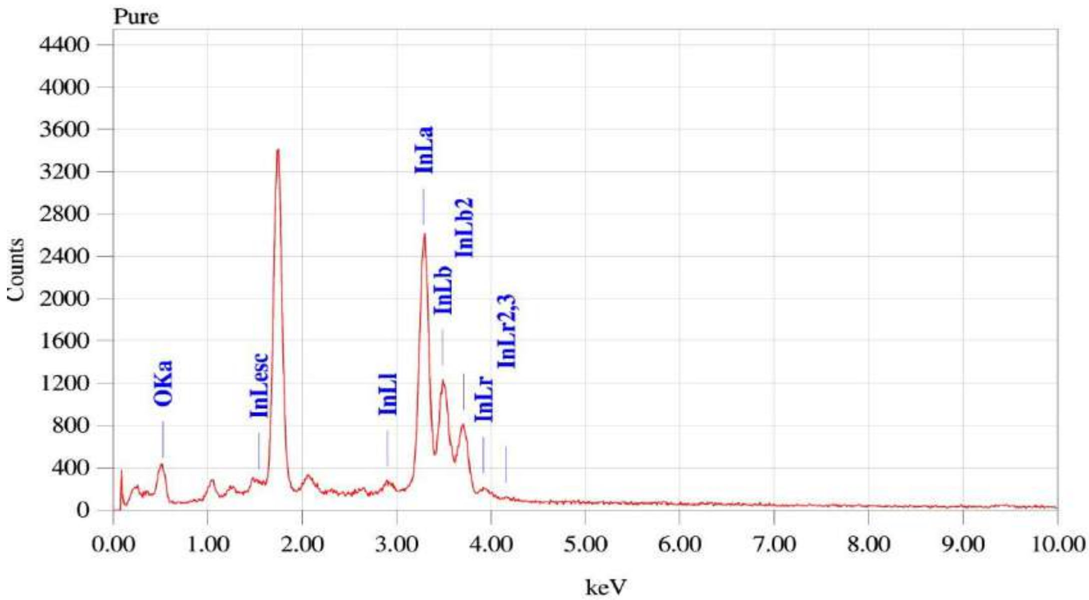


Figure 5. EDAX spectra of In_2O_3 thin film.

Figure 4 shows SEM image of the In_2O_3 thin film on glass substrates at three different magnifications10,000×, 30,000× and 60,000×. It exhibit uniform morphology, covering the entire substrate area. The average particle size is found to be ~75 nm.

The EDAX analysis was used to examine the composition of the deposited materials. Figure 5 shows the EDAX spectra for In_2O_3 thin film composition. It is seen that the major peaks are of Indium and oxygen and no other impurity. The wt% of the constituent elements such as In and O associated with In_2O_3 thin film are 41.33 and 58.67 respectively which is not as per the stoichiometric proportion and observed to be the oxygen deficient, leading to the semiconducting nature of In_2O_3.

4.2 Gas sensing properties of In_2O_3 thin films

4.2.1 Sensitivity of In_2O_3 films with operating temperature

The In_2O_3 thin film was tested to various gases such as CO_2, CO, H_2S, Cl_2, H_2, NH_3, O_2, LPG, ethanol vapor etc. It showed maximum response to ethanol vapor at 350°C. Figure 6 shows the variation of sensitivity of In_2O_3 thin film (fired at 550°C) with operating temperature ranging from 100°C to 400°C to ethanol vapor. The gas response goes on increasing with operating temperature and attains maximum gas response (936) at 350°C and decreases with a further increase in temperature.

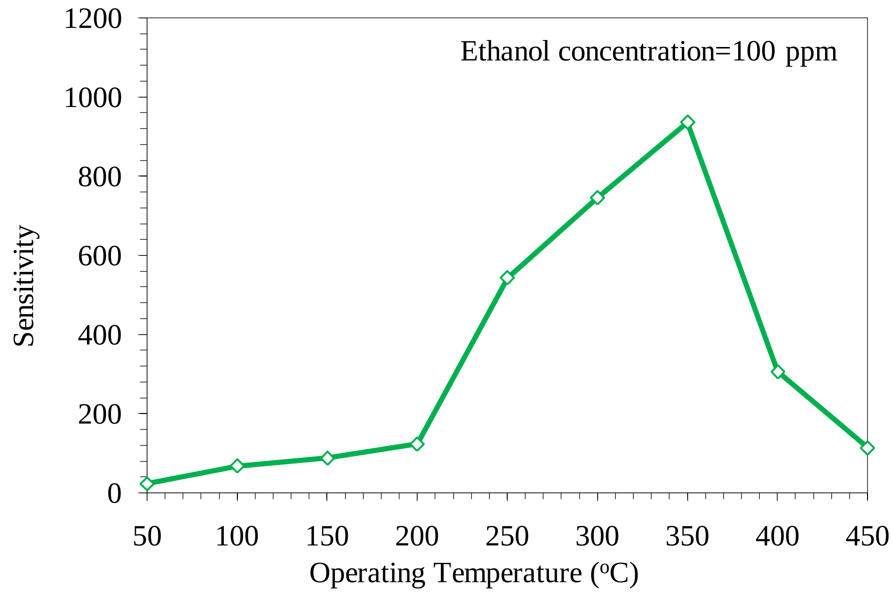


Figure 6. Variation of ethanol vapor response of In_2O_3 thin film

4.2.2 Selectivity of In_2O_3 thin film

Selectivity or specificity is defined as the ability of a sensor to respond to certain gas in the presence of other gases [8]. Figure 7 shows the selectivity profile of In_2O_3 thin film at 350°C. The film shows a maximum selectivity to ethanol vapor against the other gases.

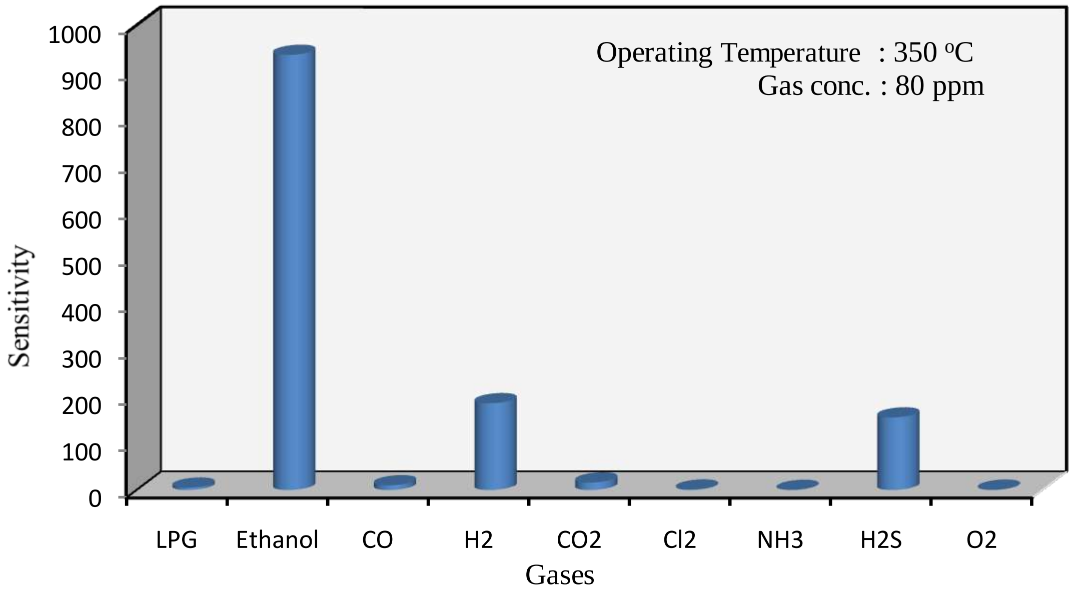


Figure 7. Selectivity of In_2O_3 thin film

4.4.3 Response Time and Recovery Time

The response/ recovery time is an important parameter used for characterizing a sensor. It is defined as the time required to reach 90% of the final change in current, when the gas is turned on and off respectively. The sensitivity vs time is shown in figure 8for 80 ppm of ethanol. From the plot, it is seen that the response time is 90 sec and the recovery time is 130 sec.

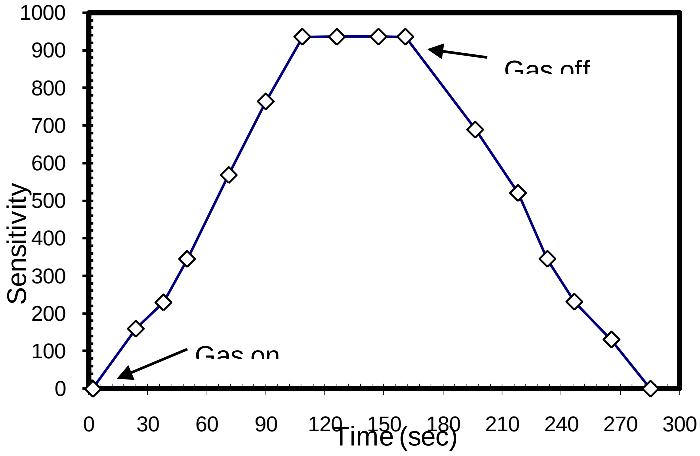
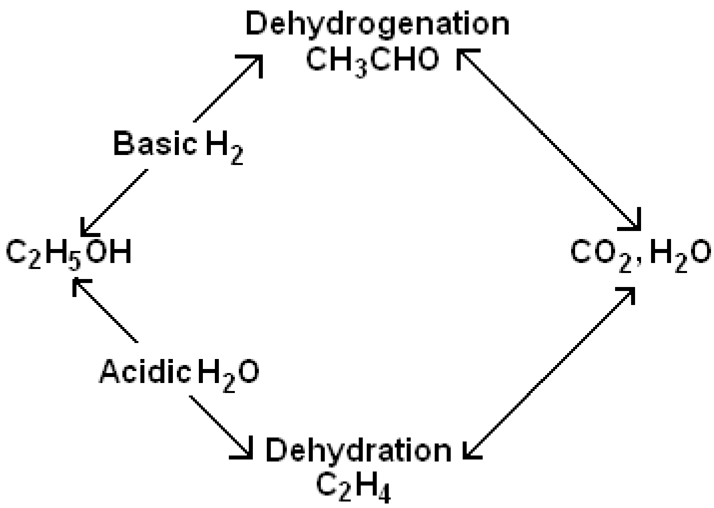


Figure 8. A dynamic response of In_2O_3 thin film sensor.

4.4.5 In_2O_3 thin film as a ethanol sensor

In_2O_3 is a basic oxide. It is well known that the sensitivity to ethanol vapor is greatly promoted by basic oxides. Being specific to ethanol vapor, the promotion would be related to the oxidation of ethanol vapor. It is known in catalytic chemistry that ethanol vapor is oxidized via two reaction routes, i.e. dehydrogenation to CH_3CHO on the basic surface and dehydration to C_2H_4 on the acid surface. These intermediates are consecutively oxidized to CO_2 and H_2O:



Out of these intermediates, CH_3CHO is known to have much higher molecular sensitivity of a semiconductor gas sensor than C_2H_4 (Seiyama et al 1992). Due to the basic nature of In_2O_3, the dehydrogenation route is more favored than the dehydration route, giving rise to the maximum gas response to ethanol vapor.

5. CONCLUSIONS

From the results, following statements can be made for the sensing performance of the In_2O_3 thin film sensor.

1. Nanocrystalline In_2O_3 thin film could be prepared by simple and inexpensive spray pyrolysis technique (SPT).
2. The sensor showed good selectivity to ethanol gas against LPG, NH_3, H_2, CO, CO_2 and Cl_2 gases.
3. The nanocrystalline In_2O_3 thin film exhibits rapid response–recovery which is one of the main features of this sensor.
4. The results obtained by SPT are promising for the preparation of sensitive and low cost ethanol sensor.

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