

# SURFACE ACTIVATED NANOSTRUCTURED ZIRCONIA THICK FILMS FOR THE DETECTION OF PPM LEVEL OXYGEN GAS OPERABLE AT ROOM TEMPERATURE

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**Abstract:** Thick films of pure and bulk zirconium oxide powder were observed to be less sensitive to polluting, hazardous and inflammable gases. So, nanostructured ZrO<sub>2</sub> powder was synthesized by disc type ultrasonicated microwave assisted centrifuge technique. Thick films of nanostructured unmodified ZrO<sub>2</sub> powder were fabricated by screen printing technique. These films were surface functionalized (activated) by SrO<sub>2</sub> for different intervals of time followed by firing at 450°C for 30 min. The characterizations, viz. surface morphology, chemical composition and crystal structure of the pure and modified nanostructured Zirconia powder by Strontium Oxide were investigated by X- Ray Diffraction (XRD), Field Effect Scanning Electron Microscope (FESEM) and Energy Dispersive Analysis by X- Ray (EDAX) techniques. Electrical characterizations, viz. I-V characteristics and conductivity profile were studied in the laboratory. Nanostructured pure and surface activated ZrO<sub>2</sub> by SrO<sub>2</sub> tested for gas sensing performance by using low cost technique for the gases, viz. H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, LPG, Cl<sub>2</sub> and H<sub>2</sub>S. The selected material gives significant response and it is highly selective to O<sub>2</sub> gas among all other gases.

**Keywords:** Synthesis, Nanostructured Zirconia, Thick Films, Surface Activation, Gas Sensor, etc.

## I. INTRODUCTION

An oxygen sensor is a device that measures the concentration of oxygen within the medium to be analyzed. Oxygen sensors are used to measure the respiratory conditions, at the production of oxygen as well as oxygen analyzers which find a lot of use in medical applications such as anesthesia monitors, respirators and oxygen concentrators within the gases or liquids. Oxygen sensors are also utilized in hypoxic air fire prevention systems to observe continuously the oxygen concentration inside the protected volumes [1-8]. Commercial oxygen sensors are already available with some limitations regarding cost, portability, power consumption, lower detection range, etc. for large applicability to laymen. Many researchers are working to fabricate and to develop the oxygen sensors at their best level. Few of the materials are utilized for fabrication of oxygen sensors are Sr(Ti, Fe)O<sub>3</sub> [2], Ceria-Zirconia [3, 4], SrTi<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> [5], SrTiO<sub>3</sub> [6], Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> [7], Ceria-Yttria [8], etc.

The aim of the present work is, to develop the low cost O<sub>2</sub> gas sensor by utilizing the easily available material in large extent and modifying the material to enhance the gas sensing performance. Pure and activated ZrO<sub>2</sub> thick films are used to monitor the toxic and hazardous gases and activated the thick films by dipping technique, so that, they could be able to detect the O<sub>2</sub> gas at trace (ppm / ppb) levels.

## II. MATERIALS AND EXPERIMENTAL METHODS

### 2.1 Synthesis of Nanostructured ZrO<sub>2</sub> Powder

Nanostructured ZrO<sub>2</sub> powder was synthesized by disc type ultrasonicated microwave treatment followed centrifuge technique [9-11], by hydrolysis of AR grade zirconium oxychloride in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol within the ratio of 1:1. This solution was then mixed with 1M aqueous solution of zirconium oxychloride within the ratio 1:1. The special arrangement was made to add drop wise aqueous ammonia (0.1 ml / min) with constant stirring until the optimum pH of solution becomes 7.9. After complete precipitation and centrifugation, the hydroxide was washed with distilled water until chloride ions were not detected by AgNO<sub>3</sub> solution. Then the precipitate was allowed for ultrasonication and then kept 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 precipitate was 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. Thus, the dry white powder of nanostructured ZrO<sub>2</sub> has been prepared to use.

### 2.2 Thick Film Fabrication

The thixotropic paste was formulated by mixing the synthesized nanostructured powder of pure  $ZrO_2$  with a solution of ethyl cellulose in a mixture of organic solvents like butyl cellulose, butyl carbitol acetate and turpeneol. 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 [11-14]. Films prepared were dried at  $80^\circ C$  under an IR lamp, followed by firing at  $500^\circ C$  for 30 min in an ambient air. Silver contacts were made by vacuum evaporation for electrical measurements and monitoring the gas sensing performance of thick films. Thus, the thick films of pure  $ZrO_2$  are now able to use for the desired applications.

### 2.3 Surface Activation of $ZrO_2$ Thick Films

Surface activation of as prepared thick films of pure  $ZrO_2$  was achieved by dipping [12-14] them into a 0.01 M aqueous solution of strontium chloride for different intervals of time, viz. 5 min, 15 min, 30 min and 45 min and dried at  $80^\circ C$  under an IR lamp, followed by firing at  $500^\circ C$  for 30 min in an ambient air. The particles of strontium chloride dispersed on the film surface would be transformed to strontium oxide ( $SrO_2$ ) upon firing process. Thus, the sensor elements with different mass % of  $SrO_2$  incorporated in to thick films of pure  $ZrO_2$  were prepared.

## III. MATERIAL CHARACTERIZATIONS

### 3.1 Structural Properties (X-Ray Diffraction Studies)

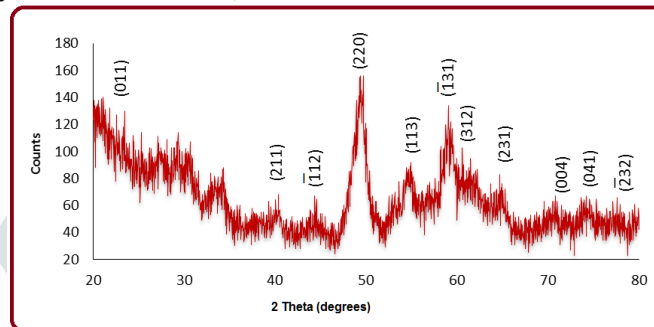


Fig. 1: XRD of pure  $ZrO_2$  powder

X-ray diffraction study of pure  $ZrO_2$  powder (Fig. 1) was carried out using BRUKER AXSD 8 (Germany) advance model. X-ray diffraction with  $CuK\alpha_1$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation is in  $2\theta$  range of  $20^\circ$  to  $80^\circ$ . The  $2\theta$  peaks observed at 23.96, 40.22, 44.60, 49.21, 54.93, 59.17, 61.79, 65.18, 70.78, 73.99 and 78.30 are correspond to the (011), (211), (112), (220), (113), (131), (312), (231), (004), (041) and (232) planes of reflections. The XRD spectrum reveals that, the material is polycrystalline in nature and monoclinic in structure. The observed peaks are matching well with JCPDS reported data of pure  $ZrO_2$ . The material was observed to be nanocrystalline in nature. The lattice parameters were found to be  $a = 5.21$ ,  $b = 5.26$  and  $c = 5.37$ . The unit cell volume was evaluated as 145.16 (JCPDS card no. Zr-002-0464). The average crystallite size was determined using Scherer's formula. It was also observed from XRD analysis that, the synthesized pure  $ZrO_2$  powder has slightly less amorphous nature (46.5%) and slightly more crystalline nature (53.5%).

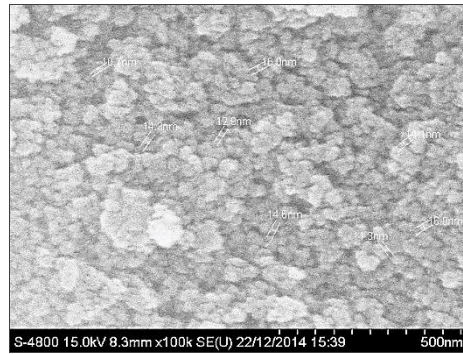
### 3.2 Energy Dispersive Analysis by X-Rays (E-DAX)

Table 1: Elemental analysis of pure and  $SrO_2$  activated  $ZrO_2$  thick films

Mass % of	Activation Time (min)					
	0 (Pure) (Expected)	0 (Pure) (Observed)	5	15	30	45
Zr	74.03	72.75	77.81	73.02	86.73	71.80
O	25.97	27.25	21.19	24.14	09.40	24.06
$ZrO_2$	100.00	100.00	98.63	96.14	94.72	94.34
Sr	00.00	00.00	01.00	02.83	03.87	04.15
$SrO_2$	00.00	00.00	01.37	03.86	05.28	05.66
$SrO_2 - ZrO_2$	100.00	100.00	100.00	100.00	100.00	100.00

The quantitative elemental composition of the pure  $ZrO_2$  and  $SrO_2$  activated  $ZrO_2$  thick films is represented in Table 1. Pure stoichiometric  $ZrO_2$  is expected to be insulating. Stoichiometrically, expected mass % of Zr and O (in  $ZrO_2$ ) are 74.03 and 25.97 respectively. However, the observed mass % of the respective elements are 72.75 and 27.25. Thus, the synthesized powder of  $ZrO_2$  is not exactly stoichiometric and hence is semiconducting in nature. The prepared powder of pure  $ZrO_2$  is excess in oxygen, which increases its p-type characteristic. This leads to semiconducting nature of the synthesized pure  $ZrO_2$ . Excess or deficiency of the constituent material particles leads to the semiconducting nature of the material. Also, the mass % of Zr and O in each activated samples are not as per the stoichiometric proportion and all samples are observed to be oxygen deficient or excess in zirconium, particularly on the surface of the film. Thus, the less number of oxygen molecules hold less number of electrons in the material. So, the maximum numbers of electrons are free to conduct the current and the electrons behave as the majority current carriers. This enhances n-type nature of activated  $ZrO_2$  thick films. It is clear from Table 1 that, the mass % of  $SrO_2$  ( $ZrO_2$ ) on the surface of the film increases (decreases) with activation time, which may be attributed to the chemisorption of strontium chloride particles on the surface of the thick films proving masking of the film during dipping process. Thus, activation process is the simple and low cost technique to activate the surface of the film. This forms p- $SrO_2$  / n- $ZrO_2$  heterojunctions on the surface of the film, leading to increase the resistivity.

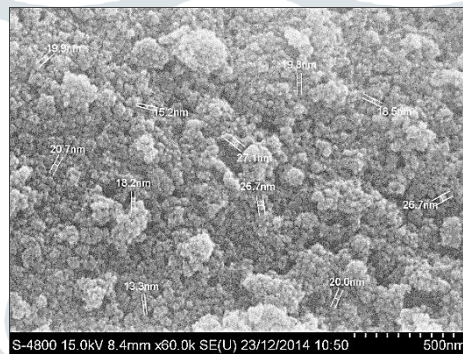
### 3.3 Microstructural Analysis (FESEM) of Pure ZrO<sub>2</sub>



**Fig. 2:** Micrograph of pure ZrO<sub>2</sub> thick film

Fig. 2 depicts the FESEM image of pure ZrO<sub>2</sub> thick film fired at 500°C for 30 min. Pure ZrO<sub>2</sub> thick film consists of voids and a wide range of randomly distributed grains with sizes ranging from 10 nm to 20 nm distributed as smaller grains. The appearance of the film looks porous, which supports the adsorption-desorption type of gas sensing mechanism. The nanoscale grains exhibit a high surface-to-volume ratio.

### 3.4 Microstructural Analysis of SrO<sub>2</sub> Activated ZrO<sub>2</sub>

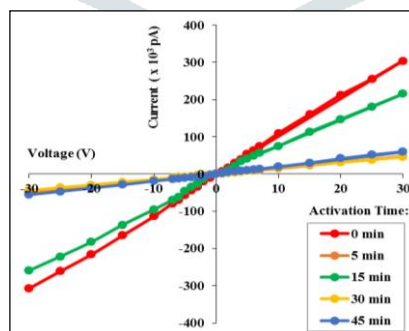


**Fig. 3:** Micrograph of 15' SrO<sub>2</sub> activated ZrO<sub>2</sub> thick film

Fig. 3 depicts the microstructure of SrO<sub>2</sub> activated ZrO<sub>2</sub> (15 min) thick film, which consists of a large number of almost similar sized grains of SrO<sub>2</sub> associated with the comparable sized grains of ZrO<sub>2</sub>. The film consists of voids and a wide range of grains with grain sizes ranging from 13 nm to 27 nm distributed non-uniformly. This film is observed to be the most sensitive to 50 ppm O<sub>2</sub> gas at room temperature, due to its porous nature, among all. Though the islands of SrO<sub>2</sub> are established on the surface of ZrO<sub>2</sub> film, the film does not look fully masked. The appearance of the film looks porous in nature, increasing surface-to-volume ratio, which enhances the large number of gas adsorption upon exposure, giving a larger response.

## IV. ELECTRICAL CHARACTERIZATIONS

### 4.1 I-V Characteristics



**Fig. 4:** I-V characteristics

Fig. 4 depicts the I-V characteristics of pure and SrO<sub>2</sub> activated ZrO<sub>2</sub>. It is clear from the symmetrical nature of I-V characteristics that the material as well as silver contacts made on the films for external connections, are ohmic in nature. The material is therefore said to possess the resistive properties, though more or less.

## 4.2 Conductivity Profile

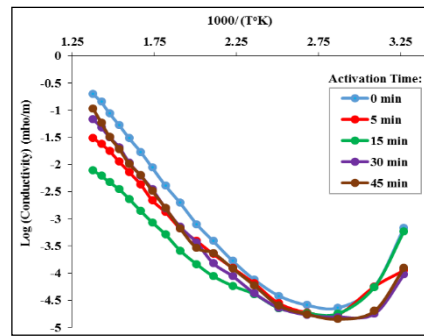


Fig. 5: Conductivity profile

Fig. 5 shows the variation of log of conductivity ( $\sigma$ ) with the reciprocal of operating temperature of SrO<sub>2</sub> activated ZrO<sub>2</sub> thick films. The conductivities of all the samples are decreasing with decrease in operating temperature from 400°C up to 100°C. The decrease in conductivity with decrease in operating temperature could be attributed to the negative temperature coefficient (NTC) of resistance and semiconducting nature of the pure and activated ZrO<sub>2</sub> thick films. It was found that, below 75°C, conductivity increases, with further decrease in operating temperature, which may be attributed to the positive temperature coefficient (PTC) of resistance and semiconducting nature of the material, even at room temperature. All the pure and activated films exhibit the lowest conductivities (nearly linear) in the temperature range from 100°C to 75°C. This is the temperature range in which all the films exhibit insulating nature, above this temperature range, the films exhibit NTC and below it, the films exhibit PTC nature. Thus the material switches its semiconducting nature from NTC to PTC through insulating nature, with decreasing temperature from 400°C to room temperature (32°C). So, the temperature range from 100°C to 75°C is the notch for which the material exhibiting insulating property. Hence, one should not expect the application of this material in the field of gas sensing or any optoelectronics field, in this particular notch of the temperature.

## V. GAS SENSING PERFORMANCE OF PURE ZrO<sub>2</sub>

### 5.1 Oxygen Gas Response of Pure ZrO<sub>2</sub>

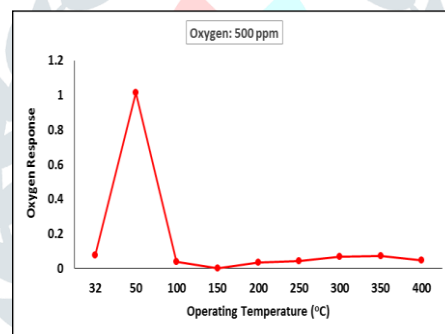


Fig. 6: O<sub>2</sub> response of pure ZrO<sub>2</sub>

Fig. 6 shows the variation of O<sub>2</sub> (500 ppm) gas response of pure ZrO<sub>2</sub> thick film with operating temperature. The maximum response obtained is of the order of 1.01 at 50°C, which is lowest. The response increases from room temperature, reaches maximum at 50°C and then falls down rapidly, further. Pure ZrO<sub>2</sub> responds to O<sub>2</sub> at lower temperature, i.e. at 50°C (<75°C). The response to O<sub>2</sub> decreases from 50°C with further increase in operating temperature (Fig. 6). The O<sub>2</sub> response at 75°C is negligibly small and can be neglected. The ZrO<sub>2</sub> sensor does not exhibit any response to O<sub>2</sub> at exactly 100°C. In the temperature notch from 75°C to 100°C, the material exhibits the insulating nature. So, the material shows no response in this notch of temperature. At higher temperatures (>100°C), pure ZrO<sub>2</sub> loses oxygen leading to increase the conductivity. However, exposure of molecular oxygen gas at this temperature would cause the adsorption of oxygen and these adsorbed oxygen molecules hold the free electrons from the material and would become oxygen ions, on the film surface, achieving the stoichiometry and enhancing insulating property of the material, showing no response to O<sub>2</sub> gas [15-17].

### 5.2 Selectivity Profile of Pure ZrO<sub>2</sub>

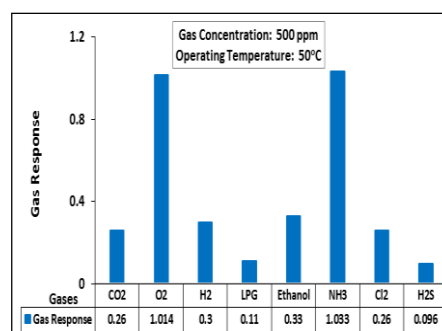
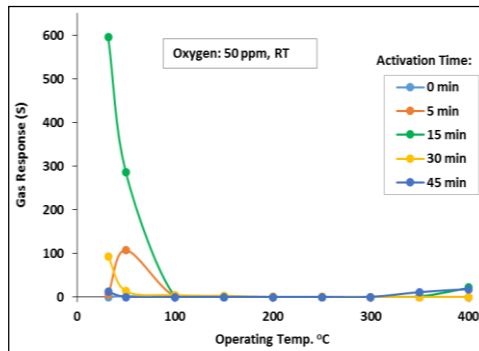


Fig. 7: Selectivity profile of pure ZrO<sub>2</sub>

It is observed from Fig. 7 that, the pure ZrO<sub>2</sub> thick films are less selective to O<sub>2</sub> against NH<sub>3</sub> at 50°C temperature, among all other gases. Pure ZrO<sub>2</sub> thick film has lack of selectivity to a particular gas among either in number of gases or in the mixture of gases. This is the major drawback of pure ZrO<sub>2</sub> thick films, while studying the O<sub>2</sub> sensing profile of the sensor. So, it is the today's need to modify the pure ZrO<sub>2</sub>, to behave as the selective gas sensors.

**VI. GAS SENSING PERFORMANCE OF SrO<sub>2</sub> ACTIVATED ZrO<sub>2</sub>**

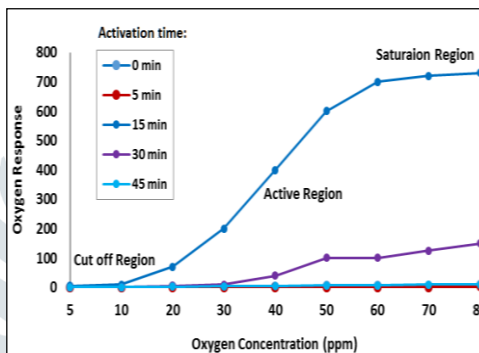
**6.1 Temperature Based Performance**



**Fig. 8:** Gas sensing profile

Fig. 8 depicts the variation of 50 ppm O<sub>2</sub> gas response with operating temperature of pure ZrO<sub>2</sub> and SrO<sub>2</sub> activated ZrO<sub>2</sub> thick films. It is clear that, SrO<sub>2</sub> activated ZrO<sub>2</sub> thick film at 15 min activation time gives highest response to 50 ppm O<sub>2</sub> gas at room temperature (32°C). But, as temperature increases, the O<sub>2</sub> response decreases and becomes negligible at 100°C, which may be attributed to notch effect of the sensor. Above 100°C, the oxygen response is negligibly small.

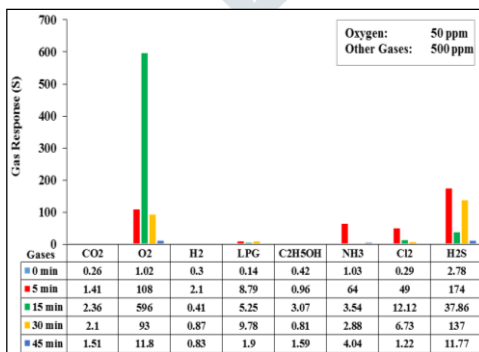
**6.2 Oxygen Concentration Based Performance**



**Fig. 9:** O<sub>2</sub> response Vs oxygen concentration (ppm)

The variation of oxygen response of SrO<sub>2</sub> activated ZrO<sub>2</sub> thick films with oxygen gas concentration are represented in Fig. 9. It is clear that, the gas responses go 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 50 ppm. The active region of the sensor would be up to 50 ppm. For proper functioning of the sensor, one should work in the active region of the sensor only.

**6.3 Gaseous Species Based Performance**



**Fig. 10:** Selectivity profile

It is observed from Fig. 10 that, the 15 min SrO<sub>2</sub> activated ZrO<sub>2</sub> thick film is most sensitive to O<sub>2</sub> at room temperature. This is the optimized condition as far as surface modification of ZrO<sub>2</sub> with the help of SrO<sub>2</sub> is concerned. Also, it has high selectivity against all other different gases, viz. carbon dioxide, hydrogen, liquefied petroleum gas, ethanol, ammonia and chlorine gas.

## 6.4 Activation Based Performance

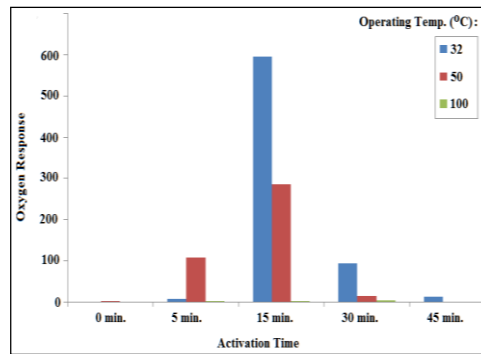


Fig. 11: O<sub>2</sub> response Vs activation time (min)

Fig. 11 indicates the oxygen response as a function of the activation time of the SrO<sub>2</sub> activated ZrO<sub>2</sub> thick film sensor. The pure ZrO<sub>2</sub> thick film was observed to be insensitive to oxygen at all temperature range. The activation of thick films of pure ZrO<sub>2</sub> by SrO<sub>2</sub> enhances the oxygen response. It was observed that, the response to oxygen increases with activation time, reaches to maximum at 15 min activation time and then falls down even with increase in the activation time. The film activated for 15 min was observed to be the most sensitive to oxygen at room temperature. At 5 min activation time, very less SrO<sub>2</sub> islands were formed creating less number of p-SrO<sub>2</sub> / n-ZrO<sub>2</sub> heterojunctions on the surface of the film. However, at 15 min activation time, the optimum number of p-SrO<sub>2</sub> / n-ZrO<sub>2</sub> heterojunctions produces better response. For larger activation time, the large number of SrO<sub>2</sub> islands would cover (mask) the entire ZrO<sub>2</sub> film, reduces response.

## 6.5 Long Term Stable Performance

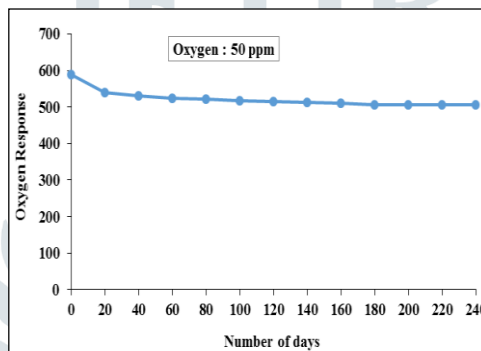


Fig. 12: O<sub>2</sub> response over long time duration (Days)

Fig. 12 indicates the oxygen response over a long time duration for the SrO<sub>2</sub> activated ZrO<sub>2</sub> (15 min) thick film sensor. The sensor was observed to be the most sensitive to oxygen at room temperature. The sensor response to oxygen was observed to be constant over a long duration (few months). It was observed that, the sensor response decreases by less than or near about 10 % after 40 days, and remains same thereafter. This proves the long term stability of the sensor.

## 6.6 Response - Recovery Performance

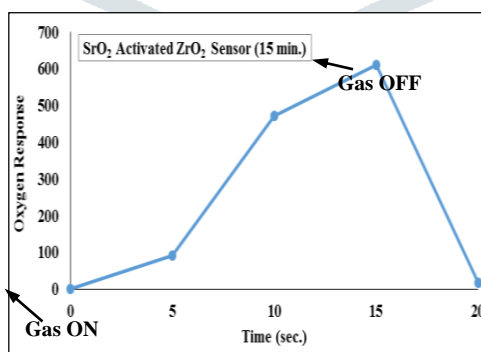


Fig. 13: Response and recovery of SrO<sub>2</sub> activated ZrO<sub>2</sub> sensor

The response and recovery of the SrO<sub>2</sub> activated ZrO<sub>2</sub> (15 min) sensor is represented in Fig. 14. The response of the sensor was fast (~12 sec.) to 50 ppm of oxygen and recovery is quick (~ 4 sec.). For better performance of the sensor, the recovery should be quick. When the gas exposure was switched off, the sensor returned back to its original chemical status, within a very short time (~ 4 sec.). This is the main feature of this sensor.

## VII. OXYGEN GAS SENSING MECHANISM

The SrO<sub>2</sub> islands established on the surface of ZrO<sub>2</sub> thick film during activation, form p-SrO<sub>2</sub> / n-ZrO<sub>2</sub> heterojunctions on the surface of thick film, leading the increase in the barrier height among heterojunctions and hence resistivity. Upon exposure, O<sub>2</sub> molecules hold the free electrons from the surface leading to decrease the n-typeness of ZrO<sub>2</sub> in the extent that, it ruptures the p-n

heterojunctions and the whole material exhibits p-type semi conductivity. The holes contribute the total flow of current within the surface of the material. This may be the reason of increase in conductivity of the sensor upon exposure of O<sub>2</sub> at room temperature.

The working principle of thick film semiconducting gas sensors is based on the change of the electronic conductivity of the semiconducting material upon exposure of O<sub>2</sub> gas (Fig. 14). The interaction of O<sub>2</sub> gas molecules with surface of the thick film causes the transfer of electrons between semiconducting surface and adsorbates.

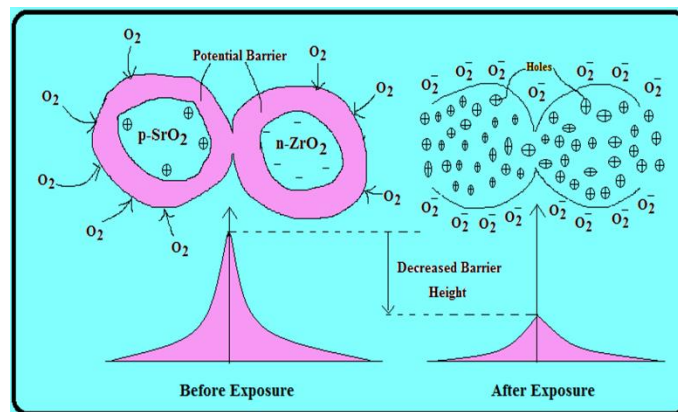
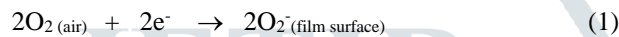


Fig. 14 Physical and Band model of the SrO<sub>2</sub> activated ZrO<sub>2</sub> thick film gas sensor

Upon exposure, the molecular oxygen O<sub>2</sub> adsorbs on the surface of the thick film. It captures the electrons from conduction band as:



It would result in conductivity only due to holes in the film. But, as the temperature increases, the O<sub>2</sub> response decreases in the range from 75°C to 100°C, due to notch effect of the sensor. Above 100°C, the oxygen response is negligibly small. This may be attributed to the fact that, as the temperature increases, slowly up to 75°C, the material may lose adsorbed oxygen ions achieving the stoichiometric proportion travelling towards insulating nature, perfectly at 75°C and up to 100°C. Above 100°C, an interesting event happens that, the material tries to lose the excess adsorbed oxygen and we are exposing the oxygen. The action of oxygen exposure is exactly opposite to that of losing oxygen by the material at higher temperatures, maintaining the material in the insulating nature. So, this material would not offer the response to oxygen at higher temperatures. This is advantageous fact for the low temperature applications viz. switches, relays, etc.

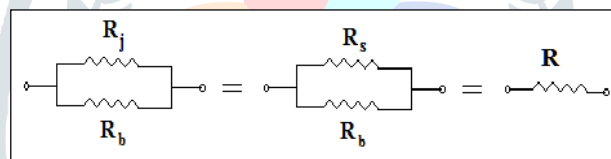


Fig. 15: Resistive model of the sensor

Gas sensing phenomenon is the surface phenomenon. So, the exposure of gas on the surface of the sensor can lead the change of surface resistance, instead of bulk resistance [18]. On the surface as well as in bulk of thick films, p-SrO<sub>2</sub> / n-ZrO<sub>2</sub> heterojunctions were formed. Thick film sensor can be represented as the resistive model as shown in Fig. 15. Total resistance (R) of the composite film sensor can be considered as the resultant of the two resistances R<sub>j</sub> and R<sub>b</sub>, connected in parallel. Where R<sub>j</sub> is the junction resistance on the surface and R<sub>b</sub> is the resistance of bulk of the sensor.

The equation of total resistance in parallel combination is as follows;

$$\frac{1}{R} = \frac{1}{R_j} + \frac{1}{R_b} = \frac{1}{R_s} + \frac{1}{R_b} \quad (2)$$

The total resistance of the film in air was very high (~10<sup>5</sup> Ω). Therefore, the values of R<sub>j</sub> and R<sub>b</sub> would also be very high, because, we know very well that, the effective resistance of the two high resistances connected in parallel is also high.

Upon exposure of oxygen gas on p-SrO<sub>2</sub> / n-ZrO<sub>2</sub> heterojunctions, the electrons are captured by adsorbed oxygen increasing the number of majority current carriers (holes) in n-type ZrO<sub>2</sub>. Thus p-n junctions get ruptured on the surface of the sensor and the whole surface acts as a p-type semiconducting material. This reduces the junction resistance (R<sub>j</sub>) drastically and becomes only the smaller surface resistance (R<sub>s</sub>), causes due to the geometry of the surface only. During such type of changes made on the surface, the bulk resistance (R<sub>b</sub>) remains same. The decrease in R<sub>s</sub> leads the decrease in R, due to decrease in barrier height.

## VIII. CONCLUSIONS

- Pure zirconium oxide thick film was almost insensitive to O<sub>2</sub> traces.
- The temperature range from 100°C to 75°C is the notch for which the pure and activated ZrO<sub>2</sub> materials exhibit insulating nature. The material switches its semiconducting nature from NTC to PTC through insulating nature, with decreasing temperature from 400°C to room temperature.
- In the temperature range of 100°C to 75°C, no one should expect the application of this material either pure or activated ZrO<sub>2</sub> in the field of gas sensing or any other field.
- It was observed that, pure ZrO<sub>2</sub> and activated ZrO<sub>2</sub> thick film sensors offer the gas responses below 75°C and does not offer even smaller response to any gas above 100°C.
- 3.86 mass % SrO<sub>2</sub> incorporated by the activation process in pure ZrO<sub>2</sub> for 15 min thick film sensor offers crucial response to 50 ppm oxygen at room temperature and it is highly selective to O<sub>2</sub> among the mixture of other gases.
- Dipping process is one of the most suitable methods of activating the surface of the thick films.

- vii. The excellent features of the sensors are highly sensitive, selective, low cost, portable in size and weight, long term stability, fast response and quick recovery.

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