RESEARCH PAPER | Physics | Volume : 3 | Issue : 5 | May 2013 | ISSN - 2249-555X

Hydrogen Sulphide Gas Interaction with Ferrite thin Film

KEYWORDS: Ferrite film, Gas sensor, Hydrogen sulphide, Hydrogen sulphide, Semiconductor sensor

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ABSTRACT *The highly sensitive nickel zinc ferrite thin films (NZF) $Ni_xZn_{(1-x)}Fe_2O_4$, as H_2S sensor films were demonstrated. The NZF films were prepared using modified chemical deposition method on the glass substrate which were annealed before application. The porous morphology of the NZF films, which was confirmed by SEM, was wisely used for gas sensing properties towards various gases such as, H_2S, CH_3OH, C_2H_5OH, NH_3 and NO_2. The film $Ni_{0.3}Zn_{0.7}Fe2O_4$ with band gap of 1.94 eV shows highest response of 37 % was observed at 100 ppm for H_2S gas.*

1. Introduction

The wide applications of gas sensors in fields such as environmental monitoring, industrial production, domestic safety, and public security have attracted many researchers worldwide for their detection of combustible and noxious gases in the air [1]. Transition-metal oxides are the most promising candidates for gas-sensing materials because of their low preparation cost, high stability, and high compatibility with microelectronic processing, and are being extensively studied for detecting toxic and pollutant gases like CO, NH_3, NO_2, ethanol, and acetone, hydrogen sulphide [2, 3]. To date, many researchers have tried to find more suitable oxide materials and/or special microstructures with better gas sensing performances such as high sensitivity, fast response, and great selectivity [4]. For obtaining better performances, the sensing materials should have large surface area for sensing activation.

Semiconducting oxides have received significant recent attention as sensor materials because of their remarkable electrical properties sensitive to oxidative or reductive type of gases [5]. The search for novel materials for chemical sensors with enhanced performance has led the scientific community that works in the field to consider ternary compounds of metal-oxide semiconductors as potential candidates [6].

Hydrogen sulfide (H_2S) is a well-known toxic gas that can be produced or can be a byproduct of several processes such as oil refining, coal or natural gas manufacturing, fuel cells, or food processing industries. This gas is dangerous for human health even at low concentrations: exposure at 250 ppm can seriously injure the human body and even cause death [7], so the threshold limit for human exposure is usually set by governmental legislation [8]. In addition, H_2S can act as a poison that severely degrades the activity of catalysts and electrochemical devices. As a result, great effort has been spent in developing materials for highly sensitive and selective hydrogen sulfide sensors and in developing new efficient and low cost devices capable of real-time, fast detection of even very small amounts of H_2S; most of the literature in this field deals with resistive electrical sensor devices, where the active materials are powders [9] or thin films [10].

In this paper we present the application of various composition nickel zinc ferrite thin films (NZF) as gas sensor for gases such as, H_2S, CH_3OH, C_2H_5OH, NH_3 and NO_2. The NZF thin films are studied in details for the H_2S gas sensor application.

2. Experimental work

2.1 Synthesis and characterization of Nickel zinc ferrite thin films

All the chemicals as ammonia and chlorides of nickel, zinc and iron used were of sd fine make. The solutions were prepared in double distilled water.

The deposition of NZF thin films was done on micro glass slides. Two-beaker system was used for the deposition onto the glass substrate by alternate immersion of substrate in cationic precursor and anionic precursor. The cationic precursor contains 0.1 M nickel chloride solution and zinc chloride solution and 0.2 M ferrous chloride. The aqueous ammonia solution was used to adjust the alkaline pH of cationic precursor, it also acts as complexing agent. First, the ultrasonically cleaned glass substrate was immersed in cationic precursor for 30 seconds termed as adsorption period, so as to get nickel, zinc and iron hydroxides adsorbed onto the substrate. Double distilled water was used as anionic precursor maintained at 300 K again the substrate was rinsed with cationic precursor for 30 seconds termed as reaction period. These thin films were dried by hot air after each cycle. These thin films were then air annealed at 450 ˚C for 6 hours to form NZF thin film with cubic spinel phase by removing any hydroxide content.

The structural details of the NZF films were evaluated from different characterization techniques. XRD pattern shows that the NZF films were oriented towards the (311) plane confirming the spinel phase. The FTIR shows absorption peaks around 600 cm^{-1} which are typical for cubic spinel structure. The porous morphology is confirmed by SEM study. The TGA was carried out to confirm the stable oxide formation which takes place at 600 ^{0}C. The surface microstructure plays vital role in the wetting properties of materials. The NZF thin films were subjected for investigation of static water contact angle measurements. Amongst the various compositions the film M-CDM37 has shown 25˚ due to regular grain like structure and porous morphology. This morphology is made use for gas sensing.

The estimated band gap is ranging from 1.98 - 2.02 eV. The band gap of different composition NZF thin film are listed in table.1. The values of band gap confirms the NZF thin films are semiconductor metal oxide.

Table.1 Band gap of NZF thin films

Thin film	Band gap (eV)
MCDM19	1.98
MCDM37	1.94
MCDM55	2.02
MCDM73	1.98
MCDM91	2.02

The resistance play vital role in the gas sensing study. The resistance of NZF thin films with temperature was measured in the range of 50˚C to 200˚C.

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The resistance of NZF thin films decreases as the temperature increases indicating a semiconducting behavior of NZF thin films. Film M-CDM37 has low resistance as compared to other NZF thin films.

NZF thin films, $Ni_xZn_{(1-x)}Fe_2O_4$ (where x is 0.1, 0.3, 0.5, 0.7 and 0.9), of different composition were prepared, as MCDM-19 ($Ni_{0.1}Zn_{0.9}Fe_2O_4$), MCDM-37 ($Ni_{0.3}Zn_{0.7}Fe_2O_4$), MCDM-55 ($Ni_{0.5}Zn_{0.5}Fe_2O_4$), MCDM-73($Ni_{0.7}Zn_{0.3}Fe_2O_4$), MCDM-91($Ni_{0.9}Zn_{0.1}Fe_2O_4$). Thin films deposited on the glass substrates were cut into the dimension of 1 cm × 1.5 cm. Two electrodes for contact were made on the top of the film using silver paste of 1mm wide and 1 cm apart from each other. This prepared NZF thin film was used as the sensor material.

2.2 Nickel Zinc Ferrite thin films based gas sensor

Now a days oxide materials are prominently used as gas sensors. The nickel zinc ferrite is one of the oxide which serves as a promising candidate for gas sensor because of its key advantages like, it exhibited tuneable conducting behavior, resistivity of the order of 10^7-10^9 Ωcm^{-1} and large excitation binding energy.

2.3 Experimental setup of gas sensor testing

For measuring gas sensing properties of NZF thin films the resistance of the thin film is measured in air and in the presence of a known concentration of the analyte gas at optimized temperature.

In this method, the nickel zinc ferrite thin film of $1cm^2$ dimension was mounted in an enclosed test chamber of a known volume. In order to measure the sensor resistance in a desired concentration of the analyte gas, a known amount of gas from calibrated canister is injected into chamber using a syringe. The resistance of the sensor as a function of time in second was measured using Rigol DMM [31] before and after exposure of gas. The recovery of the sensor was studied by exposing chamber to air. Nickel zinc ferrite thin films are tested for hazardous gases such as H_2S, NH_3, NO_2, CH_3OH, C_2H_5OH etc. at optimized temperature.

3. Gas sensing properties of NZF thin films

It is interesting to investigate the gas sensing properties of nanocrystalline NZF thin films. To study gas sensing properties of NZF thin films by M-CDM, parameters the selectivity of gas, selection of thin film, effect of the gas concentration were considered

3.1 Selectivity

The nickel zinc ferrite is mixed metal oxide and shows high resistivity. Different hazardous gases like H_2S, NH_3, NO_2, C_2H_5OH and CH_3OH, were tested for the NZF thin films. By taking in account the good morphology of film M-CDM37, it is used for the gas sensing measurement, the concentration of gas was 100 ppm and operating temperature was maintained at 200˚C. The bar chart in Fig.1 shows selectivity of NZF films for H_2S gas operating at 200˚C. The coefficient of selectivity (S_A/S_B) for H_2S: NH_3, H_2S:NO_2, H_2S: C_2H_5OH and H_2S: CH_3OH were 4.73, 6.00, 18.00 and 180.00 respectively. This implies that the H_2S is more selective to NH_3 and NO_2 against C_2H_5OH and CH_3OH. Thus, the NZF thin films are selective for H_2S gas.

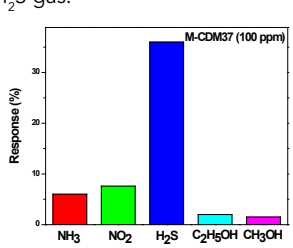

Fig. 1 Selectivity of NZF thin film towards different gases (at 200˚C)

It is observed that NZF thin film shows best response to the H_2S gas whereas exhibits negligible response to C_2H_5OH, CH_3OH, NH_3 and NO_2 gas. H_2S is reducing gas which strongly interacts with the ferrite material and shows high response. The operating temperature plays vital role in the gas sensor study. Fig.2 shows the plot of response versus temperature, which confirms the optimized operating temperature for NZF sensor as 200˚C. So the operating temperature 200˚C is fixed for the further gas sensor study [12].

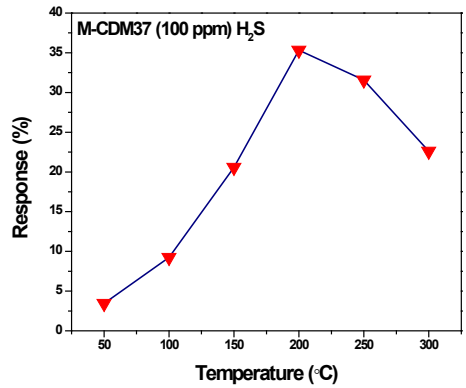

Fig. 2 Selectivity of operating temperature

3.2 Mechanism of H_2S gas sensor

The nickel zinc ferrite behaves as n-type semiconducting oxide. With the increase in the temperature, the state of oxygen adsorbed on the surface of sensor undergoes the following reaction [13],

$$O_2(gas) \leftrightarrow O_2(ads) + e^- \leftrightarrow O_2^-(ads) + e^- \leftrightarrow 2O^-(ads) \quad (1)$$

With the introduction of the H_2S gas, it would react with oxygen ions adsorbed on the surface of the sensor. The reaction process is as follows [14].

$$H_2S + O_2^-(ads) \rightarrow SO_{2(g)} + H_2O_{(g)} + 6e^- \quad (2)$$

Reaction of these oxygen species with reducing gases, or a competitive adsorption, and replacement of the adsorbed oxygen by other molecules causes reverse band bending, resulting in an increased conductivity. The water molecule gets released and surface layers enriches by charge carrier electrons due to that resistance decreases [12].

3.3 Selection of thin film

To select the thin film from different composition of NZF thin film which shows higher response to the H_2S gas, the NZF thin films M-CDM19, M-CDM37, M-CDM55, M-CDM73 and M-CDM91 of various compositions were tested. Fig.3 shows the selection of NZF thin films.

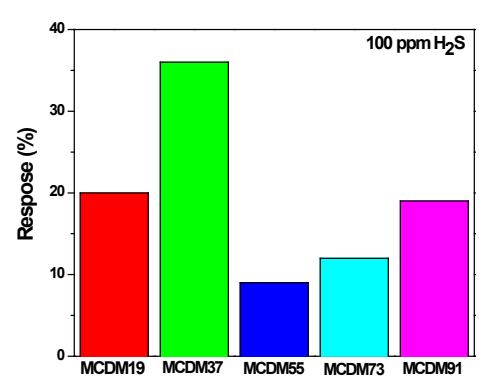

Fig.3 Selection of thin film

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Table.2 Response of NZF thin films

Thin film	Response (%)
MCDM19	20
MCDM37	36
MCDM55	09
MCDM73	12
MCDM91	19

Table 2 represents the response of NZF thin films for 100 ppm H_2S gas at 200˚C. Thin film M-CDM37 exhibits the high response (36 %) as compared to other composition of NZF thin films. Thin film M-CDM37 ($Ni_{0.3}Zn_{0.7}Fe_2O_4$) has small crystallite size as compared to other thin films i.e. 21 nm and the SEM images shows the nanostructured grains like morphology. This material has porous nature, which increases the surface area of material. Since the competence of material is significantly influenced by its surface area and morphology, it increases the surface to volume ratio. Thin film M-CDM37 has static water contact angle was 25˚ and show hydrophilic nature. The wettability of any solid surface by a liquid increases with its porosity, due to such properties, thin film M-CDM37 shows best response and significant for gas sensor application. Thus, film M-CDM37 is selected for the further gas sensor study.

3.4 Effect of H_2S gas concentration on nickel zinc ferrite thin films

The H_2S gas of different concentrations was tested on the thin films M-CDM37. The concentration varies as 20, 40, 60, 80 and 100 ppm of H_2S. The change in resistance with respect to time on exposure to H_2S gas is shown in Fig. 4. It is observed that the resistance of the thin film decreases dramatically on exposure of the H_2S gas and increases slowly when exposed to clear air. This decrease in the resistance on exposure to H_2S gas is due to the strong interaction between sensor film and analyte gas. The response of M-CDM37 film sensor to H_2S gas was calculated using the following formula,

$$S\ \% = \frac{|R_a - R_g|}{R_a} \times 100 \qquad (1)$$

The Fig.5 shows the response of M-CDM37 film sensor to H_2S gas. The M-CDM37 thin films shows good response time i.e. 27 sec, but poorer incomplete recovery time is about 102 sec for 100 ppm H_2S gas. This faster response may be due to granular morphology of M-CDM37 thin film offering high surface to volume ratio. The slow recovery time may be due to the reaction site formed in the interaction of gas and sensor films; are not leaving thin film surface.

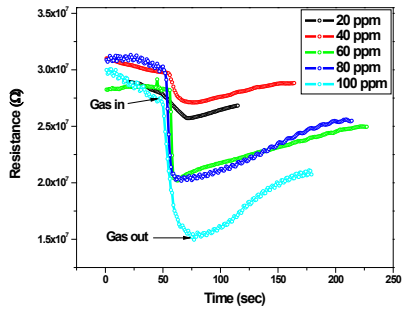

Fig. 4. Gas response of NZF thin films to H2S gas (20-100 ppm)

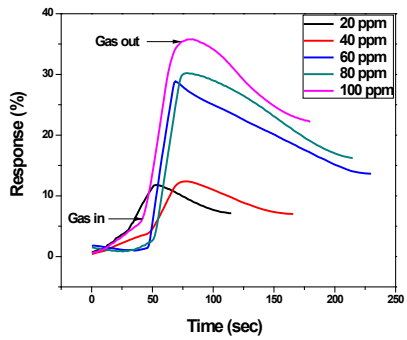

Fig. 5. Gas response of NZF thin films to H2S gas (20-100 ppm)

The effect of H_2S gas concentration on response of M-CDM37 thin films was also studied. As the concentration of H_2S gas increases the response also increases, from this it is conclude that, response is directly proportional to gas concentration. The highest response 37 % was observed at 100 ppm of H_2S gas. When the concentration of H_2S comes to some point, the reactions would reach equilibrium. The effect of equilibrium on the conductance would play a major role in leading to nearly steady sensor response.

4. Conclusion

The NZF thin films deposited by M-CDM were successfully checked for sensing of hazardous gases like H_2S, NH_3, NO_2, C_2H_5OH and CH_3OH, at concentrations of 100 ppm and 200 ˚C temperature. The coefficient of selectivity (SA/SB) for H_2S: NH_3, H_2S:NO_2, H_2S: C_2H_5OH and H_2S: CH_3OH were 4.73, 6.00, 18.00 and 180.00 respectively indicating that the H_2S is more selective than other gases. The mechanism of H_2S gas sensor is discussed in detail. The M-CDM37 thin films shows good response time of 27 sec. The highest response 36 % was observed at 100 ppm of H_2S gas.

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