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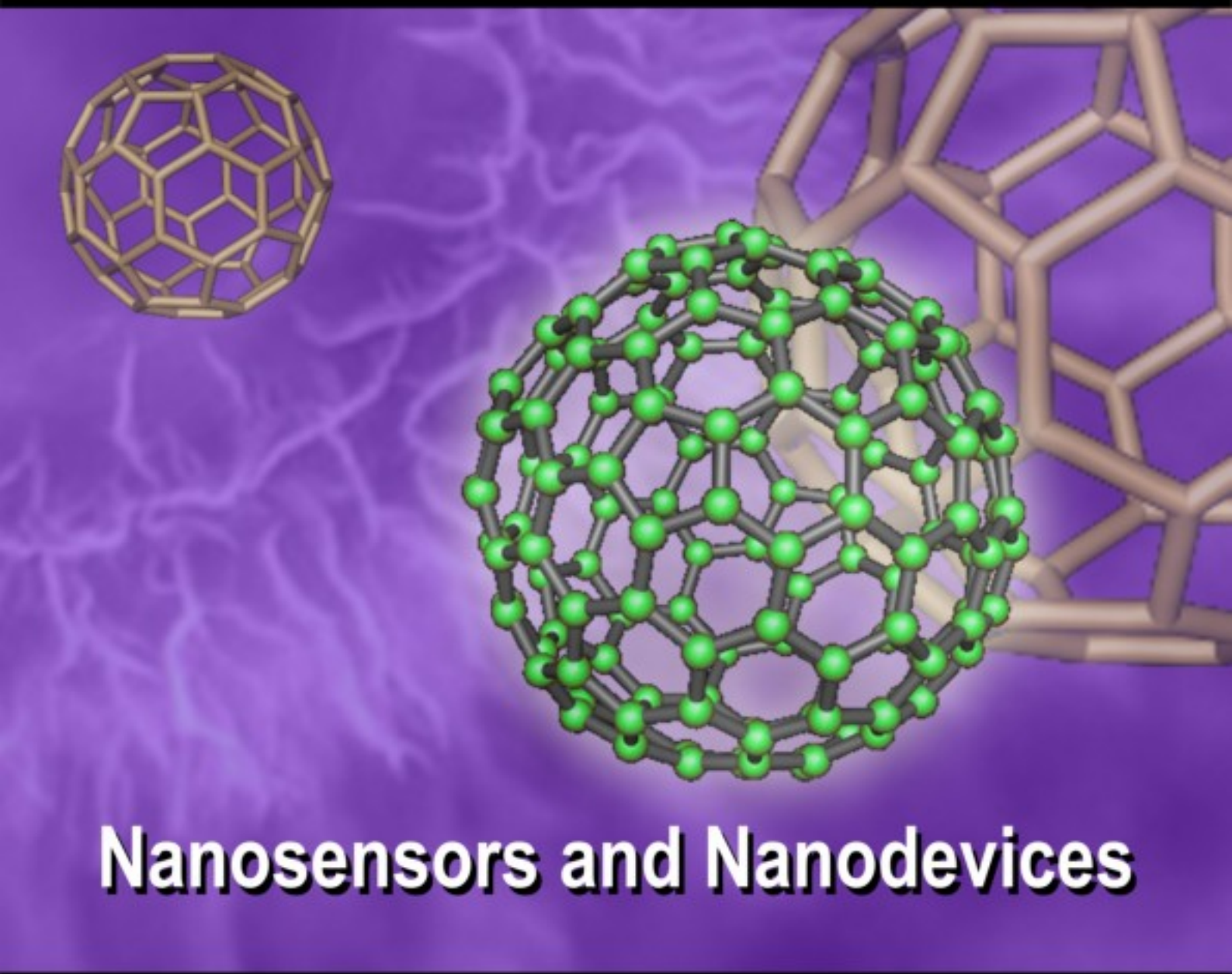

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Nanostructured ZrO_2 Thick Film Resistors as H_2-Gas Sensors Operable at Room Temperature

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Abstract: Nanostructured ZrO_2 powder was synthesized by microwave assisted sol-gel method. The material was characterized by XRD and SEM techniques. X-Ray diffraction studies confirm that a combination of tetragonal and monoclinic zirconia nanoparticles is obtained by using microwave-assisted method. The nanopowder was calcined at an optimized temperature of 400 °C for 3 h. The prepared powder had crystalline size about 25 nm. Thick films of synthesized ZrO_2 powder were prepared by screen printing technique. The gas sensing performances of these films for various gases were tested. Films showed highest response to H_2 (50 ppm) gas at room temperature with poor responses to others (1000 ppm). The quick response and fast recovery are the main features of this sensor. The effects of microstructure, operating temperature and gas concentration on the gas response, selectivity, response time and recovery time of the sensor in the presence of H_2 gas and others were studied and discussed. *Copyright © 2009 IFSA.*

Keywords: Nanostructured ZrO_2, XRD, SEM, H_2 gas sensor, Gas sensitivity

1. Introduction

ZrO_2 have been widely used for various applications such as semiconductor in dye-sensitized solar cell, catalysts, fuel cells, resistors, gas sensors, transparent optical device, optical coating etc [1-3]. Conventional method for the preparation of the oxide is normally ceramic route, preparation through sol-gel route has many advantages, like good homogeneity, less number of process steps, easy for remote operation, low sintering temperature etc. In addition to that microwave-assisted synthesis is a

new route to produce inorganic compounds because microwave heating is in situ mode of energy conversion very attractive for chemist. Microwave device is able to produce rapid bulk heating due to strong thermal gradients induced by microwave heating, strong stirring occurs for liquid leading to thermal uniformity of forced hydrolysis and very fast heating rate [4-8].

Semiconducting oxides are widely used as inexpensive and robust sensors for toxic, hazardous and combustible gases and vapors in safety and automotive applications. Few semiconducting oxide materials used in these applications are ZnO, SnO_2, Fe_2O_3, Cr_2O_3, TiO_2 and ZrO_2 etc [9-20]. Energy is the driving force of all activities in the universe [21]. Nothing moves, changes, grows or decays without consumption of energy. It flows downhill from high-potential to low-potential and high-temperature source to cosmic cold of the outer space. For most organisms, energy required is derived from food. Unlike other organisms, human not only require food energy but also energy to drive machines, produce heat, generate electricity, transport, etc. The energy is obtained from fossil fuels, solar and nuclear resources [22-26]. Fossil fuels, coal and petroleum have limited age as their consumption is tremendous. These are nonrenewable resources. They cause explosive pollution. The extraction of energy from solar radiations causes a minimal damage to environment; but not developed well till today and unaffordable in social and domestic use. Nuclear energy has the serious problems with handling and waste disposal. It is, therefore, need to turn our attention towards the development of fuel economy based on hydrogen. Hydrogen is not the primary source of energy. It is an energy carrier. On combustion, it produces only water. Hence, the advantage of hydrogen is its virtually pollution-free combustion. It is therefore, destined to become the fuel of the future. Hydrogen as an energy carrier has widespread applications. It is explosively utilized in industrial fields as a fuel. It is a colorless and odorless gas, its leakage cannot be noticed easily. This gas is potentially hazardous because explosion accidents might be caused when they leak out by mistake. So there is a great demand and emerged challenges for monitoring for the purpose of control and safety applications in domestic and industrial fields [27].

The aim of the present work is to develop sensors by synthesizing nanostructured ZrO_2 material, which could detect the trace level of H_2 gas at room temperature.

2. Experimental

The ZrO_2 nanoparticles were synthesized by the hydrolysis of Zr(IV) salts in aqueous-alcohol solution. An initial aqueous-alcohol solution was prepared from distilled water and propylene glycol [8]. This solution was mixed with aqueous solution of zirconium oxychloride ($ZrOCl_2.8H_2O$) in ratio such that the zirconium concentration was 0.1M and the alcohol to water ratio was 1:1. The special arrangement was made to add dropwise aqueous ammonia (0.1ml / min.) with constant stirring till the pH of solution becomes 8. After complete precipitation, the hydroxide was washed with distilled water until chloride ions were not detected by $AgNO_3$ solution. Then the hydroxide in a glass beaker was placed in a micro-wave oven (in put power 600 W) about 15 minutes with on off cycle [5-6].The dried precipitate was grinded by using agate pestle mortar and annealed in a muffle furnace at 400 °C for 3h.The Phase purity and the degree of crystallinity of the resulting ZrO_2 samples were monitored by XRD analysis.

Synthesized ZrO_2 powder was calcined at 300 ^{0}C for 30 min in air. Thick films of so obtained powder, were prepared by adopting the procedure explained elsewhere [13-19].

3. Results and Discussion

3.1. Structural and Surface Morphology Analysis of ZrO_2 Nanoparticles

To determine the structure of nanoparticles the powder have been, firstly, analyzed by X-Ray diffraction. After annealing treatment at 200, 300, 400 and 500 ^{0}C, the XRD patterns after heat treatment at 300^{0}C shows a slight increase of crystallinity as compared to the raw microwave powder and X-ray lines become thinner and thinner with increasing temperature due to strong growing of crystal size. The nanometric size of the particles leads to strong broadening of X-Ray diffracted lines and despite careful analysis of XRD patterns of raw powder, it is difficult to conclude about nature of the crystallographic phase produced. However, Bragg reflections intensities of tetragonal and monoclinic phase are observed after annealing treatment. Crystallinity of raw microwave powder was found to be poor compared to those obtained after annealing treatment [7].

Fig. 1 shows the XRD pattern of ZrO_2 nanoparticles within the 2θ range of 10 to 80^0.XRD of ZrO_2 annealed at 400 ^{0}C for 3h in air exhibited its characteristic diffraction peaks of tetragonal and monoclinic. The determined characteristic 2θ values and hkl planes corresponding to monoclinic-ZrO_2 were at 35.39^0(200),63.08°(222) respectively (JCPDS 36-0420) while, the determined characteristic 2θ values and hkl planes corresponding to tetragonal-ZrO_2 were at 30.35°(111), 50.49°(220) and 60.40° (311), respectively (JCPDS 17-0923). The particle size of ZrO_2 powder was calculated by using Scherrer's relation, $t = 0.9\lambda / \beta\cos\theta$. Where, λ-wavelength of X-Ray in Å, β-full width at half maximum in radian. The average particle size of ZrO_2 nanoparticles is found to be 25 nm.

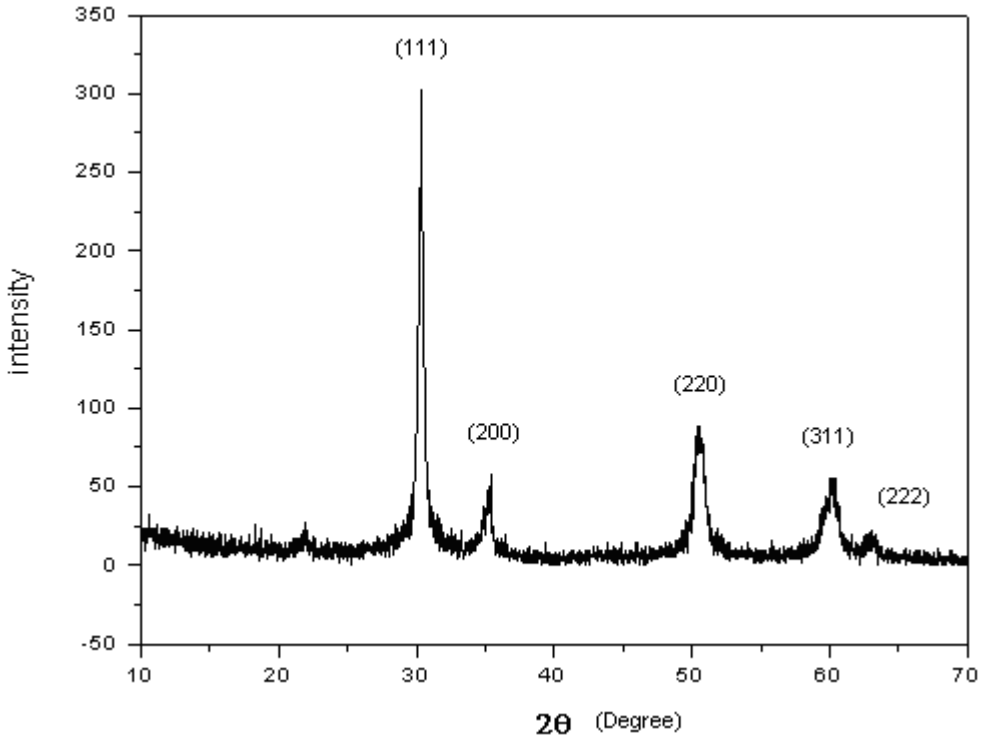
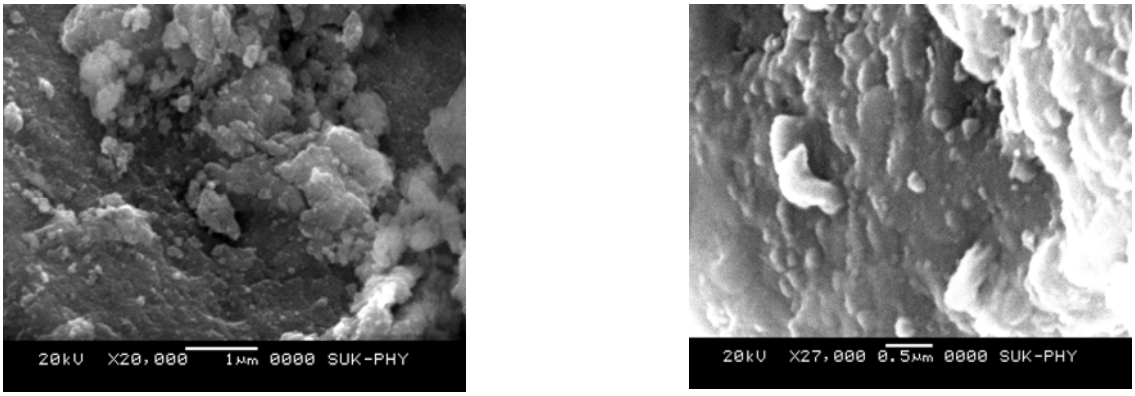


Fig. 1. XRD Pattern of ZrO_2 Nanoparticles Calcined at 400 ^{0}C, 3 h.

Fig. 2 shows the SEM photograph of ZrO_2 nanoparticles, from this figure it is seen that the grain size of the particle is found to be ~25 nm with uniform distribution. The value of particles size observed from SEM results were in good agreement with the XRD results. It reveals that the microwave

hydrolysis makes it possible to obtain particles of predominantly spherical shape with a narrow size distribution.



(a) (b)

Fig. 2. SEM micrograph of ZrO_2 nanoparticles (a) Annealed at 300 ^{0}C, (b) Annealed at 400 ^{0}C.

3.2. Sensing Performance

3.2.1. Measurement of Gas Response, Selectivity, Response and Recovery Time

Gas response (S) is defined, as the ratio of change in conductance of the sensor on exposure of the target gas to the original conductance in air medium. The relation for S is:

$$S = (G_g - G_a) / G_a ,$$

where G_a is the conductance of sensor in air medium;
G_g is the conductance of sensor in gaseous medium.

Selectivity or specificity is defined, as the ability of a sensor to respond to certain gas in the presence of more gases. Selectivity factor (K) of one gas over other is defined as, the ratio of the maximum response of other gas to the maximum response of the target gas at optimum temperature.

$$\text{Selectivity factor } K = S_{\text{target gas}} / S_{\text{gas}}$$

The time taken for the sensor to attain 90 % of the maximum change in conductance on exposure to the target gas is the response time. The time taken by the sensor to get back 90 % of the original conductance is the recovery time.

3.2.2. Gas Selectivity

It is observed from Fig. 3 that the ZrO_2 thick films are sensitive to H_2 gas and it has relatively good selectivity against different gases. This is the main feature of pure ZrO_2 thick film sensor. It is also observed that, the ZrO_2 thick film sensor also responds to CO_2 gas, though less. The efforts are therefore must be taken to enhance the sensitivity and selectivity of the sensor to H_2 and CO_2 gases at different operating conditions. From above results, it leads to conclude that the material has a potential application to develop the H_2 and CO_2 as gas sensors.

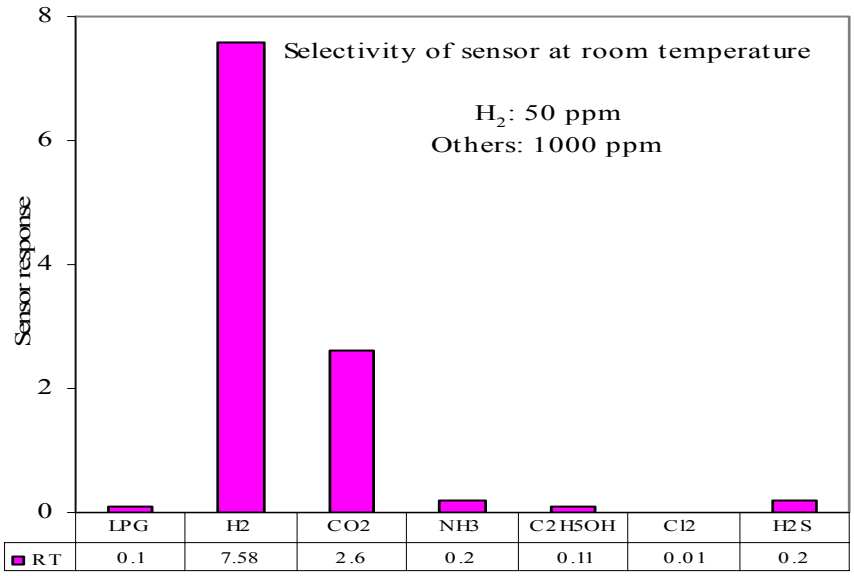


Fig. 3. Selectivity of pure ZrO_2 .

Fig. 4 depicts the gas responses of ZrO_2 thick films to different gases (1000 ppm) with operating temperature. It is observed from figures that the gas responses increase with operating temperature, reach to their respective maxima and falls down further with increase in operating temperature. The highest response was observed at room temperature and gas response decreases with increasing temperature up to 150 ^{0}C. The film surface chemistry was favorable to sense the H_2 gas at room temperature. Beyond 150 ^{0}C, the response increases up to 300 ^{0}C and again falls down with increase in operating temperature. At 300 ^{0}C, the adsorbed oxygen species O^- react with exposed H_2 gas and oxidizes H_2 gas quickly. Beyond 300 ^{0}C, the adsorbed O^- species may desorbed or H_2 gas may oxidized before reaching the film surface. Hence, gas response may decrease further. At 300 ^{0}C, the gas response may be attributed to oxygen adsorption-desorption mechanism, but without treatment to the thick film the gas response is not attributed to adsorption-desorption mechanism.

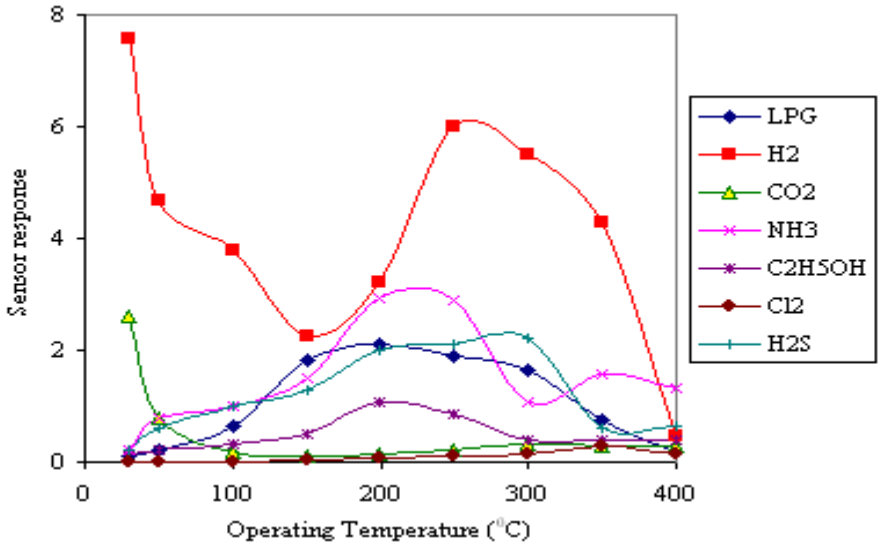


Fig. 4. Variation of gas responses for different gases.

3.2.3. Effect of Gas Concentration (Active Region)

The variation of sensor response of ZrO_2 thick film sample with H_2 gas concentration is represented in Fig. 5. It is clear from the figure that the gas response goes on increasing with gas concentration up to 50 ppm. The rate of increase in response was relatively large up to 50 ppm and saturated beyond 50 ppm. The monolayer of the gas molecules formed on the surface covers the whole surface of the film. The gas molecules from that layer would reach the surface active sites of the film. The excess gas molecules remain idle and would not reach the surface active sites of the sensor. Thus, the active region of the sensor would be up to 50 ppm.

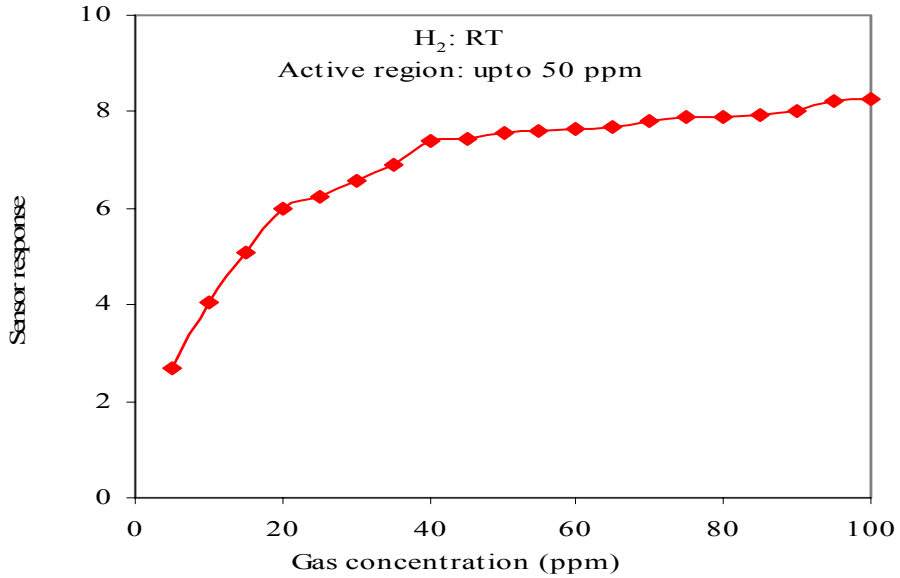


Fig. 5. Variation in sensor response with H_2 gas concentration.

3.2.4. Response and Recovery Time

The response of ZrO_2 thick film sensor was found to be quick (~ 3 s) to 50 ppm of H_2, while the recovery was fast (~ 30 s) (Fig. 6). The fast response may be attributed to faster oxidation of the gas. The negligible quantity of the surface reaction product and its high volatility explains its fast response and quick recovery to its initial chemical status.

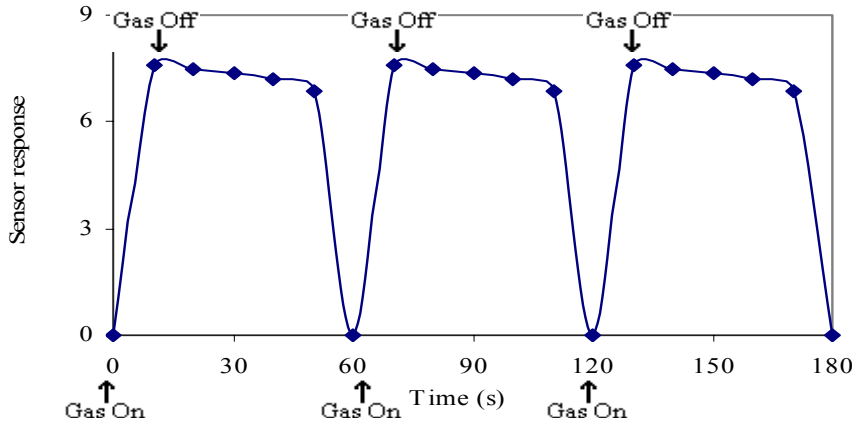


Fig. 6. Response and Recovery Time.

3.2.5. Response at 300 ^{0}C (Oxygen Adsorption-desorption Mechanism)

At higher temperature, the atmospheric oxygen O_2 adsorbs on the surface of the thick film. It captures the electrons (Fig. 7) from conduction band as:

$$O_{2\,(air)} + 2e^- \rightarrow 2O^-_{(film\ surface)}$$

It would result in decreasing conductivity of the film. When hydrogen on exposure reacts with oxygen, the following reaction takes place, ultimately converting the hydrogen to water molecules in vapors form as:

$$n\,H_{2\,(gas)} + n\,O^-_{(film\ surface)} \rightarrow n\,H_2O_{(gas)} + n\,e^-_{(cond.band)}$$

This shows the n-type conduction mechanism. For complete combustion, 1 mol of hydrogen will require the same amount of oxygen and will produce same number of water molecules. The entire surface of the sensor material is covered with chemisorbed oxygen ions O_2, O_2^-, O^- and O^{2-} depending on temperature. The adsorbed O^- species create space-charge region near the film surface at high temperature by extracting the electrons from the material. Hydrogen being a reducing gas, reacts with adsorbed O^- species on the surface and re-injects the electrons back to the material, thereby increasing the conductance of the film.

The fast response may be due to the fast oxidation of H_2 into H_2O. After evaporating water molecules from the film surface, the film recovers to its original chemical state.

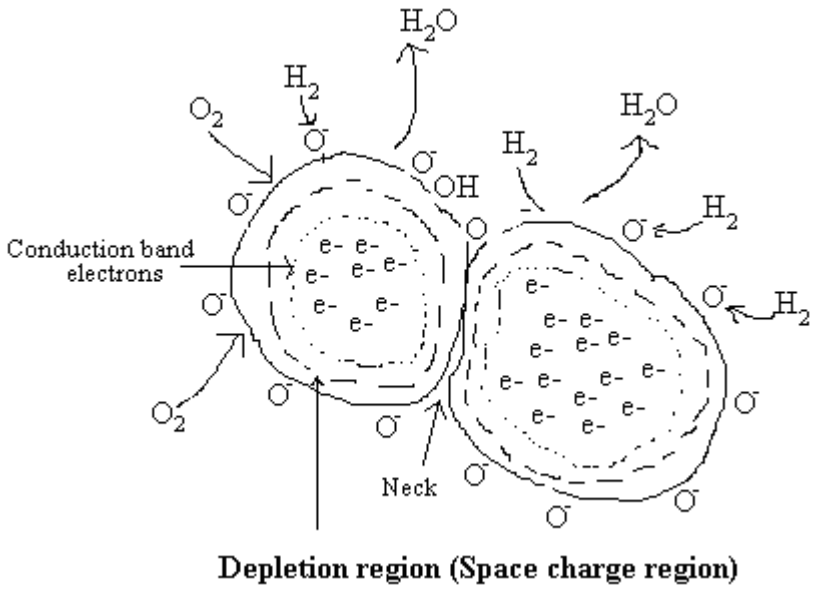


Fig. 7. Sensing Mechanism on the surface of the film.

3.2.6. Response at Room Temperature

The ZrO_2 thick films cause the formation of intergrain boundaries of ZrO_2-ZrO_2 grains. The exposed H_2 gas molecule captures the lattice oxygen from the surface of the film at room temperature. This would result the oxygen deficiency in the bulk of the material preferably at the surface. The semiconductivity in ZrO_2 may be due to large oxygen deficiency. The increase in the conductivity of

ZrO_2 thick films could be attributed to the charge-carrier generation mechanism resulted from the electronic defects due to nanostructured size of the grains. These generated electrons and the donor level in the energy band gap of ZrO_2 will contribute to increase in conductivity. This results in increasing the conductance of the film at room temperature.

4. Conclusions

The ZrO_2 nanoparticles were prepared by simple microwave assisted method .The well spherical size, narrow distribution and 25 nm size particles were obtained by this method. It is very simple, time as well as energy saving technique. The XRD pattern shows the ZrO_2 nanoparticles exists in both the phases of tetragonal and monoclinic. The ZrO_2 nanoparticles in the thick film form prepared by screen printing technique showed better response to H_2 gas at room temperature even at low concentration of H_2 gas (50 ppm).

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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