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# Gas Sensing Performance of Pure and Modified Nanostructured Screen Printed Zirconia Thick Films

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**Abstract: Metal oxide based solid state gas sensors are the best selection to the development of commercial gas sensors for a wide range of applications. The great interest of industrial and domestic solid state gas sensors comes from their versatile advantages like portable size, high sensitivity in detecting very low concentrations (ppm, ppb or sub ppb level). Zirconium Oxide (Zirconia) powder is one such challenging material for the fabrication of gas sensors. Bulk Zirconium Oxide ($ZrO_2$) powder in the form of thick film was observed to be less sensitive to the polluting gases. So, synthesized nanostructured $ZrO_2$ powder was fabricated by simple screen printing technique followed by the calcinations at 500ºC for 1 hr. Thick films of pure nanostructured $ZrO_2$ powder were surface activated by dipping them into 0.01 M aqueous solution of Strontium Chloride and Bismuth Chloride separately for different intervals of time followed by calcinations at 500ºC for 30 min. The films exhibit the semiconducting nature due to non-stoichiometry and respond to various gases. Optimizing the particular conditions, the thick films can be used for gas sensing to detect polluting and hazardous gases, viz. $H_2$, $H_2S$, $Cl_2$, $NH_3$, $C_2H_5OH$, LPG, etc. The surface morphology, chemical composition, crystal structure, electrical and thermal properties of the bulk and nanostructured $ZrO_2$ have been investigated by Field Emission Scanning Electron Microscope (FE-SEM), Energy Dispersive Analysis by X-rays (E-DAX), X-Ray Diffraction (XRD), etc.**

***Keywords - Bulk and Nanostructured $ZrO_2$, Synthesis, Thick Films, Polluting Gases, etc.***

## I. INTRODUCTION

An oxygen sensor is an electronic device that measures the concentration of oxygen ($O_2$) in 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 in the gases or liquids. Oxygen sensors are also used in hypoxic air fire prevention systems to monitor continuously the oxygen concentration inside the protected volumes [1-11]. Hydrogen sulfide has characteristic of rotten egg like odor and also it is a colourless gas. It appears naturally as a byproduct of decomposition. Hydrogen sulfide is a highly toxic gas [12-18]. It reacts with the enzymes in the blood stream which inhibit cell respiration. In other words, high concentrations of hydrogen sulfide can shut off the lungs. Even low concentration exposure of the $H_2S$ gas can burn the respiratory track and cause swelling around the eyes [19-24]. Prolonged exposure of $H_2S$ gas renders the sense of smell inoperative. Many gas sensors are already available by Figaro-Engg. Inc., Sierra Monitors Inc., IST, etc. However, many problems persist till today. These problems can be minimized by varying different parameters in the measurement of gas sensing. The different parameters, viz. operating temperature, type of gas, gas concentrations, ageing (long term), type of materials, crystallite size, film thickness, dopants, activators, calcination temperature, activation time, etc. affect the gas response of the sensor. However, the devotion is paid in fabricating the $ZrO_2$ and its compositions based low cost gas sensors. Hence, the effects of all above mentioned parameters are studied on the gas sensing performance of the nanostructured base materials and their compositions. The present work explains the comparative study of the sensors fabricated in the form of thick films.

## II. OBJECTIVES

1) To synthesize the nanostructured $ZrO_2$ by one of the simplest and cheapest process known as disc type ultrasonicated microwave assisted centrifuge technique.
2) To prepare the thick films of nanostructured $ZrO_2$ by screen printing technique. This is one of the simplest and low cost technique.
3) To ensure longer life by maintaining proper thixotropy and rheology of the thick films.
4) To achieve a suitable surface activation by dipping the thick films of $ZrO_2$ into $SrO_2$ and $Bi_2O_3$ for enhancing the gas response and selectivity.
5) To analyze the synthesized pure and modified materials by different characterization techniques.
6) To investigate the electrical and gas sensing performance of pure and surface activated $ZrO_2$ thick films.
7) To investigate and modify the response and recovery profile of pure and surface activated $ZrO_2$ thick films.

## III. LITERATURE REVIEW

Table 1: Literature Review

| Sr. No. | Material | Technique | Gas / Investigation | Year | Ref. No. |
|---|---|---|---|---|---|
| 01 | $ZrO_2$ | Thick films | $H_2$ | 2009 | 25 |
| 02 | $HfO_2$, $ZrO_2$ | Thin films | $N_2$ | 2006 | 26 |
| 03 | $ZrO_2$-$Y_2O_3$-$TiO_2$ | Thick films | Synthesis | 1999 | 27 |

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| | | | | | |
|---|---|---|---|---|---|
| 04 | $Ta_2O_5$, $ZrO_2$ | Thin films | Synthesis | 2006 | 28 |
| 05 | $TiO_2$, $ZrO_2$ | Sol gel method | Humidity | 2008 | 29 |
| 06 | $(ZrO_2)_{0.8}$-$(\alpha\text{-}Fe_2O_3)_{0.2}$ | Thick films | $O_2$ | 2000 | 30 |
| 07 | $ZrO_2$ | Thin films | Synthesis | 2002 | 31 |
| 08 | $TiO_2$, $ZrO_2$ | Sol gel method | Characterizations | 2010 | 32 |
| 09 | $CeO_2$, $ZrO_2$ | Thick films | $O_2$ | 2008 | 33 |
| 10 | Pt, ZrO2 | Thick films | $O_2$ | 2000 | 34 |
| 11 | $ZrO_2$, $Fe_2O_3$ | Thick films | $O_2$ | 2003 | 35 |
| 12 | Ceria, Yttria, Zirconia | Thick films | $O_2$ | 2009 | 36 |
| 13 | $ZrO_2$ | Thin films | Synthesis | 2003 | 37 |
| 14 | $ZrO_2$ nanopowder | Wet chemical route | Synthesis | 2006 | 38 |
| 15 | $ZrO_2$ nanopowder | Precipitation methods | Synthesis and characterizations | 2008 | 39 |
| 16 | $Al_2O_3$-$ZrO_2$ | Sol gel method | Synthesis and characterizations | 2000 | 40 |

## IV. MATERIALS USED

*A. Zirconium Oxide (Zirconia, $ZrO_2$)*

Zirconium dioxide ($ZrO_2$) is also known as zirconia. It is a white crystalline oxide of zirconium. It's most occurring form, with a monoclinic crystalline structure having wide band gap of 5.8 eV. The band gap energy of $ZrO_2$ is dependent on the phase (cubic, tetragonal, monoclinic or amorphous) and preparation methods with typical estimates from 5-7 eV. Zirconium dioxide is one of the very important ceramic materials. Pure $ZrO_2$ has a monoclinic crystal structure at room temperature and found transitions to tetragonal and cubic at increasing temperatures. Zirconia is used in the production of ceramics with other uses including protective coating on particles of $TiO_2$ pigments, as a refractory material, abrasives, enamels and insulations. Zirconium dioxide is also used in fuel cell membranes and oxygen sensors since; it has the ability to allow oxygen ions to move freely through the crystal structure at high temperatures. The high ionic conductivity makes it one of the most useful electro-ceramics.

*B. Strontium Oxide ($SrO_2$)*

Strontium is a chemical element with symbol Sr and atomic number 38. Strontium is an alkaline earth soft metal in silver white or yellowish color. When it is exposed to air, the metal forms a dark oxide layer. Strontium occurs naturally found mainly in the minerals celestite and strontianite. The properties of strontium are intermediate between and similar to those of its group neighbors, calcium and barium. It is harder than barium and softer than calcium. The melting point of strontium is 777°C and boiling point is 1377°C. The density of strontium is 2.64 gm/cc. When Strontium metal burns in air, it produces strontium oxide as well as strontium nitride. However, it does not react with nitrogen below 380°C. It spontaneously forms only oxide at the room temperature. Strontium is widely used in fireworks and flares. It is also used for refining zinc and manufacturing of ferrite magnets.

*C. Bismuth Oxide ($Bi_2O_3$)*

Bismuth occurs as silver, pink and white in its original form as with an iridescent oxide tarnish showing many colors from yellow to blue. The Bismuth oxide has base centered monoclinic crystal structure. Bismuth burns with a blue flame and its oxide forms yellow fumes, when burnt in oxygen. It is less toxic as compared with its other neighboring elements in the periodic table, viz. lead, antimony and polonium. Bismuth occurs as the native metal, and in ores such as bismuthinite and bismite. Bismuth oxide is a high-density metal. As Bismuth is a brittle metal, it is usually mixed with other metals to make it useful. Bismuth can be used in fire detectors and extinguishers, solders and electric fuses when it is mixed with low melting point metals, viz. tin or cadmium. Bismuth oxide is also used as cosmetics and paints.

## V. EXPERIMENTAL

*A. Synthesis of Nanostructured $ZrO_2$ Powder*


Fig. 1: Disc type ultrasonicated microwave assisted centrifuge technique

Nanostructured $ZrO_2$ powder was synthesized by disc type ultrasonicated microwave assisted centrifuge technique [41-46], by hydrolysis of AR grade zirconium oxychloride in aqueous-alcohol solution (Fig. 1). An aqueous-alcohol solution was prepared in the ratio of 1:1 from distilled water and propylene glycol. This solution was then mixed with 1M aqueous solution of zirconium oxychloride in 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 $AgNO_3$ 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 $ZrO_2$ has been prepared to use.

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*B. Thick Film Fabrication Technique*

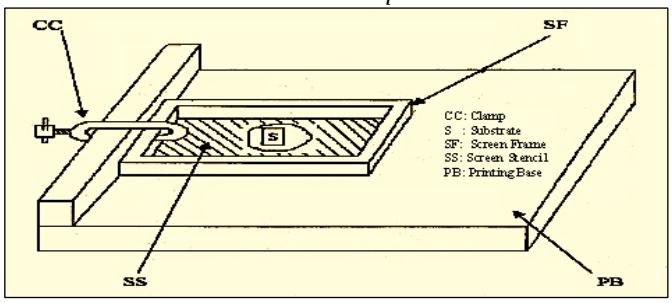


Fig. 2: Screen printing set-up board

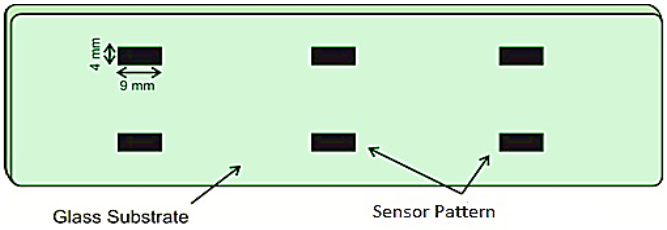


Fig. 3: Sensor patterns printed on the glass substrate

Thick film fabrication technique using screen printing mechanism is the most suitable, simple and economical method in the fabrication of sensors. The screen is held at about few millimeters above the substrate on a printing set up board (Fig. 2). The required thixotropic paste is kept on the top surface of stencil and squeegee pushes the paste and poured through the pores while it moves from one end to the other. The sensor patterns printed on the glass substrates are in rectangular form. The length of the sensor pattern kept was 9 mm and the width 4 mm (Fig. 3). The desired amounts of samples are prepared by repeating the above procedure. These samples are then subjected to a temperature in the range of 70-130ºC for drying under an IR lamp. Next, curing is done in order to avoid the blistering of the film. It has two steps: removal of organic binder and high temperature curing / firing. In the first step, the residues of organic binder are eliminated by heating at low temperature. In the second step, the film is subjected to a furnace under controlled conditions. The chemical reactions that take place, give the required electrical and physical properties of the film.

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 has opened up the possibility of manufacturing sensors in a cost effective manner. Such properties of a thick film sensor are highly desirable for chemical applications. Furthermore, thick film technology has the ability to produce the sensors from nano-scaled materials. This is an advantage because minute sample volume is required. Also, the portability of the interface instrument for the sensor can be realized. The thixotropic paste was prepared by mixing the synthesized nanostructured powder of pure $ZrO_2$ with a solution of ethyl cellulose in a mixture of 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 [43-46]. Films prepared were dried at 80ºC under an IR lamp, followed by firing at 500ºC for 30 min. in 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 ready to use in the desired applications.

*C. Surface Activation of $ZrO_2$ Thick Films*

Surface activation of as prepared thick films of pure $ZrO_2$ was achieved by dipping them into a 0.01 M aqueous solution of strontium chloride and bismuth chloride, separately, for different intervals of time, viz. 5 min., 15 min., 30 min. and 45 min. and dried at 80ºC under an IR lamp, followed by firing at 500ºC for 30 min. in ambient air. The particles of strontium chloride and bismuth chloride dispersed on the film surface would be transformed to strontium oxide ($SrO_2$) and bismuth oxide ($Bi_2O_3$) respectively, upon firing process. Thus, the sensor elements with different mass % of $SrO_2$ and $Bi_2O_3$ incorporated in to thick films of pure $ZrO_2$ were prepared.

*D. Static Gas Sensing System*


Fig. 4: Static gas sensing system

The sensor element, heating unit, dc power supply, gas inject unit, temperature measuring unit, current meter (pico-ammeter), glass dome and steel base plate are the major components of static gas sensing system. The static gas sensing system is built in the laboratory (Fig. 4). There are electrical feeds on the base plate. Heating unit is fixed on the base plate. It provides the desired temperature to sensor for its proper performance. Sensor sample to be tested was mounted above the heater. Cr-Al thermocouple is mounted to measure the temperature. The thermocouple is connected to digital temperature indicator. Inlet gas port was fitted at one of the ports of base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas by gas inject syringe. A d. c. voltage of 0 - 30 V is applied to the sensor element constantly and current is measured by pico-ammeter.

## VI. CHARACTERIZATION TECHNIQUES

The studies on microstructures and surface morphology of thick film samples were carried out by using X- Ray Diffractometer (XRD) and Field Effect Scanning Electron Microscopic (FE-SEM) techniques, respectively. Also, electrical characteristics, viz. I-V characteristics and

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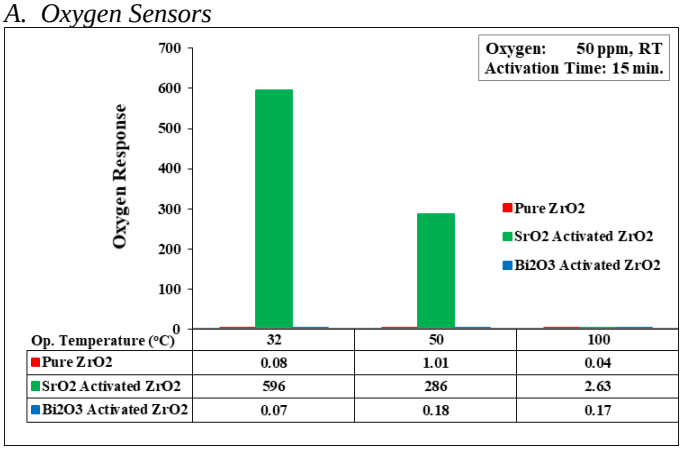
conductivity profile of all the samples were also studied in the laboratory [41-47].

## VII. RESULTS AND DISCUSSION

### A. *Oxygen Sensors*

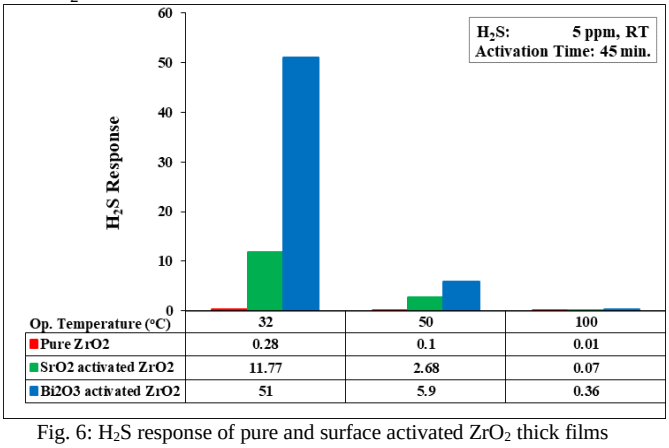



| Op. Temperature (°C) | 32 | 50 | 100 |
|---|---|---|---|
| Pure ZrO2 | 0.08 | 1.01 | 0.04 |
| SrO2 Activated ZrO2 | 596 | 286 | 2.63 |
| Bi2O3 Activated ZrO2 | 0.07 | 0.18 | 0.17 |

Fig. 5: Oxygen response of pure and surface activated $ZrO_2$ thick films

Fig. 5 depicts the $O_2$ response of pure and surface activated $ZrO_2$ (15 min.) thick films. From Fig. 5, it is observed that, the 15 min. $SrO_2$ activated $ZrO_2$ thick film is most sensitive and selective to $O_2$ (50 ppm) at room temperature. Upon exposure of $O_2$, the n-typeness of $ZrO_2$ decreases in the extent that ruptures the p-$SrO_2$ / n-$ZrO_2$ heterojunctions and the whole material exhibits p-type semiconductivity. The holes contribute the net flow of current in the surface of the material. This may be the reason of increase in conductivity of the sensor upon exposure of $O_2$ at room temperature. But, as the temperature increases, the $O_2$ response decreases in the range from 75°C to 100°C. Above 100°C, the oxygen response is negligibly small [47]. However, $Bi_2O_3$ activated $ZrO_2$ thick films are insensitive to $O_2$ at all temperature range.

### B. *$H_2S$ Sensors*




| Op. Temperature (°C) | 32 | 50 | 100 |
|---|---|---|---|
| Pure ZrO2 | 0.28 | 0.1 | 0.01 |
| SrO2 activated ZrO2 | 11.77 | 2.68 | 0.07 |
| Bi2O3 activated ZrO2 | 51 | 5.9 | 0.36 |

Fig. 6: $H_2S$ response of pure and surface activated $ZrO_2$ thick films

Fig. 6 depicts the $H_2S$ response of pure and surface activated $ZrO_2$ (45 min.) thick films. From Fig. 6, it is observed that, the 45 min. $Bi_2O_3$ activated $ZrO_2$ thick film is most sensitive and selective to $H_2S$ (5 ppm) at room temperature. Upon exposure, $H_2S$ gas gets oxidized by utilizing the molecular oxygen adsorbed on the surface of the thick film, trapping behind the free electrons in the material and enhances the conductivity of the material. The high performance of this film in $H_2S$ sensing may be attributed to the enhancement of active surface to volume ratio [47]. But, as the temperature increases, the $H_2S$ response decreases. However, $SrO_2$ activated $ZrO_2$ thick films are comparatively less sensitive to $H_2S$ at room temperature and insensitive at high temperature range.

## VIII. CONCLUSIONS

A review of the existing literature suggests that, the modified and unmodified $ZrO_2$ thick films possess in several important areas of application of modern microelectronic techniques, because of their uses in production of advanced infrared detectors and sensors for sensing toxic gases and magneto-resistive sensors. The gas response of the sensor must be as high as possible to trace level (ppm / ppb) of the gas with very high selectivity and no cross sensitivities. The response and recovery times must be very low (~ few seconds). Pure semiconducting oxides are expected to be stoichiometric and hence are less sensitive and less selective to toxic, hazardous and polluting gases.

It was studied that, the non-stoichiometric zirconium oxide behaves as semiconductors and act as gas-sensing varistors. Various techniques are employed to modify the stoichiometric zirconium oxide to disturb their stoichiometry. Few most suitable techniques viz. sintering at higher temperatures, surface functionalization, etc. can be used. Sintering at higher temperatures would cause the elimination of undesired impurities in the material. Also, it would create the oxygen vacancies in the pure materials, modifying the various characteristics of the materials. The nanostructured $ZrO_2$ material has the great potential to fabricate the gas sensors which have most advanced and highly applicable features. The review also reveals that, very few researchers studied on $ZrO_2$ thick films but almost no attempt has been made to study dipping time variation with the response of gas. Hence, it is the need to study the effect of surface activation on structural, electrical and gas sensing properties by changing dipping concentration. So, there is a great space to work for the development of $ZrO_2$ based gas sensors.

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