



APPLICATION OF METAL OXIDE THICK FILM AS A NH₃ GAS SENSOR

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Abstract

The sensors are prepared in the form of thick films prepared by screen-printing technique on chemically clean optically plane glass substrate. From the FTIR spectra it is observed that the hydrocarbon chains of surfactant incorporated in the samples. We have found the A3 (80 TiO₂-10 In₂O₃-10 Al₂O₃) exhibited high sensitivity and fast response time to NH₃ at room temperature. In all the samples the sensitivity increases by increasing concentration of NH₃ gas in ppm. The resistance of thick films decreases by increasing concentration of NH₃ gas in ppm at room temperatures due to surface oxygen vacancies of SnO₂/TiO₂ act as electron donors.

Keywords: Metal oxide thick films, TiO₂-In₂O₃-Al₂O₃, Gas Response, NH₃ gas Sensing.

I. INTRODUCTION

Ammonia sensors have applications in many areas therefore detection of Ammonia is necessary for many purposes like leak-detection in air-conditioning systems [1-2], environmental sensing of trace amounts ambient NH_3 in air [3-4], breath analysis for medical diagnoses [5-6], animal housing [7], and more. Ammonia is toxic to humans at low ppm levels so there should be rapid detection of Ammonia at very low concentration, it is also important to detect the ammonia at high concentration.

Among the metal oxides that undergo appreciable change in electrical conductivity when exposed to a gas atmosphere, the most studied material have been SnO_2 , TiO_2 , Fe_2O_3 , ZnO , MgO , V_2O_5 [8,9]. Takao *et al* [10] investigated sensing properties of the In_2O_3 -doped MgO ammonia sensor and examined some double layer sensors with a catalyst on the sensing layer. The resistance of all these n-type oxide semiconductor gas sensors is decreased by exposure to ammonia gas, which is similar to the case of reducing gases. Nanto *et al* [11] reported the Al-doped ZnO thin film ammonia gas sensor which displayed resistance increase upon exposure to ammonia gas, whereas it exhibited resistance decrease to reducing gases. In this present work we have selected semiconducting oxides SnO_2 , TiO_2 , In_2O_3 and Al_2O_3 in the form thick films in presence of ammonia gas environment.

II. EXPERIMENT

The semiconducting oxides SnO_2 , TiO_2 , In_2O_3 and Al_2O_3 (AR grade) chemicals in powder form were mixed in different stoichiometry in mol % as A1 (80 SnO_2 -10 In_2O_3 -10 Al_2O_3), A2 (90 SnO_2 -5 In_2O_3 -5 Al_2O_3), A3 (80 TiO_2 -10 In_2O_3 -10 Al_2O_3) and A4 (90 TiO_2 -5 In_2O_3 -5 Al_2O_3) where A1, A2, A3 and A4 are sample code. The materials used for gas sensors are generally prepared in the form of bulk, pellet or a film (thin or thick). The films were deposited on glass and alumina substrates. In this present study, the sensors are prepared in the form of thick films prepared by screen-printing technique on chemically clean optically plane glass substrate. It is most simple and less expensive way of preparing the sensors as compared to chemical vapour deposition, thermal evaporation, etc. methods. Initially all the chemicals were calcinated at 900°C for 4–5 h. After calcinations the fine powder was formed. The paste was prepared by mixing calcinated fine powder with nitrocellulose and *n*-amylacetate for screen-printing. The paste was screen-printed on the glass substrate in the form of thick film having thickness of the order of 16 – 24 μm . The films were subjected to heating at 100°C for an hour to decompose intermediate compounds. For surface resistance measurement, electrodes of conducting silver paint were formed on adjacent sides of the film and then the films were subjected to heating at 70°C for 15 min for drying. Infrared spectra of Thick films samples after calcination were recorded on a Shimadzu FTIR IRAffinity-1 spectrometer (Japan Make) at a resolution of 4 cm^{-1} with an average of 45 scans per sample. FTIR measurements are taken in the range of 400 – 4000 cm^{-1} .

The gas chamber having volume $30 \times 30 \times 30$ cc with an attached NH_3 gas flow meter (FLOWTRON make, India having range 0.1–0.5 ml/min) was used for keeping the sensors for testing. The gas flow was adjusted to 0.5 ml/min. The readings were carried out in a NH_3 gas

environment at different ppm levels and various temperatures. The experiment was carried out 4–5 times for reproducibility of the characteristic. Also the stability of the sensors was checked at a fixed concentration of NH_3 gas for 4–5 h. The thickness of the sensor films was measured by Digimatic Outside Micrometer (Series-293, Japan Make) having a resolution of $\pm 0.001\text{mm}$ and found to be 16.75, 14.75, 18.75, and $24.25\mu\text{m}$ for A1 (80 SnO_2 -10 In_2O_3 -10 Al_2O_3), A2 (90 SnO_2 -5 In_2O_3 -5 Al_2O_3), A3 (80 TiO_2 -10 In_2O_3 -10 Al_2O_3) and A4 (90 TiO_2 -5 In_2O_3 -5 Al_2O_3) sensors respectively. The resistance of the sensor was measured by voltage drop method adopted by Yawale *et al* [12, 13]. By knowing sensor resistance the sensitivity was calculated. It is the device characteristics of perceiving a variation in electrical property of the sensing material under testing gas exposure and it can be defined as in Eq. (1),

$$\left. \begin{aligned} \text{Sensitivity (S)} &= \frac{(R_g - R_a)}{R_a} && \text{If } R_g > R_a \\ \text{Sensitivity (S)} &= \frac{(R_a - R_g)}{R_a} && \text{If } R_a > R_g \end{aligned} \right\} \quad (1)$$

Where, R_g is the change in resistance of the sensor in presence of gas /vapors and R_a is the original resistance of sensor in presence of air.

Sensitivity (Gas response), selectivity, response time and recovery time are the important characteristics in gas sensing. Selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of other gases. Response time is defined as the time needed for a sensor to attain 80 % of maximum change in conductance upon the exposure to a test gas, while recovery time as the time taken by a sensor to get back 80 % of the original conductance in air.

III. RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) spectroscopy is one of the widely used optical methods to study the interaction of electromagnetic radiation in the infrared region with chemical compounds. The large band width ($400\text{--}4500\text{ cm}^{-1}$) and the distinct absorbance bands render the FTIR technology suitable for sensor applications. Fig.1.(a),(b),(c),(d) shows the FTIR spectra of A1 (80 SnO_2 -10 In_2O_3 -10 Al_2O_3), A2(90 SnO_2 -5 In_2O_3 -5 Al_2O_3), A3(80 TiO_2 -10 In_2O_3 -10 Al_2O_3) and A4(90 TiO_2 -5 In_2O_3 -5 Al_2O_3) sensors respectively. Anatase phase of TiO_2 changes to rutile when heated above temperature 500°C along with SnO_2 and Al_2O_3 [14, 15]. Hence the structure of TiO_2 and SnO_2 is quite similar after the calcinations of samples therefore all IR spectra has quietly similar in nature. From the spectra it is observed that bands at 2920 and 2850 cm^{-1} are due to the asymmetric and symmetric C–H stretching vibrations [16] of the hydrocarbon chains of the surfactant incorporated in the sample, while the sharp bands in the range of $1400\text{--}1700\text{ cm}^{-1}$ are attributed to the deformation of $-\text{CH}_2-$ and $-\text{CH}_3$ [16] of the incorporated surfactants. Other samples also gave similar results. The results are in good agreement with those reported by Hudson *et al.* [17] on mesoporous ZrO_2 . The broad band between $3200\text{--}3600\text{ cm}^{-1}$ are observed on samples, which are assigned to O–H stretching and deformation vibrations of weak-bound water. The bands between $400\text{--}800\text{ cm}^{-1}$ are attributed to the vibrations of tin oxide [18].

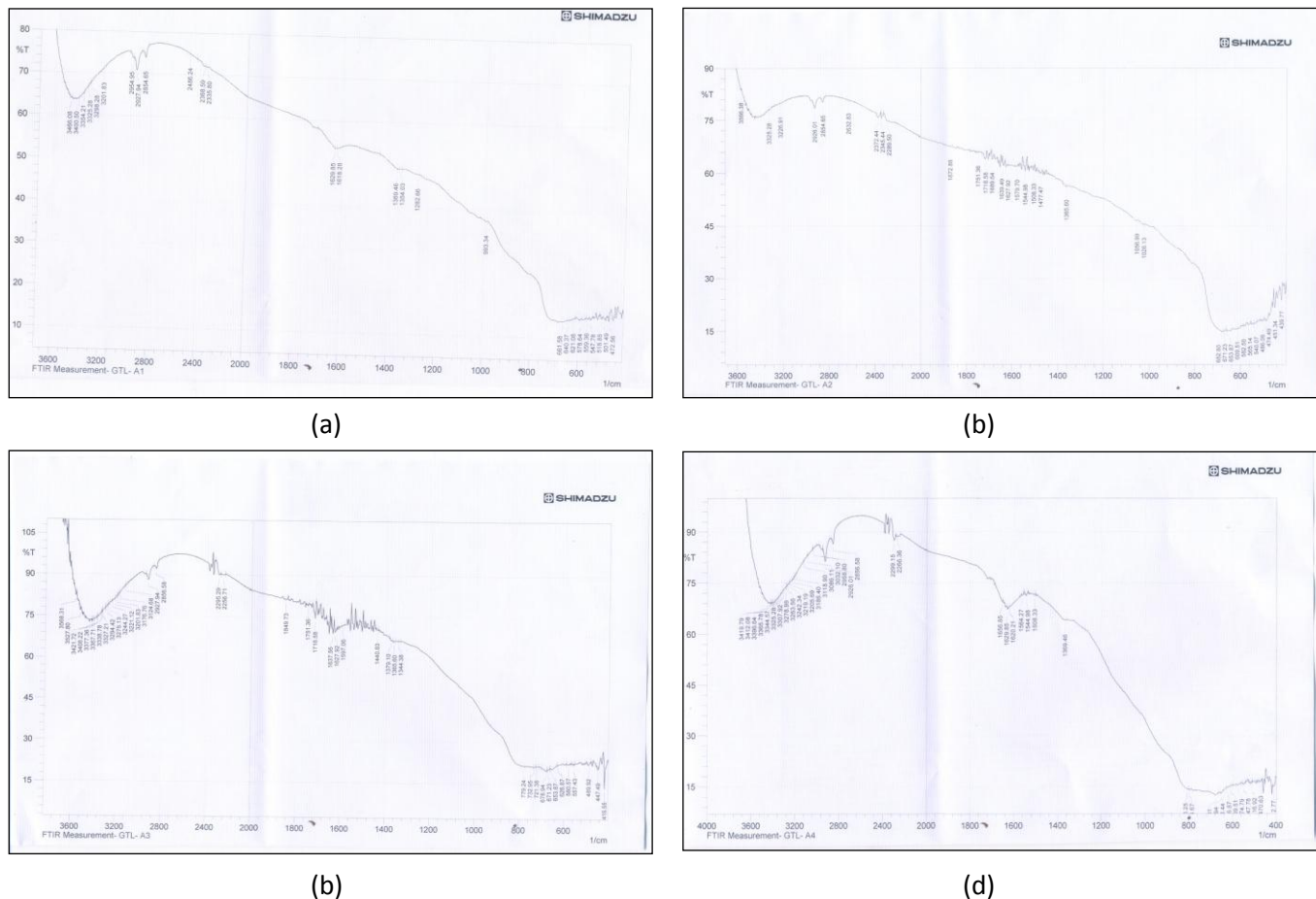


Figure 1: (a),(b),(c) and (d) FTIR Spectra of A1, A2, A3 and A4

Figure 2 shows the variation of resistance with change in concentration of NH_3 gas (ppm) at room temperatures (313K) for sensors A1, A2, A3 and A4. From figure 2, it appears that the resistance of thick films decreases by increasing concentration of NH_3 gas in ppm at room temperatures. In all the samples resistance decreases rapid up to 25ppm of NH_3 gas but after that there is slowly decrease. The thick film A2 ($90 \text{ SnO}_2\text{-}5 \text{ In}_2\text{O}_3\text{-}5 \text{ Al}_2\text{O}_3$) has found lowest resistance among all the samples.

Figure. 3 shows the variation of sensitivity with change in concentration of NH_3 gas for A1, A2, A3 and A4 thick films at constant temperature (313K). In all the films the sensitivity increases linearly for the lower concentration range but for higher concentration range it deviates from linearity. It is also observed that the sensitivity of thick film A3 ($80 \text{ TiO}_2\text{-}10 \text{ In}_2\text{O}_3\text{-}10 \text{ Al}_2\text{O}_3$) is more than other ones. At lower concentration of gas a linear behavior is observed whereas at higher concentration, the plot deviates from linearity but at higher temperature range the change in the sensitivity with concentration is small. The sensor sensitivity (S) is proportional to the number of active centers on the surface of sensor. The number of active centers is the product of surface area and surface density of the active centers. The specific surface is a ratio of surface area to mass of the sensor therefore; the sensor sensitivity is proportional to the product of

specific surface, density of active centers and the sensor mass. So if the specific surface is more, the number of active centers will be more and therefore the higher sensitivity of the material [19].

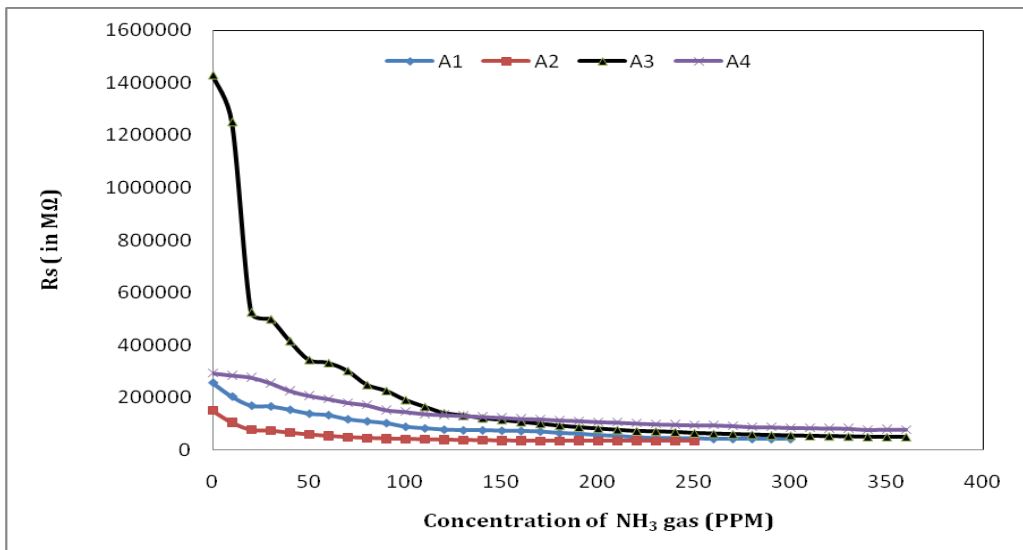


Figure 2. Variation of Resistance with change in concentration of NH_3 gas at room temperatures (313K) for sensors A1, A2, A3 and A4.

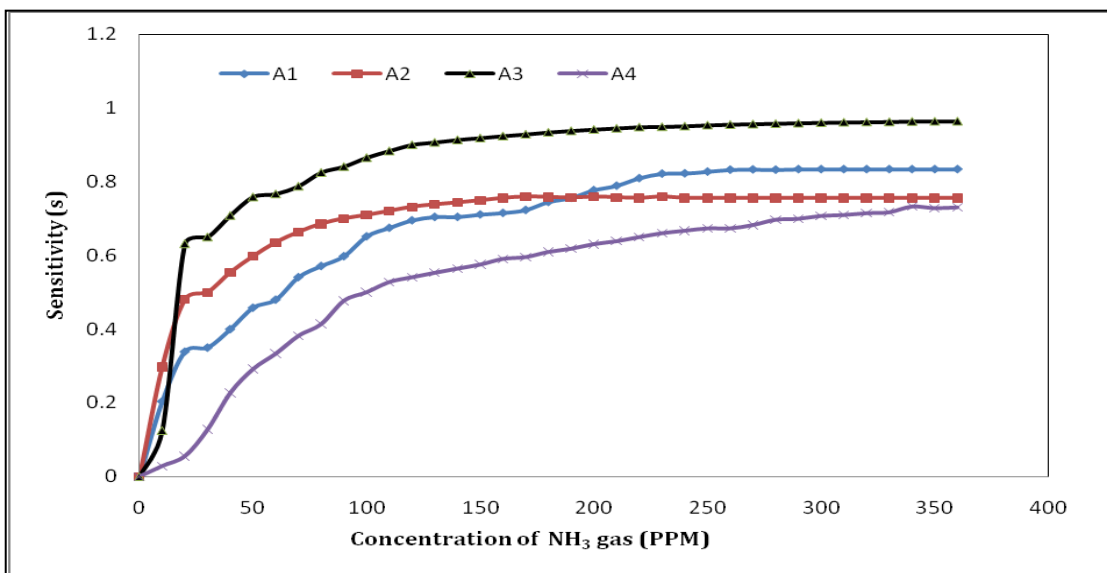


Figure 3. Variation of sensitivity with change in concentration of NH_3 gas for A1, A2, A3 and A4 thick films at constant temperature (313K).

Figure 4. shows the variation of sensitivity with change in sample composition at constant concentration (50, 100, 150, 200, 250 ppm) of NH₃ gas. From figure 4, it appears that the sensitivity increases by increasing concentration of NH₃ gas of thick films. It is seen that the sensitivity of is A3 (80 TiO₂-10 In₂O₃-10 Al₂O₃) more than other ones at higher and lower concentration of NH₃ gas.

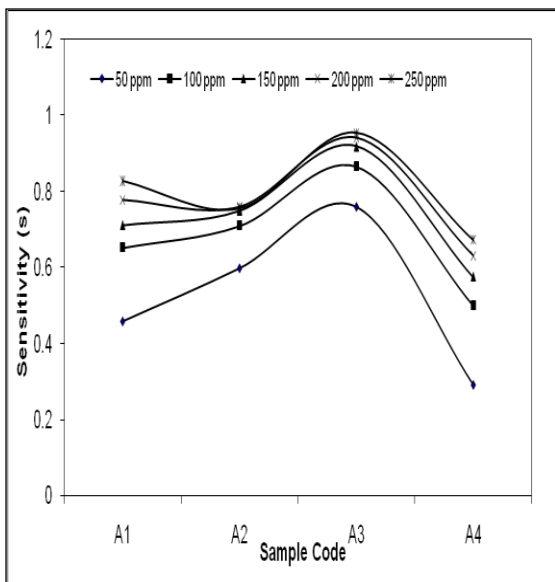


Figure 4: Variation of sensitivity with change in sample composition at constant concentration (50, 100, 150, 200, 250 ppm) of NH₃ gas

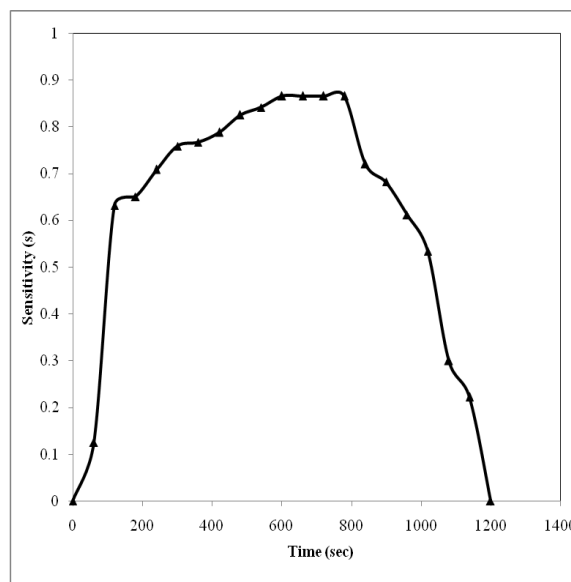


Figure 5: Transient response of the thick film A3 (80 TiO₂-10 In₂O₃-10 Al₂O₃) at 100-ppm concentration of NH₃ gas.

Figure 5 shows the transient response of the thick film A3 (80 TiO₂-10 In₂O₃-10 Al₂O₃) at 100-ppm concentration of NH₃ gas. It is observed that the thick film A3 shows 180 s ON time and 300 s OFF time. Hence the thick film A3 sensor element has a fast response time of about 180 s and high sensitivity when compared to A1, A2 and A4. The lack of a quick response to NH₃ of A1, A2 and A4 may be due to the low surface catalytic activity.

IV. CONCLUSIONS

Finally concluded that the thick film A3 (80 TiO₂-10 In₂O₃-10 Al₂O₃) has high sensitivity and fast response time to NH₃ at room temperature. In all the films the sensitivity increases linearly for the lower concentration range but for higher concentration range it deviates from linearity. The resistance of thick films decreases by increasing concentration of NH₃ gas in ppm at room temperatures due to surface oxygen vacancies of SnO₂/TiO₂ act as electron donors.

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