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Fabrication of Indium Oxide thin films sensor for H_2S

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Abstract

The present work is based on fabrication of Indium oxide with Tellurium dispersed thin film sensor for H_2S gas detection. The study reveals the capability of Indium Oxide (IO) thin films as selective H_2S gas sensor when Tellurium (Te) layer was dispersed. The inbuilt heater was fabricated from Indium Tin Oxide (ITO) thin films. Sensor showed promising results as the study of sensitivity was carried out for different concentrations of H_2S gas. The ratio of electrical conductance when, the sensor is operating at a higher temperature and to that at lower temperature is unaffected by water vapour but is sensitive to H_2S gas. Hence the detrimental effects of humidity on the sensing properties of the IO thin film gas sensors are almost negligible. The gas sensor was operated at concentrations of 40, 100, 200 & 400 ppm of H_2S gas at room temperature and was found to have good sensitivity and fast response.

Keywords: H_2S Gas Sensor, Indium Oxide, Thin films.

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1. Introduction

The semiconducting metal oxide thin film based sensors have attracted much attention in the field of gas sensing under atmospheric conditions due to their low cost and flexibility in production; simplicity of their use; large number of detectable gases and possible application fields. The sensing properties of various semiconducting oxides, especially tin oxide materials have been extensively studied [1-2]. One of the main problem with tin oxide gas sensors is their lack of selectivity. The chemi-adsorbed oxygen tends to react with wide spectrum of reducing gases. SnO_2 materials have been studied for different pollutants and it is claimed that sensitivity and selectivity to H_2S gas are improved by adopting quick cooling methods [3-4]. Single crystal In_2O_3 whiskers are able to detect H_2S gas [5]. WO_3 nanoparticle-based H_2S sensor has also been reported [6]. Looking into the need for health care and environmental applications, H_2S gas monitoring can be very useful because of its high toxicity. It has no odor and when inhaled in higher concentrations can cause accidental death. The authors have fabricated IO thin film based gas sensors to study response in terms of sensitivity for different gases like ammonia and ethanol vapour [7]. During the study it has been found that IO thin films with Te as dispersed element have good prospects to sense H_2S gas. Also the oxide semiconductor based thin film sensors normally operate at elevated temperature and therefore require a heater. This increases the power consumption and complexity. The present work is focused on fabrication of IO / Te dispersed thin film sensor for detection of H_2S gas at low temperature with an integrated miniature Indium Tin Oxide (ITO) based thin film heater. This integrated assembly helps to provide continuous temperature to the sensing film.

Principle:

Due to change in ambient parameter the doped and undoped IO thin films exhibit significant variation in their conductivity. The formation and eradication of oxygen vacancies is responsible for the large conductivity changes in the IO thin films. This is achieved with two step process:

i. Atmospheric oxygen gets adsorbed on the surface and removes a carrier from the conduction band of n-type semiconductor gas sensor to produce O^{-2} or O^- species. This phenomenon reduces the overall conductance.

ii. The reducing gas H_2S will react with chemisorbed oxygen to reinject the carriers and increase the sensor conductance.

The significant output of the present study is the relatively low temperature analysis with sufficient conductance variation for the H_2S gas. Thermal cycling technique takes the advantage of the fact that different types of reducing gases have different reaction rates. Sensors run at different temperature show degree of selectivity amongst these gases, but continuous cycling between low and high temperature will display conductance signatures indicative of tested gas like H_2S in present study.

2 Experimental Details

2.1 FABRICATION OF IO THIN FILMS AND ITO HEATER

Thermal evaporation method was used to prepare thin films. 250µ thick alumina substrates with 5mm x 5mm of surface area were used for the deposition of the thin films. The optimized growth parameters [8 - 10] were utilized for the growth of IO thin films. The Tellurium (Te) particles with thickness of 20nm were finely dispersed on the top of IO thin film by thermal evaporation under high vacuum to serve as a selective detection of H_2S gas. The ohmic contacts were established by special types of contact pads for sensing. A post deposition annealing of IO films in the furnace at different values of relative humidity was carried out. The annealing temperature was kept constant at about 700K. The method of introducing humidity into the furnace tube during annealing of IO films is commonly used when water is the oxidizing species. In this experimental setup air slowly enters the inlet side of bubbler and becomes saturated with distilled water as it rises through the water and then exits through the outlet into the furnace. The % relative humidity (RH) is monitored by controlling the temperature of the air that enters in the bubbler, or the temperature of the water in the bubbler. Heater was fabricated from ITO by a flash-thermal evaporation technique and was integrated with the IO thin film sensors on rear side [11]. The fabrication process of heater is reported elsewhere [7]. Table-1 summarizes growth parameters.

Table 1. Parameters for thin films fabrication:

Parameters	**IO thin films**	**ITO heater**
High Vacuum	10^{-4} Pascal	10^{-4} Pascal
Thickness of films	150 – 300 nm	300 – 400 nm
Substrate temperature	573 K	673 K
Post Deposition annealing	700K for an Hr	750K for an Hr

The low power consumption was achieved during the sensing operation with this system.

A potential of +6V was supplied to ITO miniature heater incorporated with a sensor when the H_2S gas was injected within the chamber. The conductivity change in air and in pollutant gas depends on the physiochemical interaction between the gas and the surface of sensing film. The sensor response is defined as **$S = R_a / R_g$**, where R_a is the resistance of the sensor in the atmospheric air, and R_g the resistance in presence of reducing gas H_2S.

2.2 CHARACTERIZATION

A λ-19 UV-VIS Spectrophotometer (Perkin Elmer, USA) was used for measurements of the optical properties of IO thin films. The square of absorption coefficient (α^2) versus photon energy (hν) curve obtained for the IO thin films grown on the cleaned glass surface is shown in figure 1. The direct band-gap of IO thin films was found to be 3.62 eV from the optical absorption studies. The calculated value is in good agreement with the value already reported [12]. A visible transmission greater than 75% with a film thickness of about 150 nm for IO thin films is obtained.

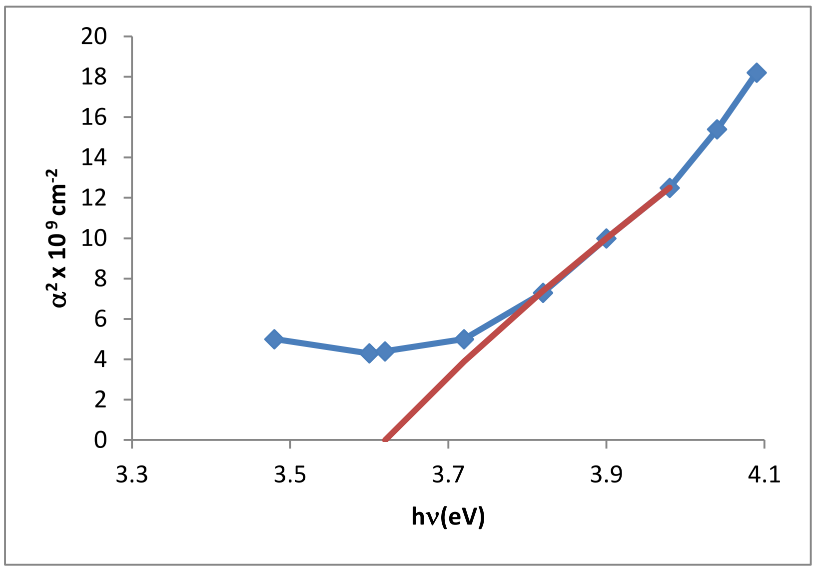

Figure -1 Optical absorption spectra plotted as α^2 vs pohton Energy

A moderately lower transparency and resistivity show the existence of donor levels due to oxygen vacancies or in other words an excess of free metal, which makes it stable and sensitive gas sensor. Electrical and optical properties of IO and ITO thin films have been summarized in table 2.

Table 2. Electrical & Optical Parameters:

Parameters	IO	ITO heater
Electrical Resistivity	1.1 x$10^{-3}\Omega$.cm	5.6 x10^{-4} Ω.cm
Carrier Concentration η	4.2 x 10^{20} cm^{-3}	4 x 10^{20} cm^{-3}
Carrier mobility μ	55 cm^2/Volt-sec	35 cm^2 /Volt-sec
Conductivity	N-type	N-type
Optical Transp.	75 %.	75%
Optical Bandgap	3.62 eV	---

Surface structure orientation and band gap energy verification of thin films were analyzed by X-pert MPD Philips XRD. Here the specimen mounted at the centre of Diffractometer was rotated by an angle theta around the axis in the plane of film. The counter attached to an arm rotating around the axis by angle twice as large as those of specimen rotation. Only (hkl) planes parallel to the film plane contribute to diffracted intensity. The effect thickness of the film is given by equation ($t/\sin^{\theta}$) which decreases with increasing diffraction angle.

The result of XRD shown in figure-2 is similar to those reported by other authors [13-14] for IO having cubic structure. At 448°K the peak obtained at 2θ = 30.5° is examined and identified as the reflection from (222) plane using ASTM data cards. Table 3 shows inter planner spacing corresponding to 2θ angle.

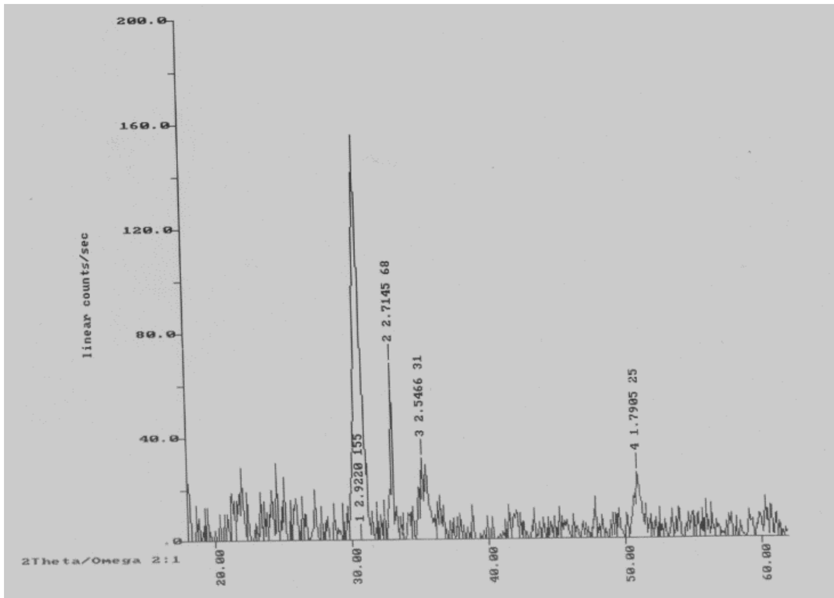

Figure-2. XRD of fabricated IO thin film

Table 3. Inter planner spacing and relative intensity

Angle 2θ	I / I0	Calculated	ASTM	I/I0	hkl
21.5	12.92	4.12	4.13	14	211
30.5	100	2.92	2.92	100	222
35.46	24	2.53	2.529	30	400
45.7	7	1.98	1.984	10	431

The grain size is determined from the full width at half max (FWHM) of X-ray peak using Debye Scherrer's formula : $L = 0.9 \lambda / \beta \cos\theta$, $\lambda = 0.154056$, $0.9 \times \lambda = 1.38654$, $P1 = \beta - b$,

where β is the full width at half maximum intensity of the peak (in Rad) and b is effect of instrument determined by broadening of microcrystalline Silicon diffraction values. The value of grain size of IO films at 448° K is 47.77 nm. The grain size was found to increase with substrate temperature. The vacuum evaporated In_2O_3 films may dissociate to species like InO, In or O_2 [15]. The value of lattice constant 10.118 A°, agrees well with the literature value reported for IO. The film thus deposited and annealed at 700K is single-phase indium oxide. The Te particles, which were deposited for the purpose of contact, dispersed as a few angstrom layer over the sensing surface. For gas sensing devices the dependence between gas concentration and response has critical parameters as thickness, temperature and annealing.

2.3 MEASUREMENT OF GAS SENSITIVITY

A saturated solution of Cadmium Chloride was prepared by dissolving sufficient amount of $CdCl_2$ powder in 50% solution of NH_4OH and was filtered to have the clear transparent solution (250ml). This solution was taken in a jar of 2L volume. The H_2S gas was purged in the jar where the sensor was placed using Kipps reactor for fixed interval of time i.e. gas was introduced for different time interval and the variation in resistance of the sensor was observed with respect to time. After closing the gas flow from Kipps reactor, the yellow precipitate (ppt) was filtered out. The ppt was dried in the oven. The weight of Sulphur was calculated from the amount of weight percent from CdS which is directly proportional to the ppm of H_2S.

2.4. THE ELECTRONIC CIRCUIT WITH ALARM

The block diagram of electronic circuit with alarm for H_2S gas sensor is shown in figure -3. This circuit consists of a bridge, high impedance amplifier, Arduino board, buzzer and fan. The change in concentration causes change in the resistance of the bridge arm. The signals picked up are amplified by the high impedance amplifier. Output of the gas sensor is connected to the analog input pin A0 of the Arduino. Digital pin 10 of the Arduino is used for controlling the buzzer and the pin 2 for controlling the relay to drive fan. Arduino controller through buzzer indicates change in concentration of gas. It is used to drive relay for fan control which is used for safety purpose when the concentration exceed safety value.

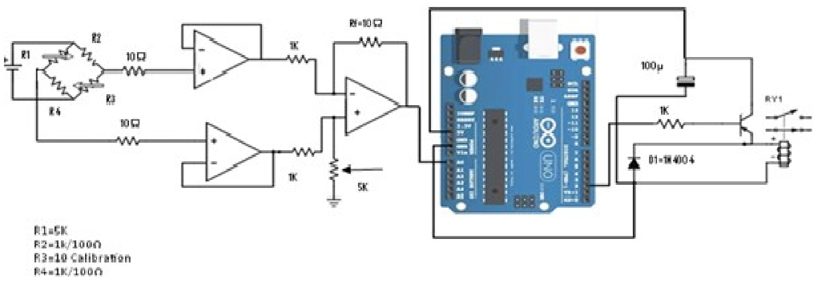

Figure-3. Electronic circuit for H_2S gas indication and fan control.

3 Results and Discussions

For the evaporated IO films X-ray diffraction and UV-VIS spectroscopic data were analyzed to study their surface structure, orientation and band gap energy verification. Crystallinity of the IO thin films of thickness 100 nm to 150 nm was analyzed by X-ray diffraction method with CuK_{α} radiation. Glancing angle X-ray diffraction (XRD) measurements indicate that the thin film consist of IO in rutile phase. The deposited IO thin films are found to have almost similar X-ray reflection peaks as that of IO profiles observed in ASTM data for powder diffraction.

The interfering effect of relative humidity on the response to IO with dispersed Te thin film to H_2S gas consist of switching a single sensor between two well defined temperatures. The sensor was tested in Laboratory with exposed to different amounts of humidity.

The graph of sensitivity as a function of temperature of IO thin film H_2S sensor is shown in figure-4. It has been observed that adsorption of H_2S gas is in temperature range 300K to 523K and was found to have maximum sensitivity of 2.2 at about 423K. Above 423K the sensitivity is saturated. It was also observed that IO sensing surface with dispersed Te (20nm) showed higher sensitivity and selectivity for H_2S gas operating at room temperature with concentrations 40ppm, 100ppm, 200ppm and 400ppm (figure-5). The sensor exhibited a significant increase up to concentration of 100ppm in air. At about 200ppm the sensitivity reaches a saturation value. The intermittent periodic heating of the sensors at two set of temperatures in H_2S gas gave larger variations in their conductance compared to continuous heating. The ratio of electrical conductance when, the sensor is operating at a higher temperature (423K) to that at lower temperature (323K) is unaffected by water vapour but is sensitive to H_2S gas, figure-6. Hence the detrimental effects of humidity on the sensing properties of the IO thin film gas sensors are almost negligible. The gas sensor was operated at different concentrations of H_2S gas at room temperature and was found to have good sensitivity and fast response.

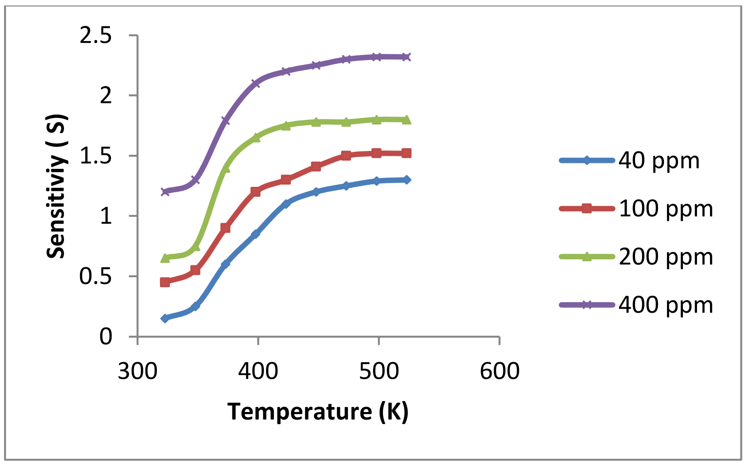

Figure 4. Gas sensitivity as function of Temperature

CONCLUSIONS

IO thin films grown on alumina substrates followed by annealing in humid environment are used as a gas sensor for monitoring H_2S gas. IO thin film gas sensor with thickness of about 150nm show maximum sensitivity at 423K. The interfering effects of humidity on the H_2S gas response of IO thin film is almost negligible by intermittent heating at two set temperatures.

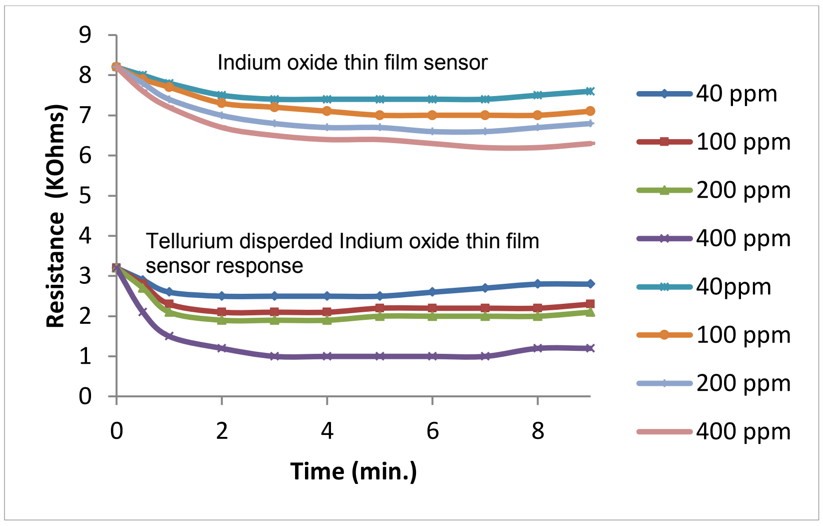

Figure 5. Response of IO thin films and Te dispersed IO thin films.

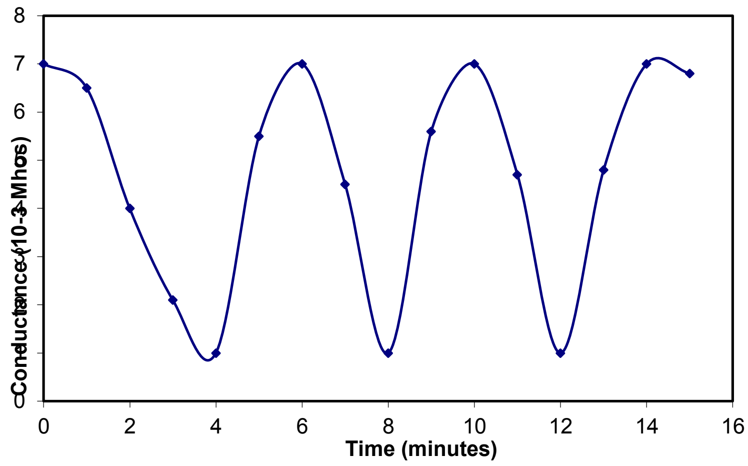

Figure 6. Response of Intermittent heating at two set temperatures.

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