REALIZATION OF H2S GAS SENSOR USING SOL-GEL PROCESSED ZnFe2O4 THIN FILM

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Abstract: *The rapid growth in technology has led the convenience for society but it also inevitably brought many problems to the environment and different lives. Hydrogen Sulfide (H_2S) is one of the major pollutants considered toxic gas. Significant sources of H_2S gas are fossil fuels, natural gas production, and other chemical industries. The higher concentration of H_2S (>500 ppm) in breathing can cause unconsciousness or even death. Thus, selective detection of H_2S traces in the ambient atmosphere is highly desirable. In this study, we demonstrated low-cost and highly sensitive $ZnFe_2O_4$ nanostructured thin film with spinel structure using the Sol-gel method. The $ZnFe_2O_4$-based sensor device shows the highest sensitivity of 81% for 100ppm of H_2S concentration at 250°C. It also exhibits fast response and good selectivity. The work implies the potential application of sol-gel prepared $ZnFe_2O_4$ in H_2S gas detection at 250°C.*

Keywords: *$ZnFe_2O_4$, spinel ferrite, H_2S, operating temperature, selectivity, response.*

Introduction

$ZnFe_2O_4$ has a spinel ferrite structure with a unit cell consisting of an array of FCC O^{2-} anions with Zn^{2+} at tetrahedral interstices and Fe^{3+} at octahedral interstices formed of O^{2-}. $ZnFe_2O_4$ is a narrow band gap around 1.9 eV ternary metal oxide semiconductor. $ZnFe_2O_4$ detects target gas via a complex interaction of the surface gas-solid phase process. $ZnFe_2O_4$ is multifunctional material used in the gas sensing field, photocatalyst, Li-ion batteries, solar cells, and magnets. In the gas sensing field, an excellent exploration of properties has been demonstrated by $ZnFe_2O_4$ with its co-substances such as porous $ZnFe_2O_4$ NRs to acetone, RGO- $ZnFe_2O_4$ to ethanol, $ZnFe_2O_4$-NRs to Formaldehyde, porous $ZnFe_2O_4$ NSs to H_2S and so on.

The mechanism for gas sensing of $ZnFe_2O_4$ gas sensors is as follows: At the time of the surface gas-solid phase reaction process, O_2 molecules adsorbed on the surface of $ZnFe_2O_4$ and the sensor captures free electrons from the conduction band and the formation of O^{2-} anions occur shown in E. (1). Depending on operating temperature, oxygen is present in molecular (O_2^-) or atomic (O^- and O^{2-}) form. The dependency of oxygen forms on temperature is shown in Eq. (2) and Eq. (3) as follows:

$$O_2(gas) + e^- \rightleftharpoons O^{2-}(ads)\ , T < 147℃ \quad (1)$$

$$O^{2-}(ads) + e^- \rightleftharpoons 2O^-(ads)\ 147°C < T < 397°C \quad (2)$$

$$O^-(ads) + e^- \rightleftharpoons O^{2-}(ads)\ T > 397°C \quad (3)$$

Due to unique ferrite crystal structure and high surface activation energy and by lowering the limit of detection with the coexistence of familiar substances makes $ZnFe_2O_4$ a good sensing material. ZnFe2O4 due to its low-cost synthesis, small size, low power consumption, and portability explores for the application of industrial problems and diagnostic clinical events. The redistribution of cations in the $ZnFe_2O_4$ structure changes its various properties which gives a new direction to gas sensing research. Doping suitable metal on $ZnFe_2O_4$ with restriction $MxZn_{1-x}Fe_2O_4$ can improve the sensing performance of $ZnFe_2O_4$ due to their good surface activity (M=Ni, Cu, Ca, etc.) Various methods have been used to improve the gas sensing properties and reduce the operating temperature of Metal Oxide Semiconductor nanomaterials like functionalization of surface and doping of noble gaseous atoms [1-2].

Wie Zhang et al [3]. reported, In Cu- $ZnFe_2O_4$, generally there is no effect of Copper doping on the growth process but it increased the dispersibility of products. Fen Liu et al [4]. reported, the sensor based on 0.125% G- $ZnFe_2O_4$ (180℃,10h) exhibits good selectivity and reproducibility to 10ppm acetone vapour at 275℃. X.Chu et al [5] reported ZnFe2O4- GQDs nanocomposite with 15 ml GQD suspension exhibited good response and good selectivity to acetone vapor at room temperature.

Methodology

$ZnFe_2O_4$ solution is prepared by dissolving 0.2 M and 0.4 M of $Zn(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ respectively in 5ml water. This mixed solution was magnetically stirred for 2 hours and then 0.6 M of Citric acid was added to the prepared solution and then the final solution was stirred for 20 hours at room temperature. Next, 150 µL Acetylacetone and 150 µL Triton X- 100 were added. Then, cleaned Si was spin-coated at 1500 rpm for 20 seconds five times with the above-prepared solution. Afterward, it was annealed at 700°C under a tubular furnace for 3 hours.

Then, an IDE (Interdigitated Electrode) pattern with Au-Cr with a thickness of 200 nm-20 nm was created on a thin film. Gas sensor performance was measured by a sensing system. By measuring the electrical resistance or current of a gas sensor by applying 3 V of voltage between the two electrodes. The gas sensor resistance is first measured in air, and then a certain amount of H_2S gas injected into the test chamber by injection or any other controlled apparatus. All gas sensing tests were performed at about 250 °C. The response to H_2S was defined as (Ig-Ia)/Ig, where I_a and I_g were the currents of the gas sensors in the air and H_2S respectively. The response and recovery time of a sensor is defined as the times taken to achieve up to 90% change of the total resistance in the case of adsorption and desorption of injected gas, respectively.

Results and Discussion

XRD and SEM images tell us about the crystal structure and morphology of the sample as shown in Fig. 1(a) and Fig. 1(b) respectively.

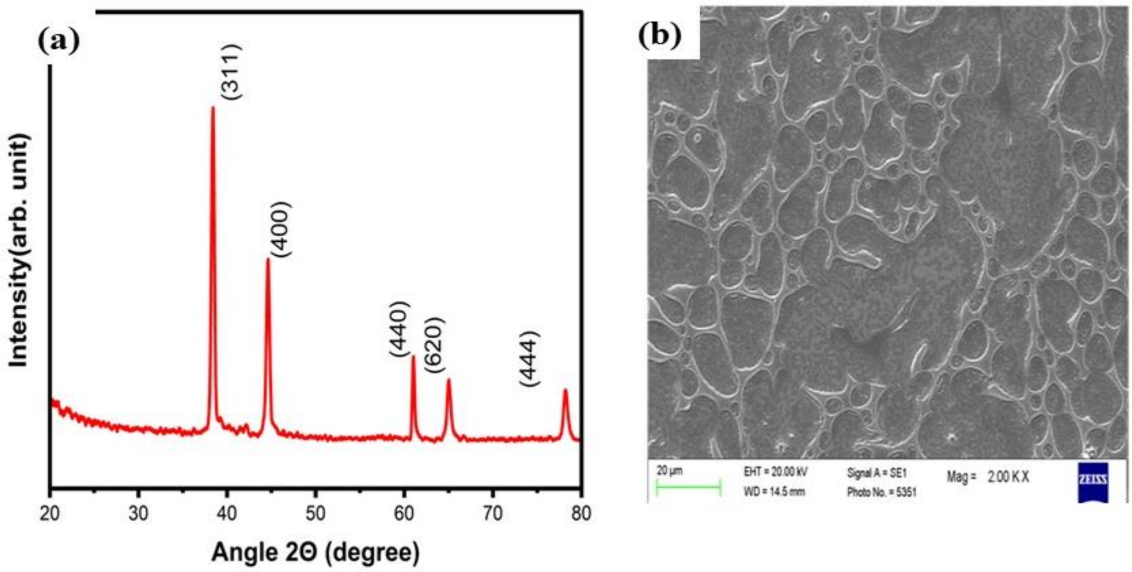

Figure 1. (a) XRD of $ZnFe_2O_4$ thin film (b) SEM image of $ZnFe_2O_4$ thin film

UV visible study is also being done to determine the band gap of the samples as shown in Fig. 2(a) and IV characteristics as shown in Fig. 2(b).

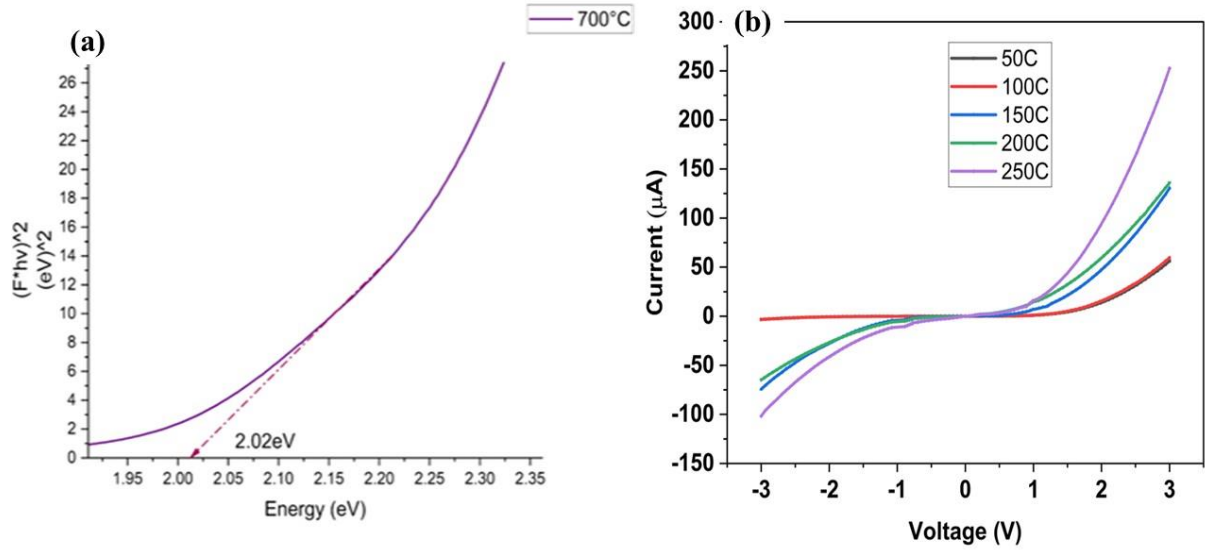

Figure 2. (a) UV Vis graph (b) IV Characteristics.

Gas Sensing Characteristics

Gas sensing selectivity can be figured out by the above-mentioned graph of bare ZFO which shows good selectivity for H_2S gas as for 100ppm gas at 250 ° C temperature. CO, NO_2, NH_3, SO_2, and H_2S show relative responses as 31%, 35%, 36%, 37%, and 57% respectively. Sensing response and selectivity as shown in Fig. 5 and Fig. 6 respectively.

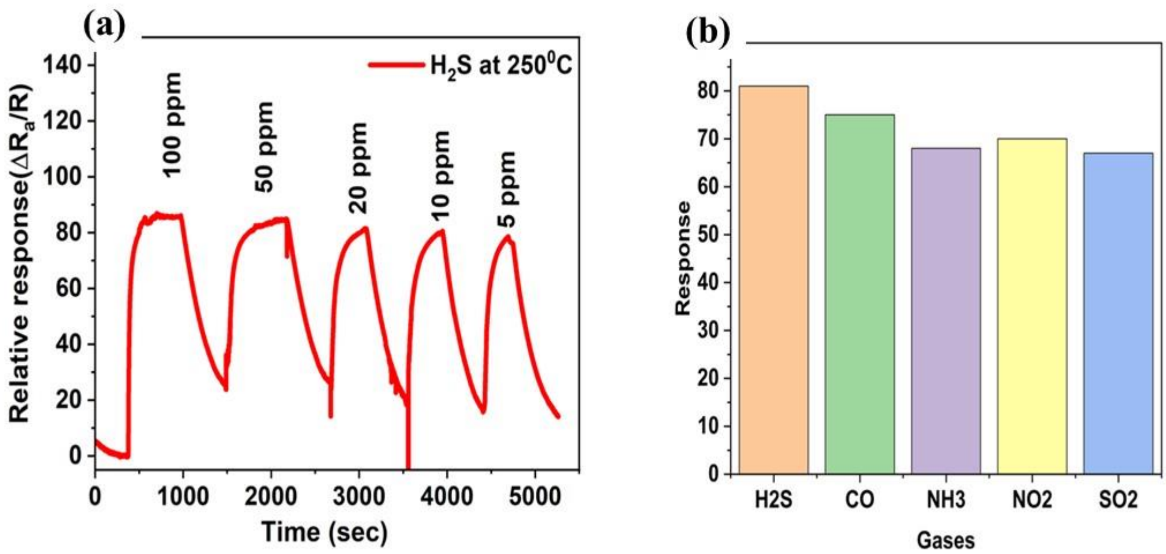

Figure 3. (a) Relative response (b) selectivity of different gases.

Conclusions

$ZnFe_2O_4$ is an n-type spinel ferrite structure having an energy band gap of around 1.9 eV confirmed by UV-visible spectroscopy. The above-studied thin film sample of $ZnFe_2O_4$ has the morphology of nanofibres confirmed by SEM characterization technique with good elemental composition confirmed by EDAX. Material that is pure without any other impurity is also confirmed by XRD characterization having all major peaks of $ZnFe_2O_4$ with a signature peak of it as (311) also gives firm evidence of $ZnFe_2O_4$ presence. Electrical properties and chemical properties are also characterized by gas sensing characteristics as discussed above with good results of sensing selectively 100ppm H_2S gas at 250° C.

References

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