Low Temperature H_2S Gas Sensor Based on Fe_2O_3 Modified ZnO-TiO_2 Thick Film

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Abstract: Nanocrystalline ZnO-TiO_2 (~ 49-56 nm) was synthesized by hydrothermal method. Thick films were prepared by using synthesized nanocrystalline ZnO-TiO_2 (with molar ratio 9:1, 7:3 and 1:1) and their gas sensing characteristics were investigated at different operating temperature. ZnO-TiO_2 thick film (with molar ratio 7:3) exhibited good response to H_2S as compared to other investigated compositions. Further, ZnO-TiO_2 thick films (with molar ratio 7:3) were modified by different concentrations of Fe_2O_3 and their H_2S sensing characteristics were investigated. The 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) exhibited excellent H_2S sensing characteristics such as, high response (~ 314.67 at 40 ^oC), quick response time (~ 8 s), less recovery time (~ 30 s), excellent repeatability and stability, good selectivity towards H_2S as compared to the other test gases like CO_2, LPG and NH_3 at 40 ^oC. The experimental results demonstrated that the Fe_2O_3 modified ZnO-TiO_2 thick film is a very promising material to fulfills the practical requirement for the fabrication of H_2S sensors with good sensing characteristics.

Key words: Nanocrystalline, ZnO-TiO_2; Fe_2O_3, gas sensor, H_2S.

1. Introduction

Hydrogen sulfide (H_2S) is a toxic and inflammable gas. It is released from coal mines, oil and natural gas industries [1]. Also, H_2S gas is used in different chemical industries, research laboratories, as a process gas in the production of heavy water, etc. Human exposure to higher concentration of H_2S gas results in neurobehavioral toxicity [2]. Therefore it is essential to monitor and control the concentration level of H_2S gas. Consequently, it is today's need to have H_2S sensors with high sensitivity, excellent selectivity, reproducibility, stability, quick response and fast recovery. There are many parameters of materials for gas sensor applications such as adsorption ability, catalytic activity, sensor response, stability, etc. Semiconductor metal oxide like ZnO, SnO_2, In_2O_3, WO_3, ZrO_2, CeO_2, Fe_2O_3, have been reported as gas sensors [3]-[13]. But very few of them are suitable to fulfilled all the requirements. To overcome these limitations recently researchers focus on composite materials, like SnO_2-ZnO [14], Fe_2O_3-ZnO [15], ZnO-CuO [16] etc. In addition to binary metal oxide there are number of ternary and complex metal oxides which are emerged as promising candidates for gas detection [17]-[20]. It has been recognized that sensor based on the two components mixed together are more sensitive than individual component alone due to synergistic effect

between two metal oxides [15]. Preparation of mixed oxides leads to the alteration of the electronic structure of the system, which causes changes in the bulk as well as in the surface properties. Surface properties are expected to be affected by new boundaries between grains of different chemical composition. It is anticipated that all these phenomena will contribute favorably to the gas sensing mechanism [21], [22].

A careful control of the sensor operating temperature and adequate selection of specific impurities is concerned with an optimum response for a specific gas. Materials like CuO, Cr_2O_3, CeO_2 etc. when dispersed onto the semiconductor oxide films, enhance the sensor response to the reducing gas [23]-[25].

It is important to mention here that physical and chemical properties of materials depend on synthesis routes, governed by the synthesizing conditions. In literature, several routes are described for synthesis of nanomaterials, such as chemical, mechanical, gas phase and molten salt synthesis. Hydrothermal technique is one of the chemical synthesis routes that allow in fabrication of shaped and size oriented materials without melting steps. There are a number of advantages of this technique such as: the short duration of the experiments as compared to classical synthesis methods, crystal size and the level of agglomeration can be controlled, costs of the instrument and energy requirement is low as compared to other synthesis routes and it is an eco-friendly method [26], [27].

The objective of this work is to synthesize nanocrystalline ZnO-TiO_2 by hydrothermal method and to study the effect of Fe_2O_3 modification on H_2S gas sensing properties of ZnO-TiO_2 based thick films.

2. Materials and Method

2.1. Synthesis of Nanocrystalline ZnO-TiO_2

For obtaining nanocrystalline ZnO-TiO_2 with molar ratio 9:1 (sample A), accurately weighted analytical grade ZnO (3.607 g) and TiO_2 (0.393 g) were dispersed in aqueous NaOH solution followed by hydrothermal treatment at 180 ^oC for 24 h in Teflon-lined autoclave. Then it was allowed to cool naturally and the obtained precipitate was isolated from solution by centrifugation at 5,000 rpm for 30 min. and subsequently washed with distilled water and then ethanol and dried at 120 ^oC for 12 h. The same procedure was followed for synthesis of ZnO-TiO_2 with molar ratio 7:3 (sample B) and ZnO-TiO_2 with molar ratio 1:1 (sample C). The synthesized materials were examined by X-ray diffraction (XRD, XPERT-PRO) and transmission electron microscopy (TEM, Techai G2 20).

2.2. Fabrication of Sensor Element and Gas-sensing Measurements

Thixotropic paste was formulated by mixing synthesized ZnO-TiO_2 powder with ethyl cellulose and mixture of organic solvent such as butyl cellulose, butyl carbitolacetate and terpineol. Then the prepared paste was screen printed on glass substrate. Furthermore, the thick film of ZnO-TiO_2 (with molar ratio 7:3) was modified by dipping it into 0.1M, 0.2M and 0.3M aqueous solutions of Iron (III) chloride for 30 min. These films were dried in air and then fired in muffle furnace at 450 ^oC for 24 h. These films are termed as Fe_2O_3 modified ZnO-TiO_2 thick films.

For the measurements of gas sensing properties of all these films, silver electrodes was used for electrical contacts. Gas-sensing measurements were carried out on a computer-controlled static gas-sensing system. A small Ni-Cr alloy coil was used for heating and a chromel-alumel thermocouple was used to monitor temperature. Keithley 6487 picometer cum voltage source was used to measure the sensor current. Test gas was injected into the chamber through an inlet port. The concentration of gas was kept 286 ppm and the % relative humidity was kept 20. The sensor response (S) was defined as the ratio of resistance in air (Ra) to that in target gas (Rg) [28].

$$S = R_a / R_g \quad (1)$$

3. Results and Discussion

3.1. Material Characterization

Fig. 1 shows X- ray diffraction (XRD) patterns of synthesized ZnO-TiO_2 powder samples (A to C). From XRD, it is revealed that materials are polycrystalline in nature with mixed hexagonal and tetragonal phases. The characteristic peak in the XRD pattern matches with hexagonal ZnO (JCPDS card no. 00-036-1451) and tetragonal TiO_2 (JCPDS card no 01-071-1166). Also the peaks which appeared at 2θ = 29.95°, 36.83°, 56.74°, 62.18° and 70.41° corresponds to Zn_2TiO_4 (JCPDS card no. 01-073-0578). The extra peak appeared at 2θ = 44.8° is related to surface hydroxyl groups on the ZnO-TiO_2 surface [29]. The average crystallite size (D) was determined by using Debye-Scherrer formula [30]:

$$D = 0.9\,\lambda/\,\beta\,\mathrm{Cos}\,\theta \qquad (2)$$

where λ is the wavelength of incident beam (1.5406 A°), β is the full width at half maxima (FWHM) of the peak in radians and θ is the diffraction angle.

The average crystallite size of samples (A to C) was calculated from bordering of the diffraction line and found to be in the range of 49-56 nm.

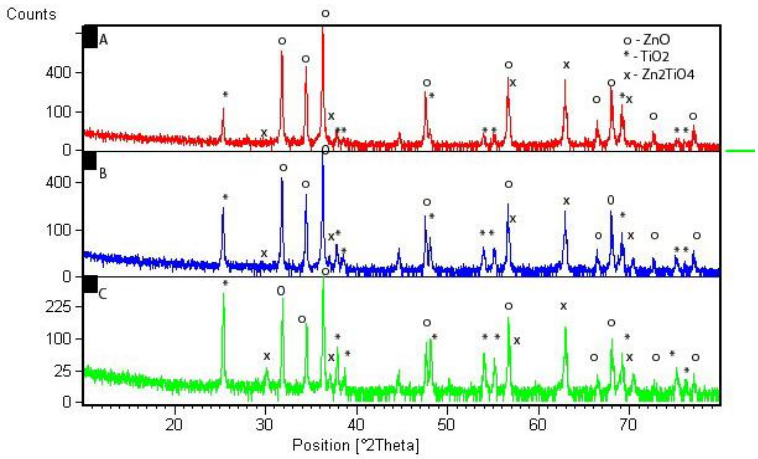
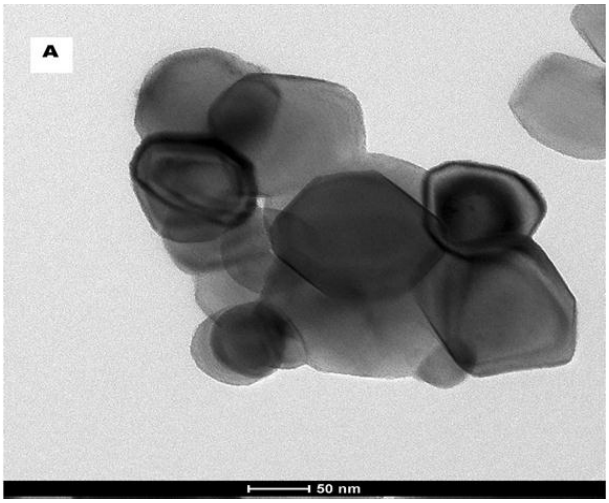


Fig. 1. XRD patterns of synthesized ZnO-TiO_2 with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.



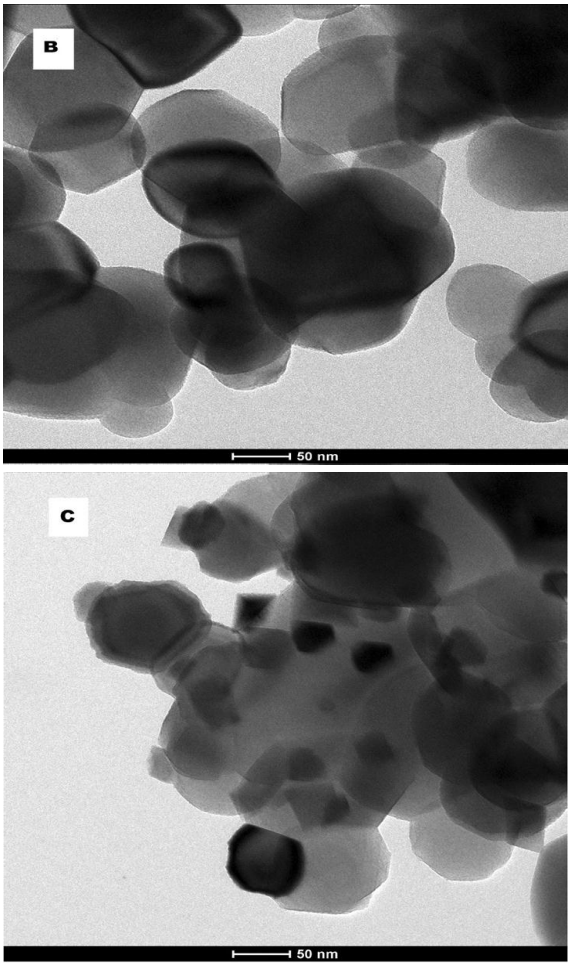
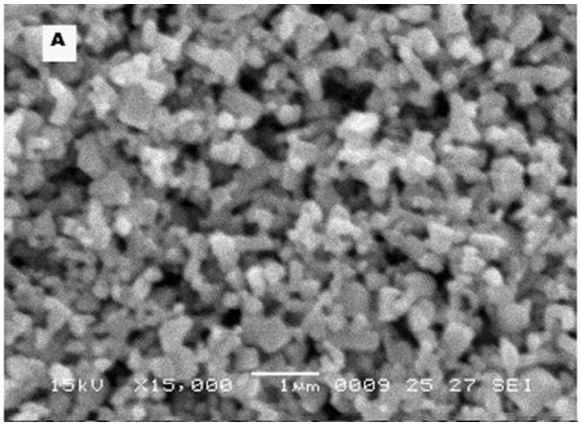


Fig. 2. TEM images of synthesized ZnO-TiO_2 with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.

The morphology of synthesized material samples was investigated by transmission electron microscopy (TEM). Fig. 2 illustrates TEM images of synthesized ZnO-TiO_2 powder samples with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1. The small amount of agglomerations can be seen in the micrographs. TEM images indicate that the average crystallite size of synthesized material is in nanometer range.

The surface morphology and nature of ZnO-TiO_2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 was analyzed by using scanning electron microscope (SEM, JEOL JSM 6380A). SEM micrographs of ZnO-TiO_2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 is shown in Fig. 3. It can be seen that the films particles are evenly distributed.



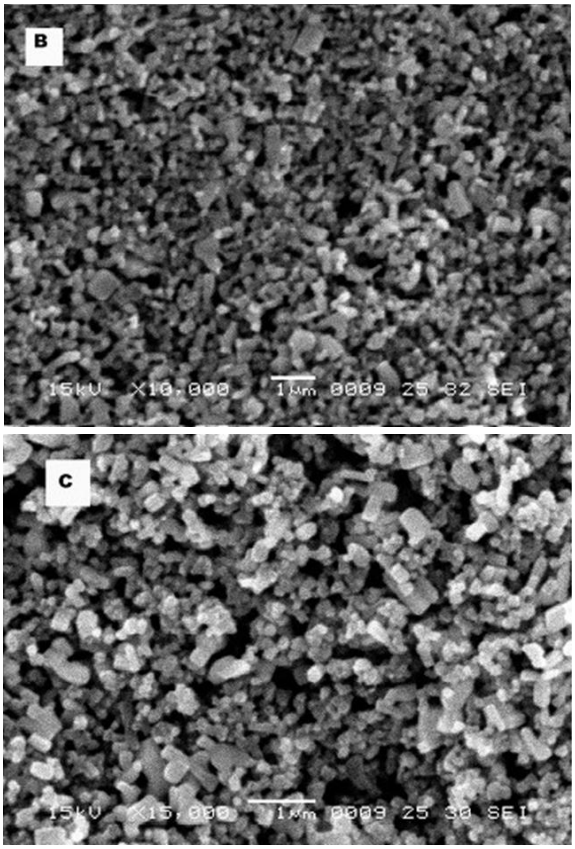


Fig. 3. SEM images of ZnO-TiO_2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1.

The elemental composition of Fe_2O_3 modified ZnO-TiO_2 thick films (with molar ratio 7:3) were analyzed by using energy-dispersive spectrometer (EDS). Fig. 4 shows EDS spectrum of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3). From the spectrum, it can be seen that there are no other elements than O, Ti, Zn and Fe in the film.

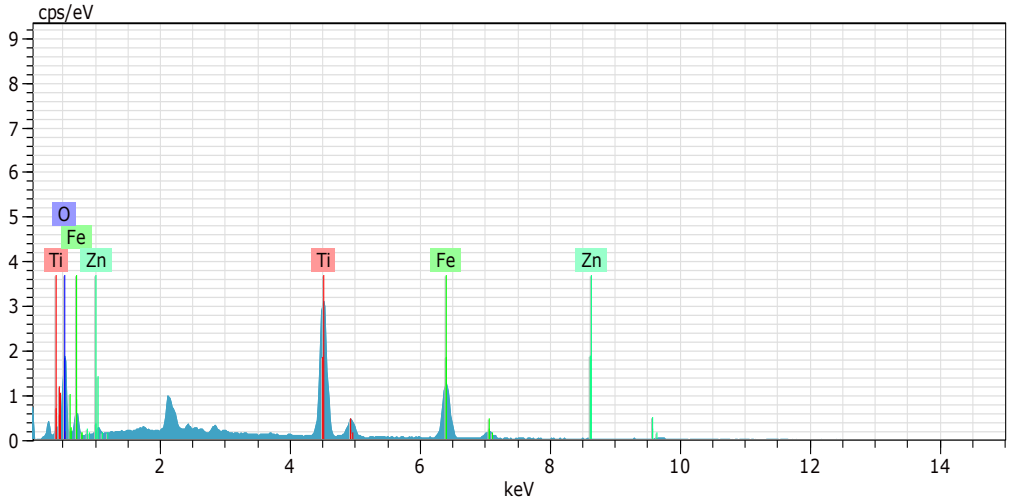


Fig. 4. EDS spectrum of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3).

Fig. 5 indicates SEM image of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3). It indicates that microstructure of 0.2M Fe_2O_3 modified film is uniform with adequate dispersion of Fe_2O_3.

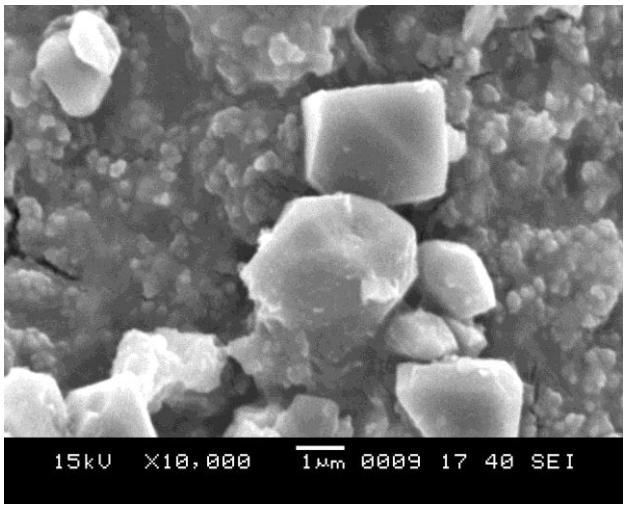


Fig. 5. SEM image of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3).

3.2. Gas Sensing Characteristics

Fig. 6 illustrates the response of ZnO-TiO_2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 towards 286 ppm H_2S. From the figure it can be seen that in the studied temperature range, among the tested compositions, ZnO-TiO_2 thick film (with molar ratio 7:3) shows good response.

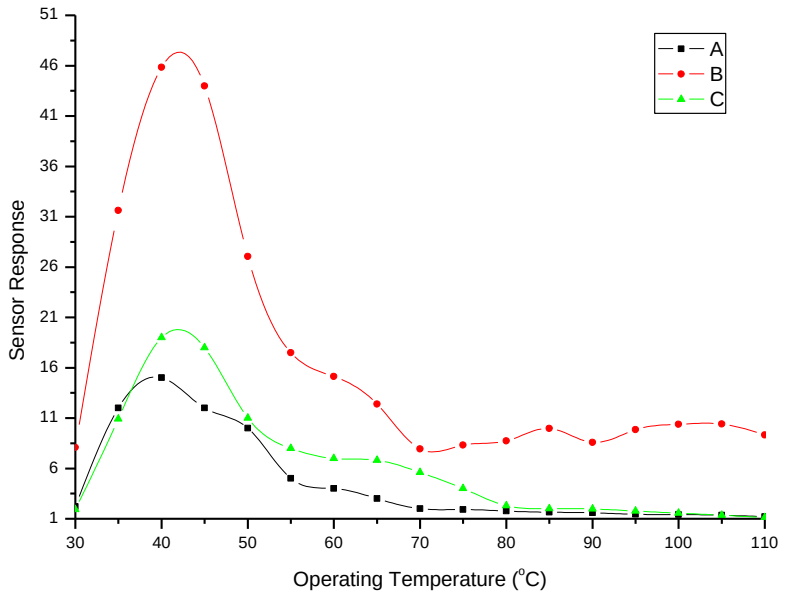


Fig. 6. Response of ZnO-TiO_2 thick films with molar ratio (A) 9:1, (B) 7:3 and (C) 1:1 towards 286 ppm H_2S.

Regarding the sensing mechanism of semiconductor oxide based materials, the sensing mechanism and change in electrical transport properties are generally depends on the oxygen molecules adsorption and desorption on the surface of materials and/or direct action of lattice oxygen or interstitial oxygen with test gases [31]-[37]. When ZnO-TiO_2 thick films are exposed to air, oxygen molecules interact with it to form adsorbed oxygen ions like O_2- or O- or O^{2-} by capturing electrons from the conduction band, which decreases the concentration of electrons in the conduction band. The reactions are as follows [38]:

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \quad \text{(i)}$$

$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads) \quad \text{(ii)}$$

$$O_2^-\,(ads) + e^- \leftrightarrow 2O^-\,(ads) \quad \text{(iii)}$$

$$O^-\,(ads) + e^- \leftrightarrow O^{2-}\,(ads) \quad \text{(iv)}$$

When we expose the H_2S to the sensor element, H_2S interact with the adsorbed oxygen and hydroxyl species present on the sensor. Fig. 6 indicates that the ZnO-TiO_2 thick film (with molar ratio 7:3) respond well to H_2S and exhibited the highest response at 40 °C among all investigated compositions. The response of ZnO-TiO_2 thick film towards H_2S can be explained by the interaction of H_2S with surface. In this interaction the adsorption of H_2S accounts for the consumption of oxygen and this reaction leads to decrease in sensor resistance. The sensor response was improved with increasing amount of TiO_2 content in the film; this indicated that there was increase in amount of chemisorbed oxygen ions. This is because electrons induced by Ti^{4+}, enter into ZnO lattice and this conformed to more chemisorbed oxygen on the surface [28]. When the optimum amount of TiO_2 in ZnO-TiO_2 thick film, TiO_2 species would be distributed uniformly throughout the surface of film. As a result the initial resistance of the film is high and this amount would be sufficient to promote the catalytic reaction effectively and overall change in the resistance on the exposure of H_2S leading to an increase in sensor response. At an operating temperature of 40 °C, the adsorption of H_2S molecules was maximum. The sensor response to H_2S can be explained with the overall reaction of H_2S molecules with adsorbed oxygen as [39]:

$$H_2S + 3/2\ O_{2\,(ad)}^- \rightarrow H_2O + SO_2 + 3/2\ e^- \quad \text{(v)}$$

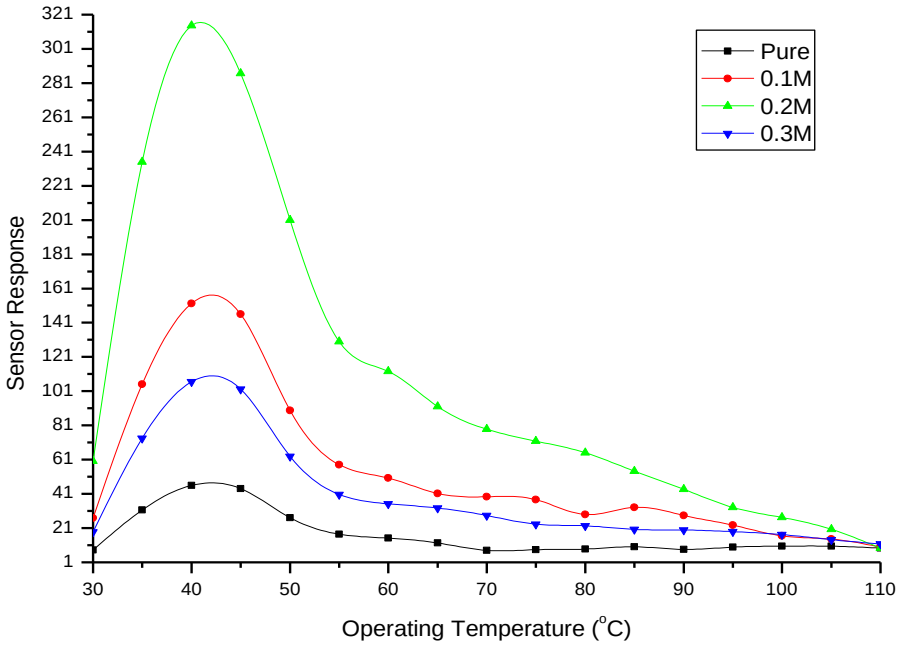


Fig. 7. Response of 0.1M, 0.2M and 0.3M Fe_2O_3 modified and unmodified ZnO-TiO_2 thick film (with molar ratio 7:3) towards 286 ppm H_2S.

Fig. 7 illustrates the sensing response of 0.1M, 0.2M and 0.3M Fe_2O_3 modified ZnO-TiO_2 thick films (with molar ratio 7:3) towards 286 ppm of H_2S with different operating temperatures. The figure illustrates that the sensing response of the film is a function of Fe_2O_3 content. It is clearly seen that the response is significantly higher for Fe_2O_3 modified ZnO-TiO_2 thick films especially at lower temperature. 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film respond at room temperature and exhibits remarkable response 314.67 at 40 °C. This can be attributed to the optimum and systematic Fe_2O_3 distribution in ZnO-TiO_2 matrix. The amount and distribution of Fe_2O_3 in ZnO-TiO_2 matrix play an important role in governing the H_2S sensing response. The maximum response may be due to Fe_2O_3 selectively catalyze the reaction rate of H_2S on the surface of film.

The H_2S sensing mechanism for Fe_2O_3 modified ZnO-TiO_2 thick film can be explain as; upon exposure of H_2S to the sensor, a surface reaction reduces the coverage of oxygen, causing returning of electron, here Fe-O sites may be acting as active centers. The adsorption of H_2S may be initiating from absorbed oxygen species on Fe, resulting H_2S dissociation with the formation of SO_2 and H_2O with the release of electrons. Due to this process electrons are made free for conduction and causing increase in sensing response.

Fig. 8 illustrates the response of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) toward different gases (286 ppm each) like NH_3, CO_2, H_2S & LPG at 40 °C. The sensor exhibited maximum response of 314.67 towards 286 ppm H_2S as compared to other gases like CO_2, LPG and NH_3. It is negligible for CO_2 and LPG. The high selectivity at low operating temperature may relate to the distribution of Fe_2O_3 which favors the adsorption of H_2S as compared with other gases. The adsorption configuration of H_2S molecules and surface reaction on the Fe-O sites are responsible for the low temperature sensing response towards H_2S selectively.

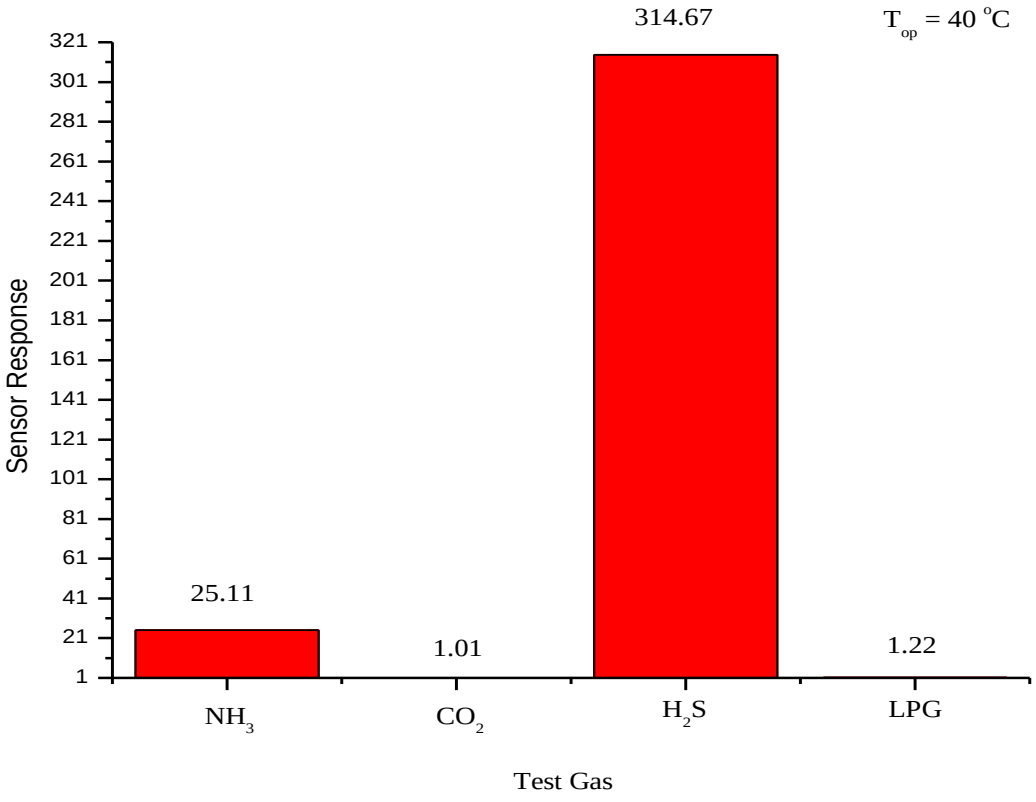


Fig. 8. Response of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) toward NH_3, CO_2, H_2S & LPG at 40 °C.

In practical application, response and recovery times of sensor for the particular gas are the important factors. Response and recovery times are defined as the time reaching 90% of the final stable values. Fig. 9 illustrates response and recovery time of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) towards 286 ppm H_2S at 40 ^oC. It indicates that response time and recovery time of sensor is 8 s and 30 s respectively. This result may be recommended for practical applicability of the sensor to detect H_2S.

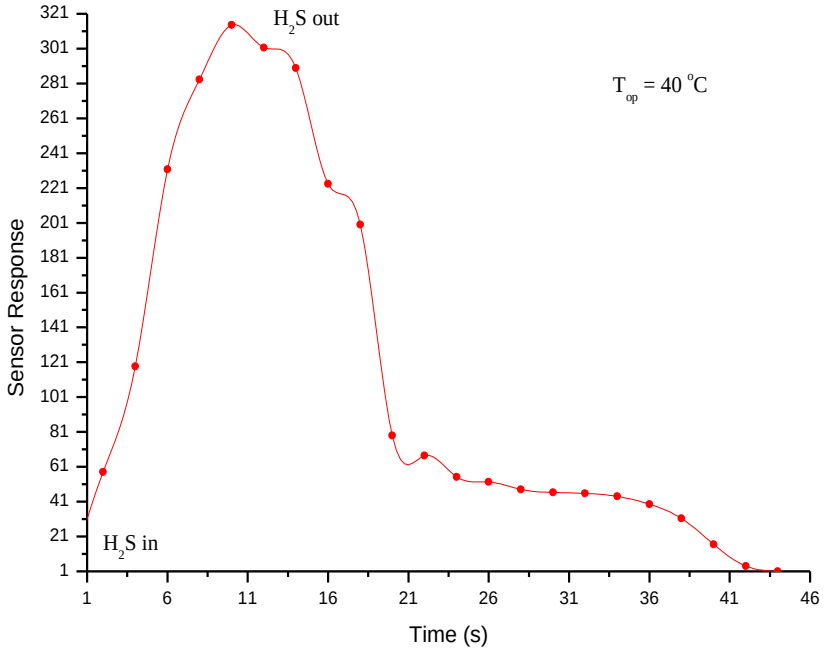


Fig. 9. Response and recovery time of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) towards H_2S at 40 ^oC.

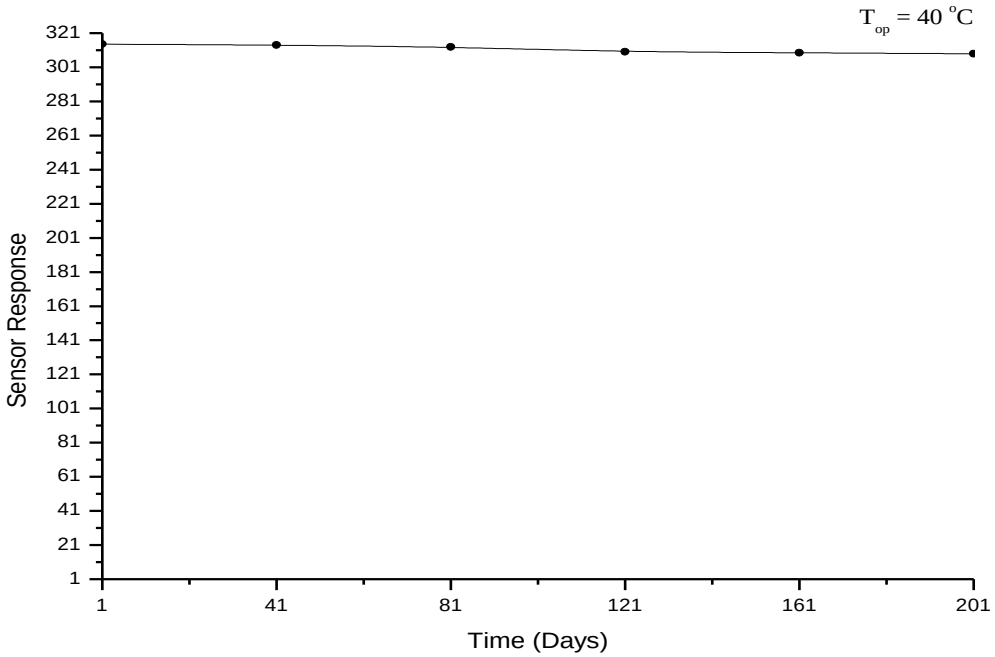


Fig. 10. Stability of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) towards 286 ppm H_2S at 40 ^oC.

Fig. 10 demonstrated response of 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) towards 286 ppm H_2S at 40 ^oC for the period of 201 days in the interval of 40 days. It is observed that there is no noticeable deviation in the sensor response. This is due to presence of TiO_2 [40].

4. Conclusions

On the basis of experimental results and its discussions, the following conclusions can be made:

(i) Nanocrystalline ZnO-TiO_2 materials were successfully synthesized by hydrothermal method. The crystallite size of synthesized materials is of the order of 49-56 nm.

(ii) The sensor element based on 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) exhibited good response to 286 ppm H_2S at room temperature and highest response of 314.67 at 40 ^oC.

(iii) The sensor element based on 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) is more selective toward H_2S as compared to CO_2, LPG and NH_3. Also it exhibited quick response (8 s), rapid recovery (30 s) and long time stability.

Hence sensor based on 0.2M Fe_2O_3 modified ZnO-TiO_2 thick film (with molar ratio 7:3) fulfills the practical requirement to detecting H_2S at low operating temperature.

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