Synthesis, Characterizations and Gas Sensing Performance of Bi_2O_3 Surface Activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ Thick Films

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Abstract : Pure and bulk ZrO_2 and SnO_2 thick films as well as their nanocomposite powders were observed to be less sensitive to polluting, hazardous and inflammable gases. Hence, nanostructured zirconium oxide and tin oxide powders were synthesized by disc type ultrasonicated microwave treatment followed centrifuge technique. The suitable proportion of as synthesized powders of ZrO_2 and SnO_2 forms the nanocomposite, $Zr_{(0.75)}Sn_{(0.25)}O_4$. Thick films of nanocomposite $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder were fabricated by screen printing technique. These films were surface activated by Bi_2O_3 for different intervals of time followed by firing at 450ºC for 30 min. The characterizations, viz. surface morphology, chemical composition, crystal structure, electrical and gas sensing performance of the pure and modified nanostructured $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder by Bismuth Oxide were investigated by X-Ray Diffraction, Field Effect Scanning Electron Microscope and Energy Dispersive Analysis by X- Ray techniques.

Keywords **– Synthesis, Thick Films, Surface Activation, XRD, EDAX, FE-SEM, NH_3 Sensor, etc.**

I. INTRODUCTION

Many gas sensors are already available by Figaro-Engg. Inc., Sierra Monitors Inc., IST, etc. However, many problems persist till today [1]. By varying different parameters in the measurement of gas sensing, such type of parameters can be effectively minimized. The different parameters, viz. operating temperature, type of gas, gas concentrations, ageing (long term), type of materials, crystallite size, film thickness, additives, surface functionalization, calcination temperature, activation time, etc. affect the gas response of the sensor [2-6]. However, the devotion is paid in fabricating the ZrO_2, SnO_2 and their compositions based low cost gas sensors, with their surface functionalization (activation). Hence, the effects of all above mentioned parameters are studied on the gas sensing performance of the nanostructured base materials and their compositions [7-11]. The aim of the present work is, to fabricate and develop the gas sensors by utilizing the pure and surface functionalized nanocomposite $Zr_{(x)}Sn_{(1-x)}O_4$ so that, they could be able to detect various gases at trace (ppm / ppb) levels.

II. OBJECTIVES

1. To synthesize the nanostructured ZrO_2 and SnO_2 powders by one of the simplest and cheapest process known as disc type ultrasonicated microwave treatment followed centrifuge technique.
2. To prepare the thick films of nanocomposites of $Zr_{(0.75)}Sn_{(0.25)}O_4$, a simple and cost effective screen printing technique is used.
3. To achieve a suitable surface activation by dipping the thick films of nanocomposites of $Zr_{(0.75)}Sn_{(0.25)}O_4$ in to Bi_2O_3.
4. To analyse the synthesized materials by different characterization techniques, viz. XRD, EDAX, FESEM, etc.
5. To enhance the gas sensing performance and selectivity of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ nanocomposite thick films by their surface activation.

III. EXPERIMENTAL TECHNIQUES

3.1 Material Synthesis

Nanostructured ZrO_2 powder was synthesized by disc type ultrasonicated microwave treatment followed centrifuge technique, by hydrolysis of AR grade zirconium oxychloride in aqueous-alcohol solution [12-16]. With the use of distilled water and propylene glycol, an aqueous-alcohol solution was prepared in the ratio of 1:1. Later this solution was mixed with 1 M aqueous solution of zirconium oxychloride by taking their equal proportion. Drop wise aqueous ammonia (0.1 ml / min.) was added with constant stirring until the optimum pH of solution becomes 7.9. After complete precipitation and centrifugation, hydroxide was washed with distilled water. The precipitate was placed for ultrasonication and then kept in the microwave oven for ten minutes with periodically continuous on-off cycles. It was further calcined at 500ºC for 2 hrs. in muffle furnace. The dried precipitate was ground by agate pestle-mortar in order to ensure sufficiently fine particle size. To eliminate the organic impurities, if present, the precipitate was re-calcined in a muffle furnace at 500°C for 2 hrs. The same procedure was followed to prepare the nanostructured SnO_2 powder by using AR grade tin chloride powder. Finally, the dry white powders of nanostructured ZrO_2 and SnO_2 have been prepared.

3.2 Thick Film Fabrication

Thick film fabrication using screen printing mechanism is the most suitable, simple and low cost technique. The thick film technique using screen printing offers a good control over the thickness and microstructure. The life time of thick films is expected to be larger. The use of thick film technology in the production of chemical sensors The thixotropic paste was prepared by mixing the synthesized nanostructured pure ZrO_2 and pure SnO_2 powders, in their desired proportion. One such proper proportion formed is nanocomposite $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder. Then, this nanocomposite $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder was added with a solution of ethyl cellulose in a mixture of butyl cellulose, butyl carbitol acetate and turpineol. Ratio of inorganic to organic materials was kept as 80:20 while formulating the paste. The thixotropic paste was screen printed on the glass substrates and the

thick films of desired patterns were obtained [17]. Screen printed thick films were dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min. in ambient air. Thus, the thick films of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ are prepared.

3.3 Surface Activation of $Zr_{(0.75)}Sn_{(0.25)}O_4$ Thick Films

Surface functionalization [18-20] of thick films of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder was achieved by dipping them separately into a 0.01 M aqueous solution of bismuth chloride for different intervals of time, that is for 5 min, 15 min, 30 min and 45 min. The dipped samples dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min in an ambient air. The chloride particles dispersed on the films surface would be transformed to oxide particles during the firing process. Hence, different mass percentage of Bi_2O_3 incorporated in to thick films of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ were prepared. Silver contacts made for the measurement of electrical parameters and monitoring the gas sensing performance of the thick films.

IV. Material Characterizations

4.1 X - Ray Diffraction

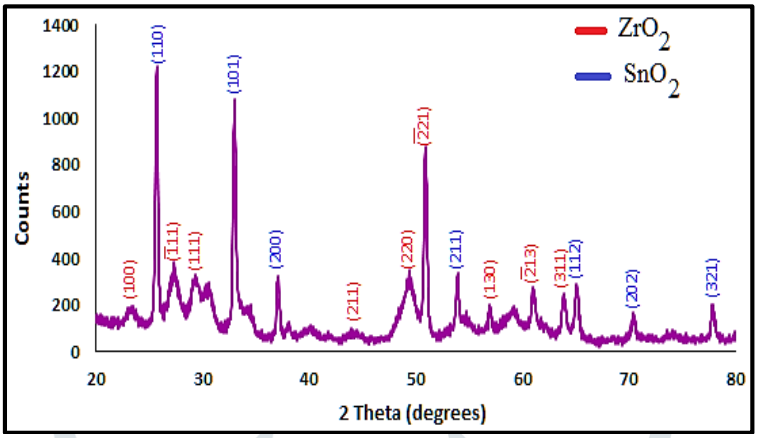


Fig. 1: XRD of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder

Fig. 1 depicts the X-ray diffractogram of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder. The 2θ peaks observed are correspond to the (100), (110), (111), ($\bar{1}$11), (101), (200), (211), (220), ($\bar{2}$21), (211), (130), ($\bar{2}$13), (311), (112), (202) and (321) planes of reflections. No peaks corresponding to Bi_2O_3 were observed in XRD pattern of surface activated films, which may be due to their very small mass % dispersed on the surface of $Zr_{(0.75)}Sn_{(0.25)}O_4$ film. The XRD spectrum reveals that, the material is polycrystalline in nature and combination of tetragonal-monoclinic in structure. The observed peaks are matching well with JCPDS reported data of pure SnO_2-ZrO_2. The average crystallite size was determined using Scherer's formula and observed to be of 6.9 nm. Hence, the material was observed to be nanocrystalline in nature. XRD analysis also confirms that, the synthesized pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ powder has less amorphous nature (31.0 %) and more crystalline nature (69.0 %).

4.2 Energy Dispersive Analysis by X - Rays (E-DAX)

Table 1: Elemental analysis of pure and Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films

Mass %	Activation Time (min.)					
	0 (Pure) (Expected)	0 (Pure) (Observed)	5	15	30	45
O	39.48	03.36	32.43	17.89	07.09	12.34
Zr	42.21	76.90	53.62	56.98	67.21	50.04
Sn	18.31	19.74	12.37	18.10	16.09	26.65
$Zr_{(0.75)}Sn_{(0.25)}O_4$	100	100	98.24	92.16	89.29	87.77
Bi	00	00	01.58	07.03	09.61	10.97
Bi_2O_3	00	00	01.76	7.84	10.71	12.23
Bi_2O_3 + $Zr_{(0.75)}Sn_{(0.25)}O_4$	100	100	100	100	100	100

The quantitative elemental composition of the pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ and Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films were analysed using an energy dispersive spectrometer and mass % of O, Zr, Sn, $Zr_{(0.75)}Sn_{(0.25)}O_4$, Bi, Bi_2O_3 and Bi_2O_3- $Zr_{(0.75)}Sn_{(0.25)}O_4$ are represented in Table 2. The mass % of Zr, Sn and O in each pure and activated sample is not as per the stoichiometric proportion and all samples are observed to be oxygen deficient. So, the maximum numbers of electrons are free to conduct the current and the electrons behave as the majority current carriers. This enhances n-typeness characteristics of pure and surface activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films. It is clear from Table 1 that, the mass % of Bi_2O_3 on the surface of the $Zr_{(0.75)}Sn_{(0.25)}O_4$ film increases or decreases with activation time, which may be attributed to the chemisorption of bismuth chloride particles on the surface of the thick films proving activation of the samples during dipping process.

4.3 Microstructural Analysis (FE-SEM)

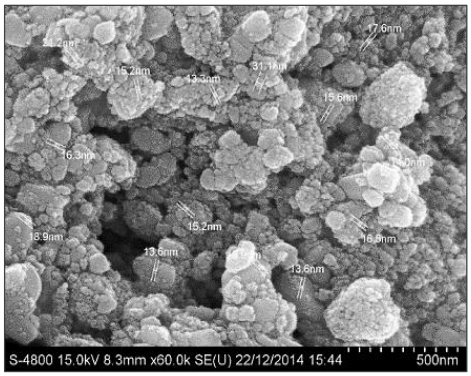


Fig. 2: Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$

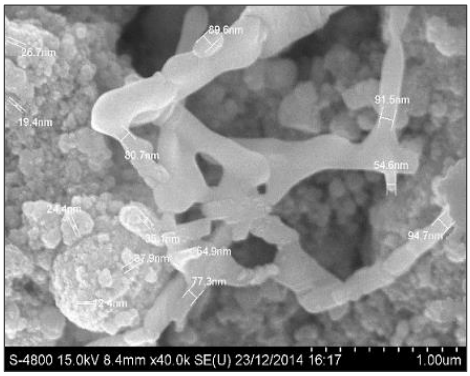


Fig. 3: 30 min. Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$

Fig. 2 depicts the SEM image of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film fired at 500ºC for 30 min. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film consists of voids and a wide range of randomly distributed grains with sizes ranging from 10 nm to 30 nm distributed as smaller grains. The appearance of the film looks porous, which supports the phenomenon of gas sensing. The nanoscaled grains exhibit high surface to volume ratio. The large numbers of smaller grains of zirconium oxide are associated with the less numbers of larger grains of tin oxide.

Fig. 3 depicts the micrograph of Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film for 30 min. activation time. The film consists of nano rods of Bi_2O_3 associated with the smaller grains of $Zr_{(0.75)}Sn_{(0.25)}O_4$. The film exhibits better response to NH_3 gas for 50 ppm at 50ºC operating temperature and much better response to H_2S gas for 5 ppm at 32ºC (R.T.) operating temperature. This may be attributed to the thin nano rods of the film. Due to large nanoscaled structure, the effective surface to volume ratio is large, which enhances the gas response. The film consists of voids, having grain sizes ranging from 10 nm to 30 nm distributed non-uniformly.

V. ELECTRICAL CHARACTERIZATIONS

5.1 I-V Characteristics

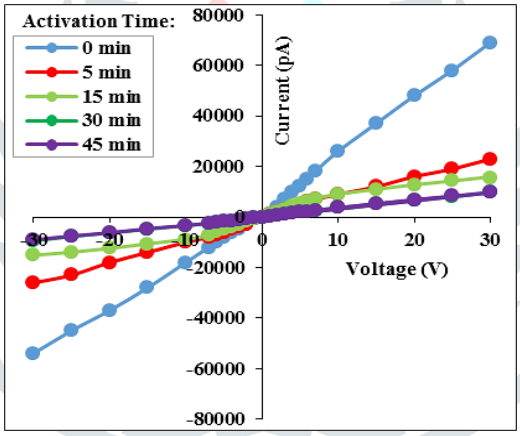


Fig. 4: I-V Characteristics

Fig. 4 depicts the I-V characteristics of pure and Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films. It is clear from the I-V characteristics that, the materials as well as silver contacts made on the films for external connections, are ohmic in nature. The materials are therefore said to have possessing the resistive properties, though more or less.

5.2 Electrical Conductivity

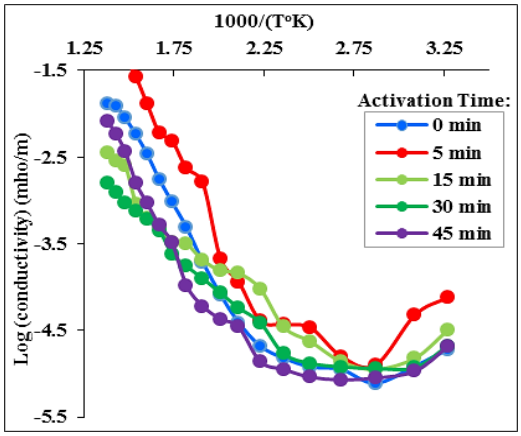


Fig. 5: Conductivity profile

Fig. 5 depicts the variation of log of conductivity with the reciprocal of operating temperature of pure and Bi_2O_3 functionalized $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films. It was found that, the conductivities of all the samples decreases with decrease in operating temperature, up to 100°C, attributed to the negative temperature coefficient (NTC) of resistance and semiconducting nature of the pure and activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films. It was also found that, the conductivity of all the samples is minimum in between 100°C to 75°C and then increases with further decrease in operating temperature from 75°C to room temperature (32°C), attributed to the positive temperature coefficient of resistance (PTC). Between 100°C and 75°C operating temperatures, no one could expect a gas sensing response to any one gas under the test.

VI. GAS SENSING PERFORMANCE

6.1 Gas Sensing Performance of Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$

6.1.1 NH_3 and H_2S response of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$

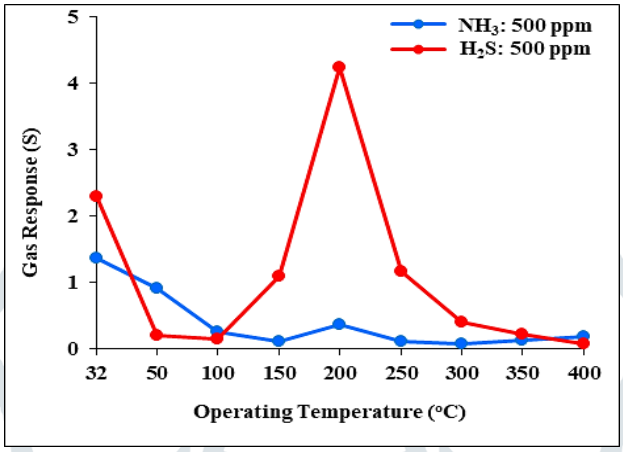


Fig. 6: NH_3 and H_2S response of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$

Fig. 6 shows the variation of NH_3 and H_2S (500 ppm) gas responses of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films with operating temperature. The maximum responses to NH_3 and H_2S obtained are of the order of 1.37 and 2.29 at room temperature (32°C), which are very less and decrease with operating temperature, up to 100°C. However, the material also responds to H_2S at 200°C. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ responds to NH_3 and H_2S at room temperature and somewhat at lower temperature (< 75°C) and it exhibits no response in the temperature range from 75°C to 100°C. In the temperature notch from 75°C to 100°C, the material exhibits the insulating nature. So, the material shows negligible response in this notch of temperature. At higher temperatures (>100°C), pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ desorbs oxygen leading to increase the conductivity. Upon exposure of electron donor gases, viz. NH_3 and H_2S, they get oxidized by using the adsorbed oxygen, exhibiting the gas response.

6.1.2 Selective Nature of Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$

It is observed from Fig. 7 that, the pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films are less selective to NH_3 and H_2S gases at room temperature among all other gases. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films have lack of selectivity to a particular gas (NH_3 or H_2S) among either number of gases or the mixture of gases. This is the major drawback of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films, while studying the NH_3 and H_2S gas sensing profile of the sensor.

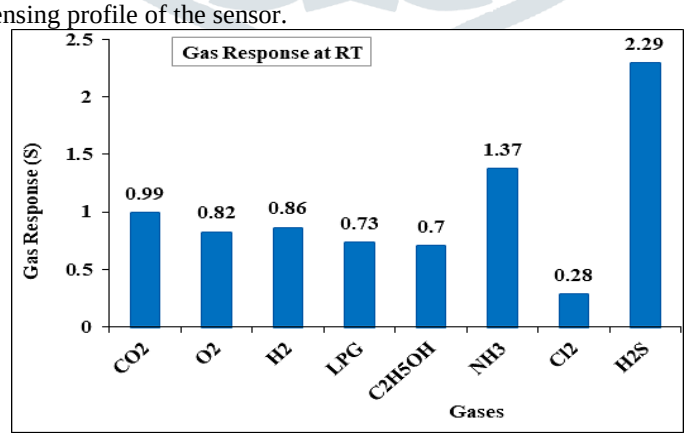


Fig. 7: Selective nature of pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film

6.2 Gas Sensing Performance of Bi_2O_3 Activated $Zr_{(0.75)}Sn_{(0.25)}O_4$

6.2.1 Temperature Dependent Performance

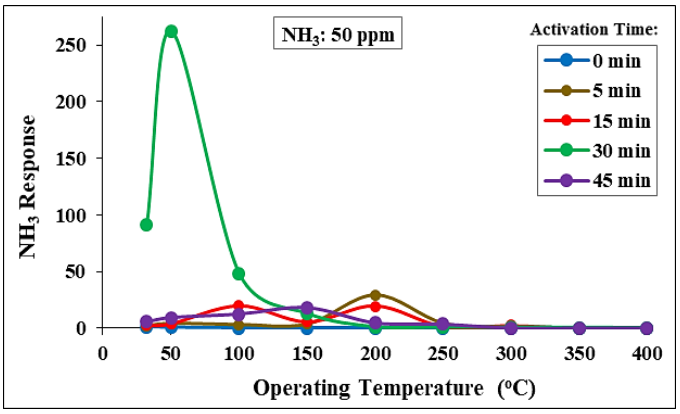


Fig. 8: Variation of NH_3 response with op. temperature

Fig. 8 depicts the variation of 50 ppm NH_3 response with operating temperature of pure and Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films. It is clear from figure that, Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films at 30 min. activation time gives highest response to 50 ppm NH_3 gas at room temperature (32°C). From elemental analysis, it is observed that, the Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) thick film is observed to be most oxygen deficient. This enhances n-typeness of activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ film. During surface activation of the film, Bi_2O_3-$Zr_{(0.75)}Sn_{(0.25)}O_4$ heterostructures were formed, decreasing the conductivity of the activated surface of the film. Upon exposure, NH_3 gas gets oxidized by utilizing the lattice oxygen from the surface at room temperature, trapping behind the free electrons in the material and enhances the conductivity of the material. This may be the reason of increase in conductivity of the sensor upon exposure of NH_3 at room temperature. However, as the temperature increases, the NH_3 response increases up to 50°C, and then decreases in the range from 75°C to 100°C, due to notch effect of the sensor. Above 100°C, the material responds to NH_3, but the response is negligibly small, which may be attributed to the desorption of oxygen from the surface of film at higher temperature. Due to desorption of oxygen, there is a less chance to oxidize the NH_3 gas molecules, reducing the NH_3 response.

6.2.2 Active Nature

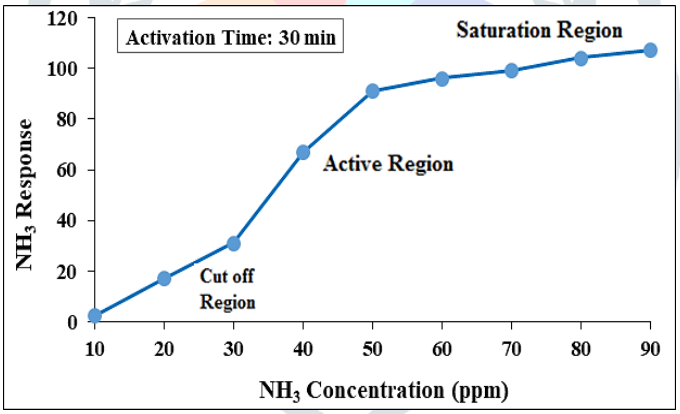
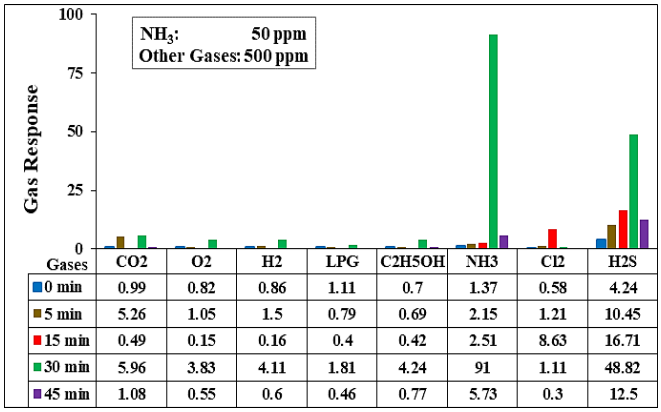


Fig. 9: Variation in NH_3 response with NH_3 concentration (ppm)

The variation of NH_3 response of Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) films with NH_3 gas concentration is represented in Fig. 9. It is clear from the figure that; the gas response goes on increasing linearly with gas concentration up to 50 ppm. The rate of increase in response was relatively larger up to 50 ppm and saturated beyond it.

6.2.3 Selective Nature



Gases	CO2	O2	H2	LPG	C2H5OH	NH3	Cl2	H2S
0 min	0.99	0.82	0.86	1.11	0.7	1.37	0.58	4.24
5 min	5.26	1.05	1.5	0.79	0.69	2.15	1.21	10.45
15 min	0.49	0.15	0.16	0.4	0.42	2.51	8.63	16.71
30 min	5.96	3.83	4.11	1.81	4.24	91	1.11	48.82
45 min	1.08	0.55	0.6	0.46	0.77	5.73	0.3	12.5

Fig. 10: Selective nature

It is observed from Fig. 10 that, the 30 min Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick film is most sensitive to NH_3 at room temperature. This is the optimized condition as far as surface activation of $Zr_{(0.75)}Sn_{(0.25)}O_4$ with Bi_2O_3 is concerned. Also, it has high selectivity against different gases, viz. carbon dioxide, oxygen, hydrogen, liquefied petroleum gas, ethanol and chlorine, except H_2S.

6.2.4 Long Term Stable Nature

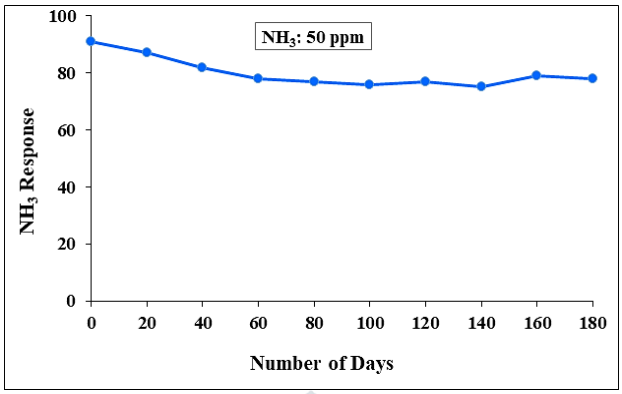


Fig. 11: NH_3 response over long time duration

Fig. 11 indicates the NH_3 response over a long time duration for the Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) thick film sensor. The sensor response to NH_3 was observed to be constant over a long duration (few months). It was observed that, the sensor response decreases by about 20 % after 40 days, and remains same thereafter. This proves the long term stability of the sensor.

6.2.5 Response - Recovery Nature

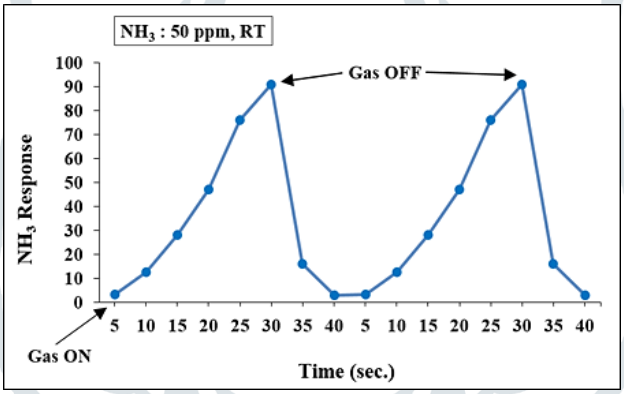


Fig. 12: Response and recovery nature

The response and recovery of the Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) sensor is represented in Fig. 12. The response time of the sensor was of the order of 25 sec. to 50 ppm of NH_3 gas and recovery time is of the order of 5 sec. For better performance of the sensor, the recovery should be very fast. When the gas exposure was switched off, the sensor returned back to its original chemical status, within a very short time (~ 5 sec.). This is the main feature of this sensor.

VII. CONCLUSIONS

From the results obtained, some important conclusions are made for the gas sensing performance of the sensor.

1. Pure $Zr_{(0.75)}Sn_{(0.25)}O_4$ thick films are almost insensitive or less sensitive to hazardous and toxic gases.
2. Bi_2O_3 surface activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) thick film gas sensor offers good response to 5 ppm H_2S at room temperature.
3. Bi_2O_3 surface activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) thick film sensor offers good response to 50 ppm NH_3 at room temperature.
4. It offers a crucial response to NH_3 at 50°C and this sensor is highly selective to NH_3 gas among the mixture of gases.
5. It was found that, with further increase in temperature, the sensor response goes on decreasing.
6. Bi_2O_3 surface activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) shows long term stable nature of the sensor.
7. The response and recovery time of Bi_2O_3 activated $Zr_{(0.75)}Sn_{(0.25)}O_4$ (30 min.) sensor is 25 sec. and 5 sec. respectively, which is quite excellent.

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