Gas sensing behavior of ZnO thick film sensor towards H$_2$S, NH$_3$, LPG and CO$_2$.

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Abstract - ZnO is synthesized by microwave assisted technique. The XRD, TEM, SAED and SEM characterization of sample is carried out for studying crystal structure, particle size, crystalline nature and surface morphology of ZnO samples. The thick films of ZnO sample were fabricated by screen printing technique and its I-V characteristics and electrical conductivity were studied. The gas sensing response of ZnO thick film sensor towards 450 ppm of H$_2$S, LPG, NH$_3$ and CO$_2$ gas was investigated. The thick film showed response 15 towards H$_2$S at 150 0C, response 3 to NH$_3$, response 2 for LPG and no response to CO$_2$. The variation of response with H2S concentration was also studied. The response time and recovery time of sensor was 70 second. It was selective to H$_2$S in presence of LPG, NH$_3$ and CO$_2$ gases. The thick film showed good reproducibility and stability for H$_2$S.

1. Introduction:
Zinc is a chemically active metal. Zinc oxide is a multifunctional semiconducting metal oxide and one of the most promising materials for gas-sensing application. It is $n$-type semiconductor and can be use as a gas sensor. The electrical conductivity of ZnO sensor changes when it exposed to reducing or oxidizing gases. ZnO is sensitive to many gases, but, its working temperature is 400 0C to 500 0C and its gas response is poor. In recent years, the study on ZnO nanostructure sensor is increased and focusing to reduce its operating temperatures up to room temperature. ZnO is the most capable semiconductor to detect the toxic and hazardous gases [1-5]. It has been proved that ZnO is a good gas sensitive material for detection of both reducing and oxidizing gases [6-14]. Various gases have been tested on ZnO nanostructure sensor, such as acetone, CO$_2$, ethanol, NO$_2$, and NH$_3$ [15-20].Recently, to improve the gas sensing properties of ZnO, various materials have been employed to modify its surface properties [21-25].

2. Experimental:
2.1. Synthesis of ZnO and fabrication of thick film:
Microwave oven is used as a heating tool for synthesizing zinc oxide. The analytical reagent Zinc chloride and liquid ammonia from Merck India Ltd were used as a basic material without further
purification. The zinc hydroxide solution was prepared by using 0.1 mol zinc chloride in de-ionized water [26]. Diluted liquid ammonia was used for adjusting the pH of solution [26-29]. For fabricating ZnO thick films, the screen printed technique is used as explained at other place [26]. The fabricated thick films called the ZnO thick film sensor.

3. Characterization:

3.1. XRD investigation of Zinc oxide:
XRD pattern of ZnO was obtained on BRUKER- D8, Advanced using Cu K as X-ray source. The XRD pattern of the Zinc oxide nanomaterial is shown in figure 1. The Width present at the half maxima of intensity patterns indicates that, the particle size is less than 100 nm. The average particle size calculated by Scherrer formula found out to be 51 nm. It is observed from the pattern that (101) reflections corresponding to 2θ = 36.246° has maximum intensity among all the peaks. This indicates that ZnO had preferred orientation in the direction of (101) plane. The respective peaks and corresponding reflection plane are as (100), (002), (101), (102), (110), (103), (200), (112) and (201). Various peaks and corresponding reflection in the XRD pattern matched with the JCPDS card number 21-1486 [30]. No other impurity peaks are seen in the pattern, suggested the formation of single phase ZnO. High intensity peaks and reflections indicates the polycrystalline nature of the sample. Particle size calculated from Scherrer formula matched with the particle size shown by TEM micrograph.

3.2. Surface morphology of ZnO:
Surface morphology of sample was studied by scanning electron microscope (SEM). The micrograph of sample is shown in figure 2. The ZnO has porous rod shape and the tube structure. The particle size of ZnO is range from 35nm to 100 nm and above and they are distributed randomly. The tube structure increases the effective surface area for adsorption of gas, which is favorable for improving gas response. Non-uniformity in particle size and tube structure of ZnO which is present in micrograph may also play the effective role for enhancing gas response [31-32].
3.3. EDAX pattern and elemental composition:

Figure 3. EDAX pattern of ZnO.

EDAX pattern of ZnO is depicted in figure 3. The presence of only Zn and O are observed in it. Table 1 shows the elemental mass % and At % in the synthesized sample. The number of intensity peaks of Zn is greater than O peak. Further the intensity of Zn peaks is quite greater than O, indicating that the mass percent of Zn is quite greater than O. The ZnO sample comprises of 64.68 mass percent of Zn and 35.52 mass percent of O.

| Sr. No. | Element | Mass %   | At %  |
|---------|---------|----------|-------|
| 1       | O       | 35.32    | 69.05 |
| 2       | Zn      | 64.68    | 30.95 |
| Total   |         | 100      | 100   |

No impurity elements are observed in EDAX pattern and elemental composition result of sample, which clearly indicates that, the synthesized sample is purely zinc oxide.
3.4. Investigation through TEM and SAED:

![Image of TEM micrograph and SAED pattern of ZnO](image)

**Figure 4.** TEM micrograph and SAED pattern of ZnO.

TEM micrograph of sample was taken by PHILIPS, CM 200 which is showed in Figure 4. The 93 nm ZnO rod can be clearly observed in micrograph. SAED pattern is showed in the inset of figure 4. It is consisted of bright spot of varying sizes in the ring depicting the polycrystalline nature of sample [33].

4. Electrical behavior:

4.1. I-V characteristics:

![I-V Characteristics of ZnO](image)

**Figure 5.** I-V Characteristics of ZnO.

The I-V characteristics of ZnO thick film at different temperature are shown in figure 5. Nature of I-V characteristics indicated that, the contacts formed on the surface of thick film are ohmic in nature [34-39].

4.2. Nature of electrical conductivity:

The electrical resistivity of ZnO thick film is studied with the help of Keithley 6487 picoammeter cum voltage source. The variation of log (conductivity) with temperature of ZnO thick film is showed in figure 6. As the temperature increases, the trapped electrons are thermally excited and the rate of desorption of adsorbed oxygen molecules increases, which releases the free electrons to the
The conduction band and produce more current, hence increase in conductivity with temperature is observed. The nature of conductivity curve shows the negative temperature coefficient of resistance ie semiconducting nature of ZnO thick films [35-40].

![Figure 6. Conductivity of ZnO.](image)

5. Gas sensing performance:
The gas sensing response can be calculated as,

\[ \text{Gas response } S = \frac{R_a}{R_g} \]

Where \( R_a \) is the resistance in air ambient and \( R_g \) is the resistance in presence of gas under test [41-45]. While measuring the resistance, the voltage applied to the sensor was 10 volt.

5.1. Gas response and operating temperature:

![Figure 7. Variation of gas response with operating temperature.](image)

The variation of gas response with operating temperature for 450 ppm of H\(_2\)S, LPG, NH\(_3\) and CO\(_2\) gases are shown in figure 7. The ZnO depicted highest response 15 towards H\(_2\)S at 150 °C; the response is 3 towards NH\(_3\) at 100 °C, towards LPG the response at 50 °C is 2 and no response to CO\(_2\). It means pure ZnO thick film sensor is insensitive to NH\(_3\), LPG and CO\(_2\). The gas sensing mechanism of sensor are reported in various reports [46-51].
5.2. **H$_2$S concentration and gas response:**
Variation of ZnO response with H$_2$S concentration is shown in figure 8. At low concentration of H$_2$S gas the response was fast, but beyond certain concentration of H$_2$S it becomes slow and at 600 ppm and above the response was saturated.

![Graph showing gas response versus H$_2$S concentration](image)

**Figure 8.** Gas concentration versus response.

At low concentration of gas maximum reaction sites are available for chemical reaction with gas leading to fast response. At higher concentration the available reaction sites decreases and response becomes slow. Above 600 ppm of H$_2$S multilayer of gas molecules form on the surface and upper layer will have no opportunity to react with oxygen molecules on the surface and response get saturated.

5.3. **Response and Recovery time:**

![Graph showing response and recovery time](image)

**Figure 9.** Response and recovery time of ZnO for H$_2$S.

The time require to reached the response 90% of its maximum value called the response time and the time required to fall the response 90% of its maximum after removal of gas called the recovery time. The Response and Recovery time of ZnO at 150 °C towards H$_2$S was 70 second and depicted in figure 9.
5.4. Selectivity and reproducibility of ZnO:

ZnO showed selectivity to H$_2$S at 150 °C in presence of 450 ppm of H$_2$S, LPG, NH$_3$ and CO$_2$ gases as shown in figure 10. It has also shown good reproducibility and stability for H$_2$S.

6. Discussion: The simple adsorption desorption mechanism can be used to explain the gas sensing mechanism of ZnO thick film sensor towards H$_2$S. It is showed in figure 11.

The free electrons from conduction band at the surface of ZnO thick film sensor are trapped by the adsorbed oxygen species from air ambient. Hence, the resistance of the thick film increases due to increase in width of the depletion region and height of potential barrier. Thus the current produced will be small. On the other hand when the thick film exposed to H$_2$S, the adsorbates oxygen molecules on the surface reacts with H$_2$S and oxidized it. Thus the oxygen molecules get extracted from the surface...
and released the free electrons to the conduction band which produce more current. The favourable temperature for adsorption of maximum oxygen molecules by ZnO surface is 150 °C.

When the sensor surface exposed to H$_2$S, it reacts with adsorbed oxygen and SO$_2$ and H$_2$O are formed which releases the free electrons to the conduction band [52].

$$2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$$

The response of ZnO towards NH$_3$ and LPG were very small. The film showed no response to CO$_2$.

7. Summery, conclusion and future scope:
The microwave technique is more cost effective and user friendly technique, therefore the Samsung microwave oven was used as a heating tool for synthesizing ZnO nanocrystalline material. The ZnO has wurtzite hexagonal structure. XRD and TEM study depicted 35 to 100 nm size of ZnO tube. The rod shape and tube structure of ZnO nanoparticles were observed in SEM study. The I-V characteristics showed the ohmic nature of silver contacts formed on the surface of the thick film. Electrical conductivity of thick film depicted the semiconducting nature. The response of sensor for 450 ppm of H$_2$S was 15 and sensor was rather insensitive to LPG, NH$_3$ and CO$_2$. Sensor showed selectivity to H$_2$S at 150 °C. The response and recovery time of the sensor for 450 ppm of H$_2$S at 150 °C temperature were 70 second. The gas sensing response of ZnO thick film to H$_2$S, LPG, NH$_3$ and CO$_2$ is poor. Therefore doping or surface modification of ZnO thick film by different metal oxide can be tried for improving gas response.

8. Acknowledgement-
I express my deep sense of gratitude to Dept. of Physics, Vidya Bharti Mahavidyalaya, Amravati (M.S.) India for providing the laboratory facility. I am thankful to Dept. of Physics, Savitribai Fule University Pune for extending help in carrying XRD and SEM of sample. I am grateful to IIT Bombay for extending help in carrying TEM and SAED of sample.

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