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RESEARCH ARTICLE

GAS SENSING PERFORMANCE OF PURE AND Bi_2O_3 SURFACE ACTIVATED NANOCOMPOSITE $Zr_{(0.50)}Sn_{(0.50)}O_4$ THICK FILMS

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ABSTRACT

Thick films of bulk SnO_2 and ZrO_2 powders were observed as less sensitive to polluting, hazardous and inflammable gases. Hence, nanostructured SnO_2 and ZrO_2 powders were synthesized by disc type ultrasonicated microwave assisted centrifuge technique. Nanocomposite material, $Zr_{(0.50)}Sn_{(0.50)}O_4$ was prepared using synthesized ZrO_2 and SnO_2 powders by taking their 1:1 proportion. Thick films of nanostructured pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder were fabricated by screen printing technique. These films were surface functionalized by Bi_2O_3 for different intervals of time followed by firing at 450°C for 30 min. The surface morphology, chemical composition, crystal structure of the unmodified and surface activated nanostructured $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder by Bi_2O_3 have been investigated by XRD, FESEM and E-DAX. Electrical and oxygen gas sensing performance of the thick films were also studied.

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INTRODUCTION

Pollution has raised its ugly head high in the global environment (Moore, 1995; Dasmann, 1976; Air Quality Guideline, 2000). It created tremendous disasters of global warming. To face such disasters, is a very challenging for mankind. Many gases released by the vehicles and industries contribute the pollution and ultimately the global warming. Gases beyond certain limit can affect the living beings. So, there is a need to detect the gaseous pollutants in the environment, even at trace levels. Many researchers are working already to detect the hazardous gases in the environment and hence to develop the gas sensors at their best level. Researchers are well known about the hazards of different gases released by any means in the open environment. Still, the action has not been initiated in the desired proportion to save the environment from the pollution and its hazards. Also, the researchers have the responsibility to aware the society from the pollution hazards (Patil, 2011). The aim of the present work is, to fabricate and develop the gas sensors by utilizing the pure and surface activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite thick films by Bi_2O_3 so that, they could be able to detect various gas traces (ppm / ppb).

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MATERIALS AND METHODS

Synthesis of $Zr_{(0.50)}Sn_{(0.50)}O_4$ Nanocomposite Powder: $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite in the form of dry powder were synthesized by disc type ultrasonicated microwave treatment followed centrifuge technique (Pandav *et al*., 2015; Sonawane *et al*., 2008), by hydrolysis of AR grade zirconium oxychloride and tin chloride in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol in the ratio of 1:1. This solution was then mixed with 1M aqueous solution of zirconium oxychloride and tin chloride in the desired proportions. The special arrangement was made to add dropwise aqueous ammonia (0.1ml / min) with constant stirring until the optimum pH of solutions become in the range from 7.9. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. The precipitates were allowed for ultrasonication and then placed in a microwave oven for 10 minutes with continuous on-off cycles, periodically, followed by calcination at 500°C for 2 hrs in muffle furnace. The dried precipitates were ground by agate pestle-mortar to ensure sufficiently fine particle size and re-calcined in a muffle furnace at 500°C for 2 hrs, to eliminate the organic impurities, if present. The crystallite size of synthesized nanocomposite was monitored by XRD analysis and confirmed on calculating by Scherer's formula.

Thus, the dry powders of nanostructured $Zr_{(0.50)}Sn_{(0.50)}O_4$ have been prepared and ready to use for screen printing.

Thick Films Fabrication and Surface Activation: The thixotropic paste was formulated by mixing the synthesized nanostructured powder of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol. While in formulating the paste, the ratio of inorganic to organic part was kept as 80:20. The thixotropic paste was screen printed on the glass substrates and the thick films of desired patterns were obtained (Patil *et al*., 2006; Gawas, 2011; Shelke, 2019). Thus, thick films of $Zr_{(0.50)}Sn_{(0.50)}O_4$ nanocomposite were fabricated by screen printing technique. The films prepared were fired at 500°C for 30 min in muffle furnace. Then the dried films were surface activated by activating them into 0.01 M aqueous solution of bismuth chloride, for different intervals of time, viz. 5 min, 15 min, 30 min and 45 min and dried at 80°C under an IR lamp, followed by firing at 500°C for 30 min in ambient air (Kapse, 2012; Khamkar *et al*., 2012). The particles of bismuth chloride dispersed on the film surface would be transformed to bismuth oxide (Bi_2O_3), upon firing process. Thus, the sensor elements with different mass % of Bi_2O_3 incorporated in to thick films of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ were prepared (Shelke, 2016). Silver contacts were made by vacuum evaporation for electrical measurements and monitoring the gas sensing performance of thick films.

RESULTS AND DISCUSSION

Material characterizations

Structural Properties (X-ray diffraction studies): Fig. 1 depicts the X-ray diffractogram of $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder. The 2θ peaks observed are correspond to the (110), (111), (111), (101), (102), (200), (211), (122), (131), (213), (311), (112), (121), (202), (140), (232) and (321) planes of reflections. No peaks corresponding to Bi_2O_3 were observed, in XRD pattern of surface activated thick films, which may be due to their very small mass percentage dispersed on the surface of $Zr_{(0.50)}Sn_{(0.50)}O_4$ 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 material was observed to be nanocrystalline in nature. The average crystallite size was observed to be of 38.7 nm, which was determined using Scherer's formula.

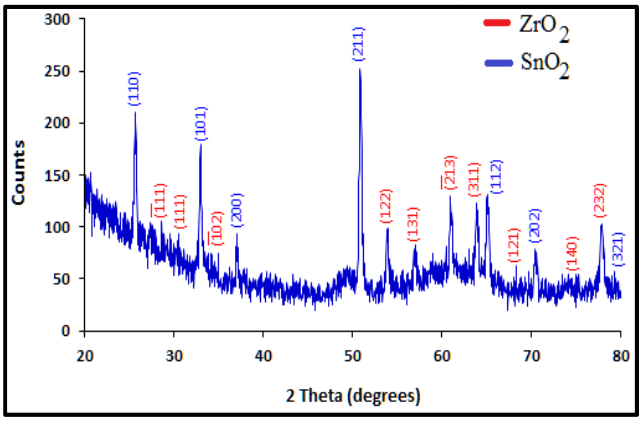


Fig. 1. XRD of $Zr_{(0.50)}Sn_{(0.50)}O_4$ powder

Quantitative Elemental Analysis (EDAX): The quantitative elemental composition of the pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ and Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films were analyzed using an energy dispersive spectrometer and mass % of O, Zr, Sn, $Zr_{(0.50)}Sn_{(0.50)}O_4$, Bi, Bi_2O_3 and Bi_2O_3-$Zr_{(0.50)}Sn_{(0.50)}O_4$ are represented in Table 1. The prepared powder of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ was deficient in oxygen, which increases its n-typeness characteristic. This leads to n-type semiconducting nature of the synthesized $Zr_{(0.50)}Sn_{(0.50)}O_4$. Also, the mass % of Zr, Sn and O in each activated samples are not as per the stoichiometric proportion and all samples are observed to be oxygen deficient. This enhances n-typeness of activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films. It is clear from Table 1 that, the mass % of Bi_2O_3 in $Zr_{(0.50)}Sn_{(0.50)}O_4$ on the surface of the film increases (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 film during dipping process.

Microstructural Analysis (FESEM): Fig. 2 depicts the SEM image of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick film fired at 500°C for 30 min, which consists of voids and a wide range of randomly distributed grains with sizes ranging from 10 nm to 30 nm. The film has porous nature, which supports the adsorption-desorption type of gas sensing mechanism. The nanoscale grains exhibit high surface to volume ratio. The smaller grains of zirconium oxide are fused with the larger grains of tin oxide. Fig. 3 depict the microstructures of 30 min Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick film. This film consist of groups of very thin nano rods of Bi_2O_3 associated with the grains of $Zr_{(0.50)}Sn_{(0.50)}O_4$. The film activated for 30 min exhibits larger response to O_2 gas, which may be attributed to the large surface active sites of the film, due to thin nano rods. The films consist of voids, having grain sizes ranging from 10 nm to 30 nm distributed non-uniformly.

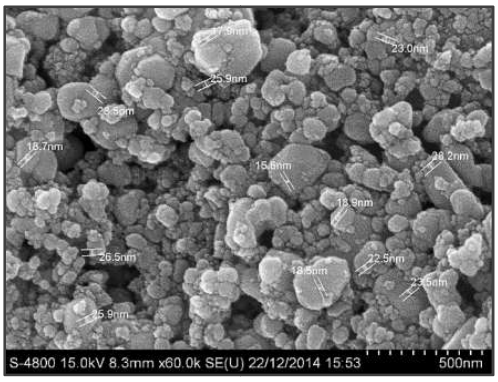


Fig. 2. Pure $Zr_{(0.50)}Sn_{(0.50)}O_4$

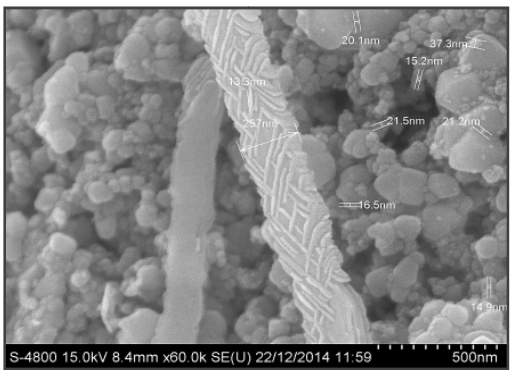


Fig. 3. 30'Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$

Table 1. Elemental analysis

Mass %	Activation Time (min.)					
	0 (Pure) (Expected)	0 (Pure) (Observed)	5	15	30	45
O	37.88	37.50	19.16	24.38	08.03	17.18
Zr	27.00	33.59	10.29	03.56	01.61	06.39
Sn	35.12	28.91	55.38	29.88	53.46	16.86
$Zr_{(0.50)}Sn_{(0.50)}O_4$	100	100	83.09	52.98	58.86	33.58
Bi	00	00	15.17	42.18	36.90	59.58
Bi_2O_3	00	00	16.91	47.02	41.14	66.42
$Bi_2O_3 + Zr_{(0.50)}Sn_{(0.50)}O_4$	100	100	100	100	100	100

Conductivity Profile and I-V Characteristics: Fig. 4 depicts the variation of log of conductivity with the reciprocal of operating temperature of pure and Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films. The conductivities of all the films are decreasing with decrease in operating temperature, up to 75°C, attributed to the negative temperature coefficient (NTC) of resistance and semiconducting nature of the pure and activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films. The conductivities of all the samples are minimum at 75°C and increase with further decrease in operating temperature, attributed to the positive temperature coefficient (PTC) of resistance.

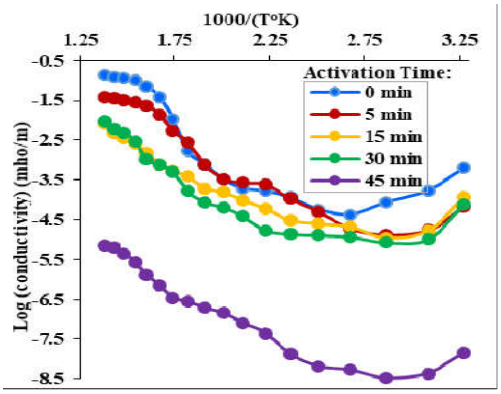


Fig. 4. Conductivity profile

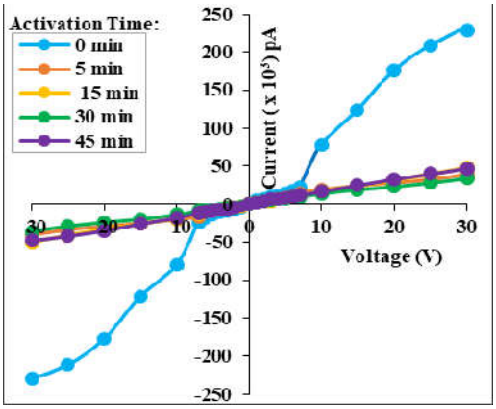


Fig. 5. I-V characteristics

Fig. 5 depict the I-V characteristics of pure and Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films. It is clear from the symmetrical nature of 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.

Gas Sensing Performance of the Sensors Pure $Zr_{(0.50)}Sn_{(0.50)}O_4$: Fig. 6 shows the variation of O_2 (500 ppm) gas response of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick film with operating temperature. The maximum response of O_2 obtained is of the order of 0.11 at room temperature (32°C), which is very less and decrease with further increase in operating temperature.

Pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick film 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 $Zr_{(0.50)}Sn_{(0.50)}O_4$ desorbs oxygen leading to increase the conductivity. It is observed from Fig. 7 that, the pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films are selective to H_2S at 150°C and NH_3 at room temperature (32°C), among all other gases. Pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films have lack of selectivity to NH_3 against LPG at room temperature. Also, pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films are less sensitive to the respective gases. This is the major drawback of pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films, while studying the gas sensing profile of the sensor.

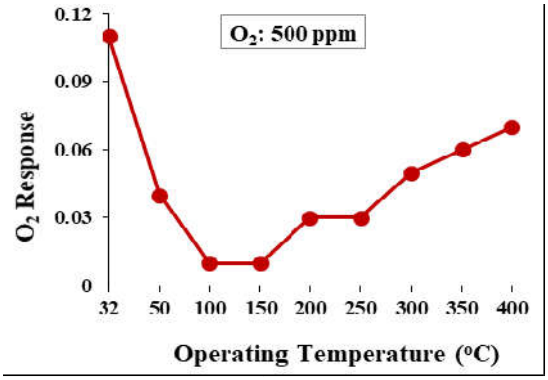


Fig. 6. O_2 response Vs. op. temperature

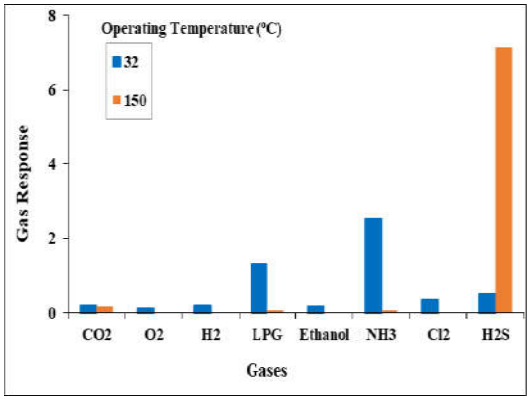


Fig. 7. Selective nature

Bi_2O_3 Activated $Zr_{(0.50)}Sn_{(0.50)}O_4$: Fig. 8 depicts the variation of 50 ppm O_2 response with operating temperature of pure and Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films. It is clear from figure that, Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films at 30 min activation time gives highest response to 50 ppm O_2 gas at room temperature (32°C) as well as at 50°C. During surface activation of the film, Bi_2O_3-$Zr_{(0.50)}Sn_{(0.50)}O_4$ heterostructures were formed, decreasing the conductivity of the activated surface of the film.

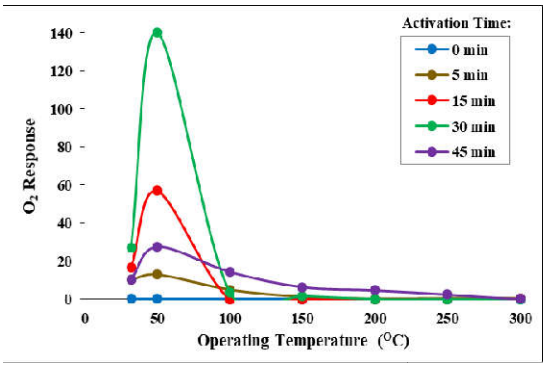


Fig. 8. Gas sensing performance

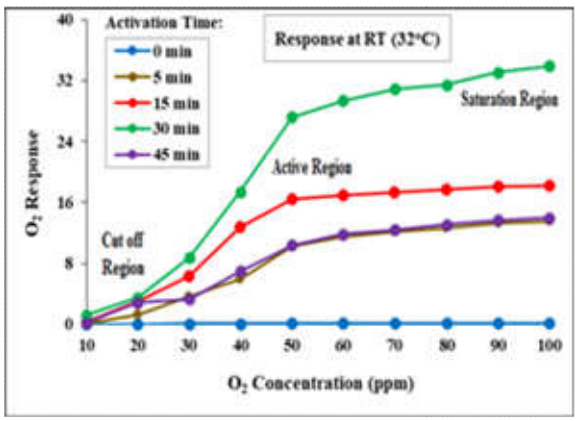
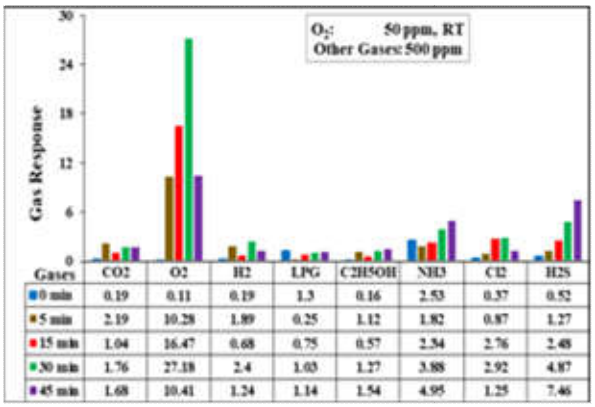


Fig. 9. Active nature



Gases	CO2	O2	H2	LPG	C2H5OH	NH3	Cl2	H2S
0 min	0.19	0.11	0.19	1.3	0.16	2.53	0.37	0.52
5 min	2.19	10.28	1.89	0.25	1.12	1.82	0.87	1.27
15 min	1.04	16.47	0.68	0.75	0.57	2.34	2.76	2.48
30 min	1.76	27.18	2.4	1.03	1.27	3.88	2.92	4.87
45 min	1.68	10.41	1.24	1.14	1.54	4.95	1.25	7.46

Fig. 10 Selective nature

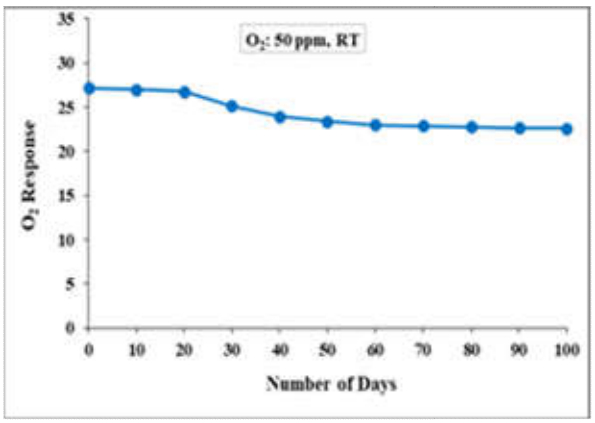


Fig. 11. Long time duration (Days)

Upon exposure, O_2 gas adsorbs on the surface capturing the free electrons from the surface of the film.

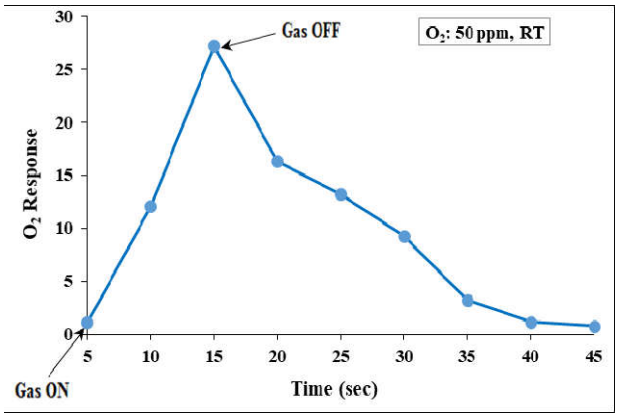


Fig. 12. Response and recovery nature

Thus, the active region of the sensor would be up to 50 ppm. It is observed from Fig. 10 that, the 30 min. Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick film is most sensitive to 50 ppm O_2 at room temperature. This is the optimized condition as far as surface activation of $Zr_{(0.50)}Sn_{(0.50)}O_4$ with the help of Bi_2O_3 is concerned. Also, it has high selectivity against different gases, viz. carbon dioxide, hydrogen, liquefied petroleum gas, ethanol, ammonia, chlorine and hydrogen sulphide.

Long Term Stable Nature and Response-Recovery Nature: Fig. 11 indicates the O_2 response over a long time duration for the Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ (30 min) thick film sensor. The sensor was observed to be the most sensitive to O_2 at room temperature. The sensor response to O_2 was observed to be constant over a long duration (few months). It was observed that, the sensor response decreases by less than 10% after 20 days, and remains same thereafter. This proves the long term stability of the sensor. The response and recovery of the Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ (30 min) thick film sensor is represented in Fig. 12. The response time of the sensor was of the order of 12 sec to 50 ppm of O_2 gas and recovery time is of the order of 20 sec. For better performance of the sensor, the recovery should be very fast. When gas exposure was switched off, the sensor returned back to its original chemical status, within a very short time (~20 sec). This is the main feature of this sensor.

Conclusions:

From the results obtained, following conclusions can be made for the sensing performance of the sensor.

- Pure $Zr_{(0.50)}Sn_{(0.50)}O_4$ thick films were almost insensitive or less sensitive to hazardous and toxic gases.
- Bi_2O_3 activated $Zr_{(0.50)}Sn_{(0.50)}O_4$ (30 min) is highly sensitive and selective to 50 ppm O_2 gas at room temperature.
- The excellent feature of the sensor is that, it is highly sensitive and selective to O_2 gas.
- The sensor exhibits long term stability, fast response and quick recovery.
- The thick film and surface activation technique is a low cost technique.
- The sensor so prepared, is portable in size and light in weight.

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