



PREPARATION AND CHARACTERIZATION OF ZIRCONIA BASED THICK FILM RESISTOR AS A AMMONIA GAS SENSOR

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Abstract - *Thick film technique is popular because of low cost, simple for construction and better sensing surface area, hence for resistive gas sensor thick films of pure ZrO₂ powder were prepared by Standard screen printing technique. The material was characterized by X-Ray diffraction pattern, surface morphology was observed by SEM, elemental composition were observed by EDAX and optical properties were studied with UV spectroscopy Techniques, electrical properties were studying with different applied voltages and at different working temperature. X-Ray Diffraction studies confirmed that the combinations of tetragonal and monoclinic structure. The energy band gap and the thicknesses of the films were evaluated, the crystalline grain size was*

determined using Scherrer's formula. The gas sensing performances of various gases were tested with working temperatures from 100° to 500°C. The sensitivity and selectivity to different gases was tested and the resistive thick films showed highest response to NH₃ (100 ppm) at 300°C. It was observed that increase in gas concentration its sensing response goes on increasing but slowly increase being still constant for higher concentration. The sensitivity and selectivity may be further enhanced by doping other element and ZrO₂ can be stabilize by mixing other oxides. The quick response and fast recovery time was recorded.

Index terms: ZrO₂ thick film; Screen printing technique; NH₃ sensors; high sensitivity; fast response and recovery time.

I. INTRODUCTION

Sensors in the form of thin and thick films are very attractive and metal oxide semiconductor gas sensors have been widely used in different industrial applications and environment monitoring. Now days it is mostly used to detect toxic gases and other gases applicable in mines[1] air cabins,[2] medication,[3] space, for cooking purposes in homes and hotels and Automobiles [4-6] etc. Such as H₂, CO₂, CO, NO₂, NO_x, CH₄, H₂S, SO₂, O₂, NH₃, C₂H₅OH, LPG etc. [7-9] The main advantages of the thin and thick film sensors are simple construction, small size, good sensitivity and selectivity, quick response and fast recovery time, low operating temperature, high stability, good accuracy, easy processing, reproducibility, low Cost and low consumption

Pure zirconia (ZrO₂) is not used in any practical application. But with other oxides such as yttria (Y₂O₃), calcia (CaO) and magnesia (MgO) are common additives in the range of 3-28 wt%. These additives are called 'stabilisers' for the following reasons: At room temperature, pure ZrO₂ has a monoclinic, which transforms to tetragonal at ~1170 C which remains stable up itself transforms to a cubic fluorite phase at 2370 C. The volume of monoclinic zirconia is change up to 9%° to the melting point of 2680 higher than tetragonal zirconia. If a component is made of pure zirconia, it would be sintered at temperatures in excess of 1200 ceramic components. During cooling from the firing temperature, the t to m transformation would occur, accompanied by sudden volume expansion which would lead to build up of stress and shattering of the component. In the presence of a stabiliser oxide, instead of monoclinic, the tetragonal or the cubic phase remains stable down to room temperature, depending on the amount of stabiliser added. This helps in avoiding the catastrophic volume

change accompanying the t to m transformation. Moreover, one can adjust the stabiliser content and the sintering temperature to stabilise a mixture of tetragonal and cubic phases down to room temperature, hence thermal stability have been achieved. Zirconia ceramics possess the amazing ability to conduct electricity through the migration of oxygen ions (O^{2-}) [10-12]. This property is seen at temperatures above $250^{\circ}C$. The story of zirconia ceramics and the environment does not end here. The ionic conductivity of zirconia is useful in making the so-called lambda sensors in modern automobiles. This sensor monitors the composition of the exhaust gases of a car engine. Based on the input from the lambda sensor, the computer of the car controls fuel injection into the engine to maximize efficiency. Along with catalytic converters, the O_2 sensors have been a boon to the automotive industry which faces increasingly tough emission control regulations and fuel efficiency standards. Zirconium exists in nature mainly as zircon ($ZrSiO_4$) and sometimes as the mineral baddeleyite ($m-ZrO_2$). [13-14] Zircon is found as sandy deposits called zircon sand the extraction of zirconia from zircon sands is carried out using the following process. Mineral beneficiation is carried out to separate and remove undesirable materials and impurities. For zircon it is mainly silica that is removed, and for baddeleyite, iron and titanium oxides. There are a few routes for extracting zirconia from zircon. These include chlorination, alkali oxide decomposition, lime fusion, and plasma dissociation and is accompanied by a large change in lattice size. ZrO_2 has been widely used for various application such as semiconductor in dye- sensitized, solar cell, fuel cell, transparent optical device, optical coatings, solid electrolytes for gas sensors, for medication, and resistive gas sensors.[15-18]. ZrO_2 is a wide band gap n-type semiconductor material with density $5.83g/cm^3$ for monoclinic phase and $6.10 g/cm^3$ for tetragonal phase.[19-21]. Zirconia is very famous as a Oxygen sensor at high operating temperature [22]. In present work it is ammonia sensitive. Ammonia is produced and utilized extensively in many chemical industries, fertilizers factories, refrigeration system, food processing, medical diagnosis, fire power plants leak system can result the health hazards. Ammonia is harmful and toxic in nature, therefore all industries working for alaram system detecting and warning for dangerous ammonia concentration levels. Detection of low level as well high level ammonia concentration is not important but also monitoring is essential aspect and hence development of ammonia sensor is need. Efforts are made to discuss the ammonia detection in the present work and shall try to focus study on development of ammonia sensor at room temperature.

II. EXPERIMENTAL RESULTS

a. Substrate Cleaning

Glass substrates were ultrasonically cleaned with acetone and then deionized water for 20 minutes and stored in hot oven on of 60 degree temperature for few minutes so as to avoid moisture and unnecessary impurities and it is prepared for good adhesion [23].

b. Preparation of pure ZrO₂ thick films

The thick film paste was formulated by mixing thourahphally pure ZrO₂ powder (AR grad99.9% pure) with low melting point Organic vehicles ethyl cellulose (temporary binder) with solvents butyl cellulose,, carbitol ethanol, butyl carbitol acetate and alpha terpineol etc. in proper weight proportion and maintained inorganic to organic compound ratio in the proportion of 75:25 percentage to achieved desired viscosity and rheology This thixotropic paste was kept in bowel for few minutes to good settlement. Then thick films were screen printed on glass substrate in desired pattern. Thickness was maintained by squeeze strokes and optimized rheology of paste. The films then kept in IR light source for drying and fired at 550⁰C to burn organic binder and grain growth and to reduce porosity for good sensing ability [24-25].

c. Thicknesss measurement

The thicknesses of the films were observed to be in the range from 50 to 55μm by gravimetric weight-loss method using formula

$$t = \frac{m}{A \sigma} \quad (1)$$

Where t is thickness of the film, A is film surface area, σ is average density if zirconia, m is weight loss after and before deposition.

III. CHARACTERIZATION

a. Structural and Morphological Analysis of ZrO₂ Particles

Figure 1 shows the XRD Pattern of Pure ZrO₂ Powder within the range of 20 to 80° X-ray diffractogram of the material was confirmed the polycrystalline structures of the ZrO₂. It is determined by 2θ values and hkl planes corresponding to monoclinic at 35.2° (200), 63.08° (222) and tetragonal at 30.2° (111), 50.4° (220), 60.2° (311), 74.7° (400).The strongest peaks for the tetragonal phase was observed. Inspection of X-ray pattern shows that no cubical

phases transformation. The observed peaks in the XRD pattern are matching with the standard recorded data (JCPDS 36-020) and (JCPDS 17-0923) [26].

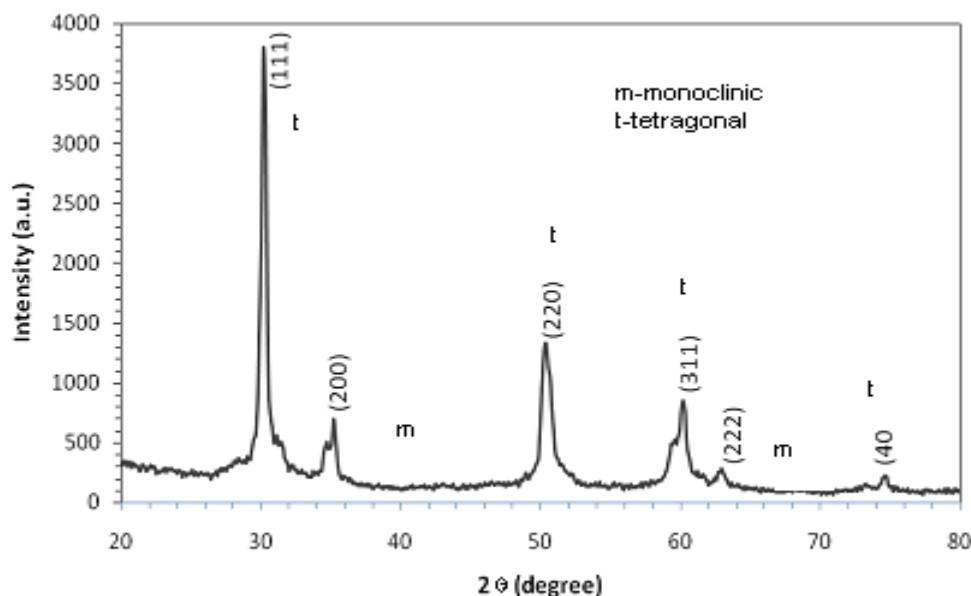


Figure 1. X-ray diffraction Pattern of ZrO_2 Pattern

The average particle grain size of ZrO_2 powder was determined using Debye-Scherrer's formula and was estimated to be 71 nm.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

Where λ - wavelength of X-Ray Cu K_α radiation in $\text{\AA}$ ($1.542\text{\AA}$) and β is the peak Full width of half maxima in radian. [27-28]

Table 1. The X-ray diffraction data results of the crystalline nature of the ZrO_2 thick film

hkl	2θ	d (Å)	I	I _o	I/I _o	TC(hkl)
111	30.2	2.95969	3541	100	354.1	4.367225
200	35.2	2.5987	690	25	27.6	0.3404
220	50.4	2.54878	1321	35	37.748571	0.46549
311	60.2	1.802286	853	45	18.9555	0.233785
222	63.08	1.5372	265	12	22.0833	0.2723609
400	74.7	1.2708	209	8	26.125	0.04471457

Determination of the a and c lattice constants were carried out from X-ray diffraction pattern using following formula, it would be calculated as a= 5.89 (nm) and c= 5.19 (nm).

$$\frac{1}{d^2} = \frac{4}{3} \left[\frac{h^2 + h^2 k + k^2}{a^2} \right] + \frac{l^2}{c^2} \quad (3)$$

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \quad (4)$$

where (hkl) are Miller indices ,d is interplaner spacing which can be calculated by using well known Bragg's formula

$$n\lambda = 2d\sin\theta \quad (5)$$

The texture coefficient (TC) represents the texture of the particular plane, deviation of which from unity implies the preferred growth , quantitative information concerning the preferred crystallite orientation was obtained from the different texture coefficient TC(hkl) defined as

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1} \sum_n I(hkl)/I_o(hkl)} \quad (6)$$

where $I(hkl)$ is the measured relative intensity of a plane (hkl), $I_o(hkl)$ is the standard intensity of the (hkl) plane taken from JCPDS data, N is the reflection number and n is the number of diffraction peaks. A sample with randomly oriented crystallite represents $TC(hkl)=1$ while the larger this value signifies crystalline nature , the larger abundance of crystallites oriented at the (hkl) direction. The calculated texture coefficient are presented in table.1,from the values calculated , it was observed that t.c. approaches less than unity for randomly distributed samples where as tc is larger than unity for a preferentially oriented (hkl) plane. The lower values of Tc reveals that the films have poor crystallinity. It was monoclinic- tetra crystallite phase is close. [29-30]

Examination of X-ray diffraction predicts the results that the strongest peaks for the tetragonal phase 30.5° for (111) and The volume fraction of the monoclinic phase, V_m , was estimated according to the equation

$$V_m = \frac{1.311 X_m}{1 + 0.311 X_m} \quad (7)$$

Where X_m is the integrated intensity ratio defined as

$$X_m = \frac{I_{pm(111)} + I_{pm(111)}}{I_{pm(111)} + I_{pm(111)} + I_{pt(111)}} \quad (8)$$

But in the present case only strongest peak observed for hkl plane (111) is tetragonal phase.

b. Surface Morphology of the Films

SEM image was observed by model JEOL-JSM 6360(LA), JAPAN coupled with EDAX. fig.2 depicts the SEM images unmodified (pure ZrO_2), From the surface morphology observation of images it is seen that an unmodified film consists of larger grains distributed, grains may reside in the intergranular regions of ZrO_2 thick film. Effective sensing surface area was expected to be increased. Average grain size of the ZrO_2 particle is observed to be 71.9 nm and matched with calculated value having uniform appearance on the film. For gas sensors, where surface reactions produce the change in electrical conduction, two factors are important: the particle (grain) size and the surface reactivity. It is evident that powders, produced by the mechanochemical preparation, contain agglomerations, to a greater or lesser degree. A micrograph of the scanning electron microscopy shows clearly several agglomerated particles of ZrO_2 film. The SEM images reveal an increase of particle size with good grain growth annealing and fired temperature dependent. The film was non-stoichiometry behavior and oxygen deficient and it is good for gas sensing.

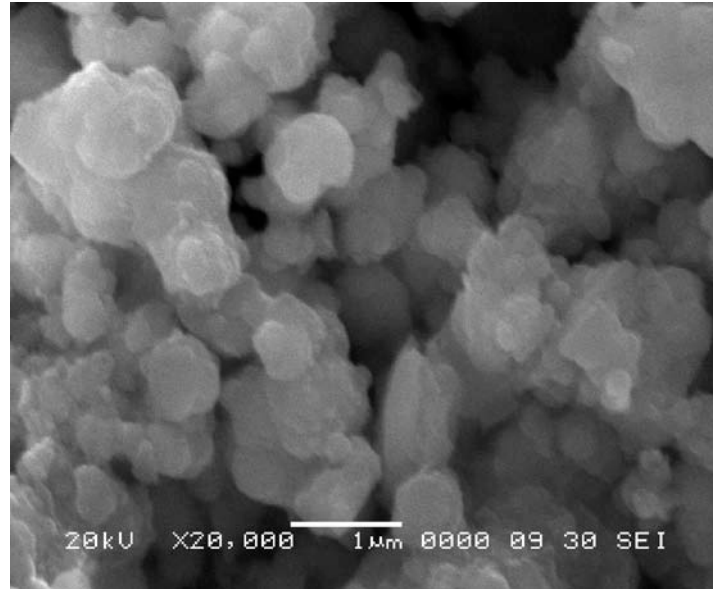


Figure 2. SEM image of Pure ZrO_2 thick film resistors

The film surface is having porous and bulk behavior and it was observed oxygen deficient and it is good for gas sensing.

IV ELECTRICAL PROPERTIES

a. I-V Characteristics

Figure 3 depicts the I-V characteristics of ZrO_2 thick film, the symmetrical nature of the I-V characteristics for samples shows that the contact is ohmic in nature. Current is function of voltage and it is temperature dependent as well as nature of gas and its concentration [31].

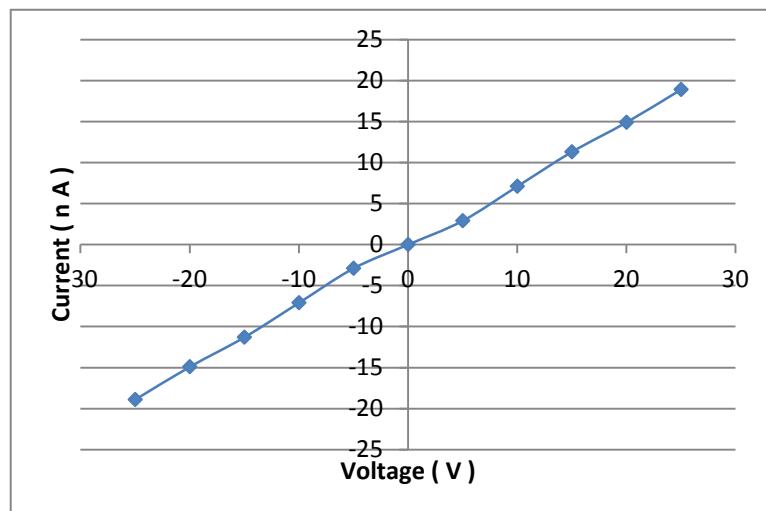


Figure 3. I-V Characteristics of ZrO_2 film

b. Electrical conductivity

The semiconducting nature of ZrO_2 film is observed from the measurements of conductivity with operating temperature. The semi-conductivity in ZrO_2 film must be due to large oxygen deficiency in it. The material would then adsorb the oxygen species at higher temperatures ($\text{O}_2^- \rightarrow 2\text{O}^- \rightarrow \text{O}^{2-}$). It is clear from figure 4 that the of conductivity of the film increases with an increase in operating temperature, indicating a negative temperature coefficient resistance. The temperature coefficient of the film is determined using following formula.

$$\alpha = \frac{R_t - R(\text{room temp})}{R_{\text{room t}} * (t - \text{room temp})} \quad (9)$$

Where R_t is resistance at working temperature, R_{rt} is resistance at room temperature and $(t - \text{rt})$ is temperature difference assumed to be 100°C . The temperature coefficient observed negative and varied between 368 to 670 ppm/ $^\circ\text{C}$.

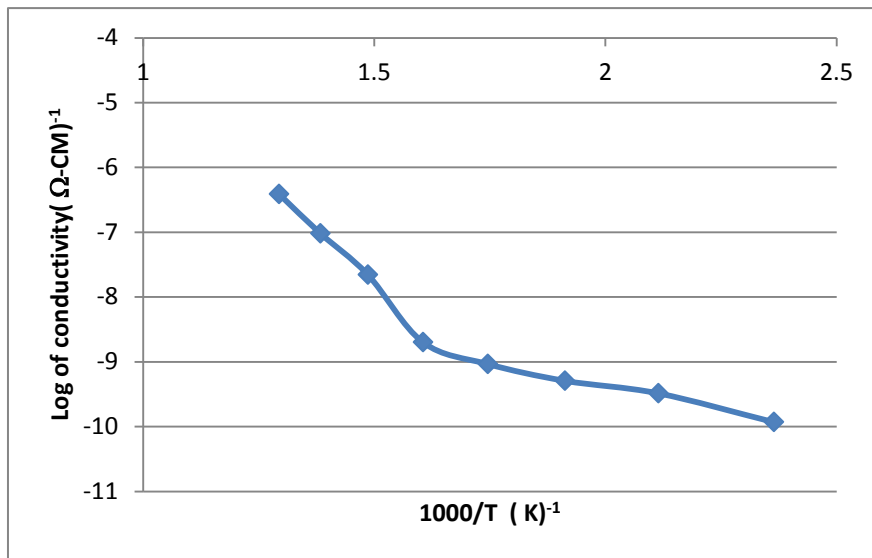


Figure 4. Conductivity graph of ZrO_2 thick film at ambient air.

IV. OPTICAL PROPERTIES

Optical absorption spectra shows the absorbance of the film decreases gradually with increase in wavelength. This is because in the thicker films more atoms are present in the film so more states will be available for the photons to be absorbed.

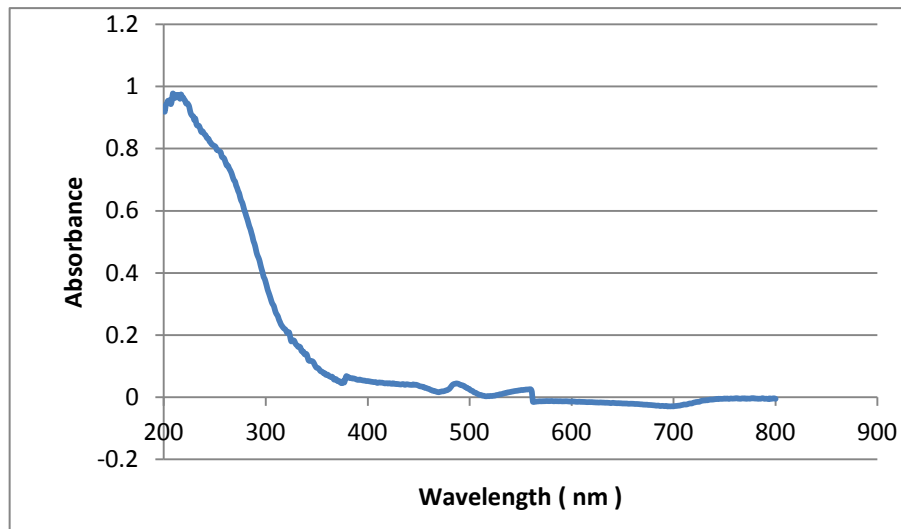


Figure 5. Variation of absorption with wavelength (nm)

The absorption coefficient (α) is calculated using Lambert's Law ,

$$\alpha = \left[\frac{2.303 A}{t} \right] \quad (10)$$

where A is absorption, t is the thickness of the film, neglecting the reflection coefficient which is negligible and insignificant near absorption edge. The absorption coefficient (α) calculated is found to be in the order of 10^5 cm^{-1} . The high α value ($> 10^4$) confirms the existence of direct bandgap value. [Tarcame, et.al.2004]. According to Tauc [Tauc,1974] it is possible to separate three distinct regions in the absorption edge spectrum of amorphous semiconductors. The first is the weak absorption from defects and impurities, the second is the exponential edge region which is strongly related to the structural randomness of the system and third is the high absorption region that determines the optical band gap.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (11)$$

Where $h\nu$ is photon energy and n is a constant. The value of n is $\frac{1}{2}$ or 2 depending on presence of the allowed direct and indirect transisition. The nature of the plot suggests direct interband transition. The optical band gap E_g was calculated using Tauc's plot $(\alpha h\nu)^2$ verses $h\nu$. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g , which is determined by extrapolation of the linear portion of the curve. The typical plots of the $(\alpha h\nu)^2$ verses $h\nu$ for undoped (pure) zirconia substrate. It is observed that band gap is 4.2 eV [32-36].

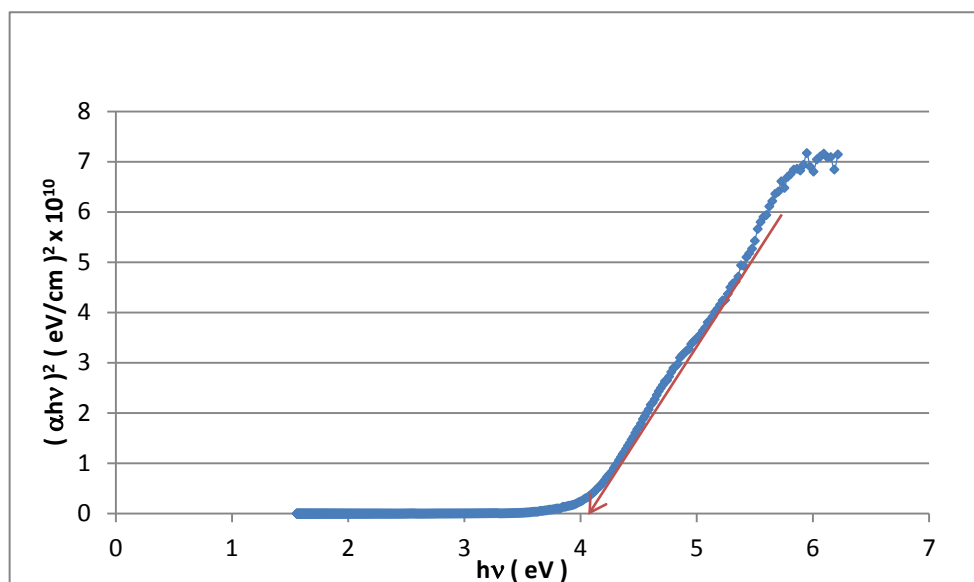


Figure 6. Plot of $(\alpha h\nu)^2$ Vs photon energy $(h\nu)$

V. GAS SENSING PERFORMANCE

a. Gas sensing performance

The sensing performance of the films was examined using a 'static gas sensing system'. In this system, the sensor element is mounted in an enclosed test chamber of a known volume. In order to measure the sensor resistance in a desired concentration of the analytic gas, a known amount of gas is injected into the housing using micro-syringe. There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with electronic circuit with adjustable ON-OFF timer intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was used to digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. A constant voltage was applied to the thick film sensor, and the current was measured by a digital pico-ammeter.

Gas sensing performance is based on the principle of change in conductance by exposure of the tested target gas. It should be calculated measuring current after exposure of gas and before exposure of gas in ambient air using the following formula.

$$S = \frac{I_{\text{gas}} - I_{\text{air}}}{I_{\text{air}}} \quad (12)$$

Where I_{gas} is current when target gas has to be injected and I_{air} current measured after ambient air has to be passed at different operating temperature .It was observed that current increases for reducing gas and decreases for oxidizing gas. The conductivity depends on intragranular bulk and geometrical effects. The voltage dependence of the current is ohmic if the voltage drop is less than KT/q at each intragranular (grain boundary) contact [37-38].

b. Sensing Characteristics of Pure ZrO_2 film

From the figure 7 shows the variation of gas response of the pure ZrO_2 films (fired at 550°C) to various gases (100 ppm) with Operating temperature ranging from 150 to 450°C . For NH_3 , the response goes on increasing with operating temperature, attains its maximum (7.17) at 300°C and further decreases with increase in operating temperature. From figure8, It is clear that the sensor gives response to NH_3 (at 250°C , 300°C 350°C) against the other tested gases. It shown maximum response at 300°C operating temperature and it is increases with increase in gas concentration and concentration depends on the deviations of the composition from the non-stoichiometry caused by oxygen vacancies, also oxygen species changes with temperatures , which are predominant atomic defects. Also the electrical properties of ZrO_2 depends on the surface of states produced by chemisorptions of oxygen and other gaseous molecules, resulting in space charge and electron barriers. NH_3 is reducing gas that interact with chemisorbed oxygen species(O_2^- , O^- , O^{2-}) leading to increase of the electron concentration in the conduction band. Depending on the temperature range, there are different adsorbed oxygen species that all affect the surface charge layer of ZrO_2 .

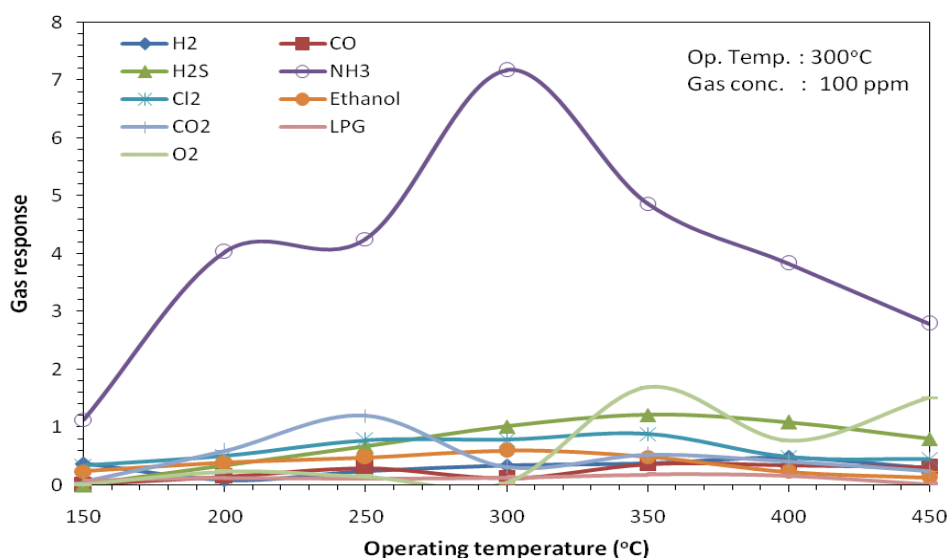


Figure 7(a). Gas response to different gases at different operating temperature

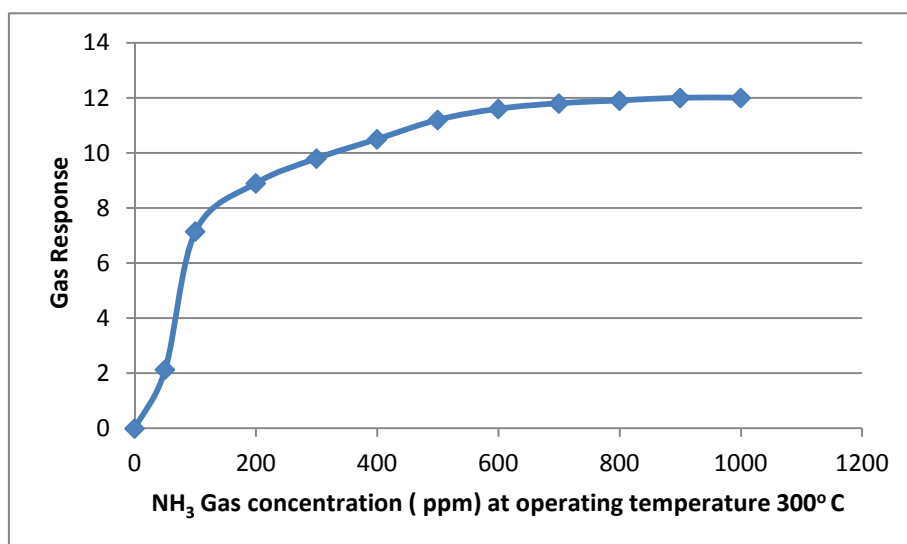


Figure 7 (b) Variation of gas response according to concentration at optimal operating temperature

As we know, The gas sensing ability depends on oxygen species, non-stoichiometric behavior, temperature, nature of gas, also gas concentration. But chemisorptions and physisorption is responsible for gas sensing, it dependent surface morphology as well as grain growth, agglomeration of particles and moderate porosity and increase in surface to volume ratio. Gas concentration and surface chemical reaction is co-related, furthermore at higher concentration, cation-anion chemical species are more due to this saturation rapid increase or decrease in current being constant resulting gas response being gradually slow even though for higher concentration. Also desorption take place at higher temperature.

c. Selectivity

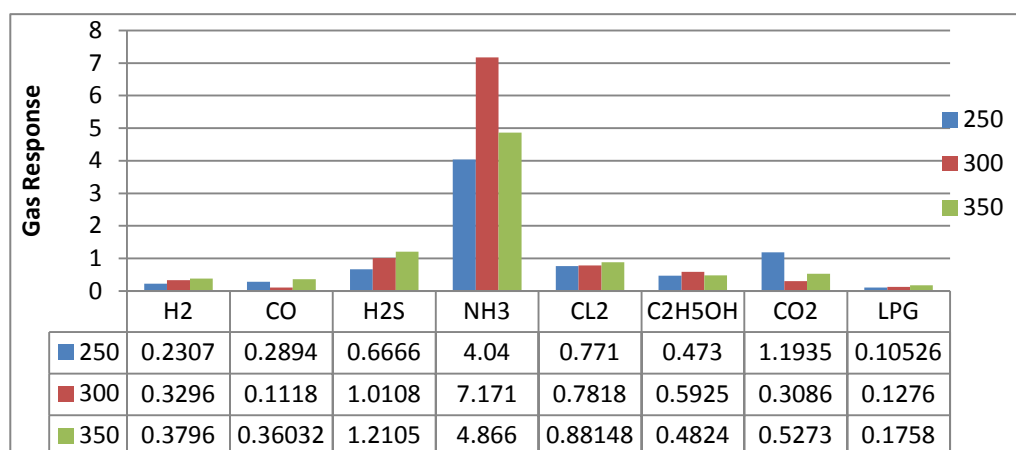
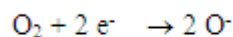


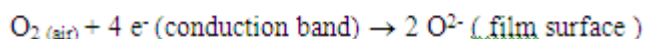
Figure 8. Selectivity of NH₃ among various target gases at operating temperature

Selectivity is defined as the ability of a sensor to respond to a certain gas in the presence of more gases and Fig.8 shows the selectivity of respond gas and shows highest sensitivity to pure ZrO₂ film for NH₃gas (measured at 100 ppm) at 300⁰C operating temperature against all other tested gases: H₂, H₂S, Cl₂,C₂H₅OH, CO₂, LPG,CO etc.[20-29]] In the presence of NH₃ gas the conductivity is strongly dependent on the surface concentration of NH₄⁺ adsorbed on Bronsted acid sites. The surface adsorbed NH₄⁺ play a role of charge carrier and thus results in an increase of electric conductivity. The variation of sensor response of ZrO₂ thick film with NH₃ concentration is shown in Fig.8. It shows that rate of sensing response increases with gas concentration and it observed maximum (7.1) for 100 ppm at 300 ⁰C operating temperature. upon exposure to NH₃ a noticeable decrease in the hydroxyl bands of these sensors has been observed which may due to the surface reaction of NH₃ with physisorbed H₂O. Further, the negligible quantity of the surface reaction product and its high volatility indirectly indicates the observed fast response of these sensors to NH₃ and quick recovery to normal condition.

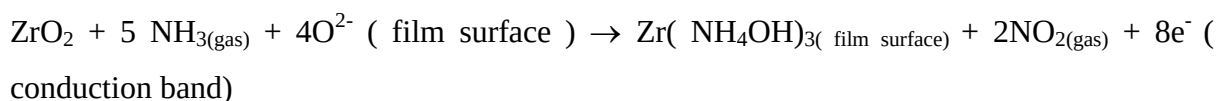
The overall Chemical reactions assumed in this gas sensing represented by



At higher temperature electrons capture from conduction band as



Gas sensing mechanism is generally explained in terms of conductance either by adsoption of atmospheric oxygen on the surface and/ or by direct reaction of lattice oxygen or interstitial oxygen with target gas. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from conduction band, in the form of superoxides or peroxides, which is mainly responsible for the detection of test target gases. At higher temperature, it captures the electron from conduction band and it would result in decreasing conductivity of the film, when ammonia reacts with the surface of the film and adsorbed oxygen on the surface of the film ,it get oxidized ammonium hydroxide, liberating free electrons in the conduction band.. The following reaction take place



This shows n-type conduction mechanism ,thus generated electron contribute to sudden increase in conductance of the thick film[39-43]

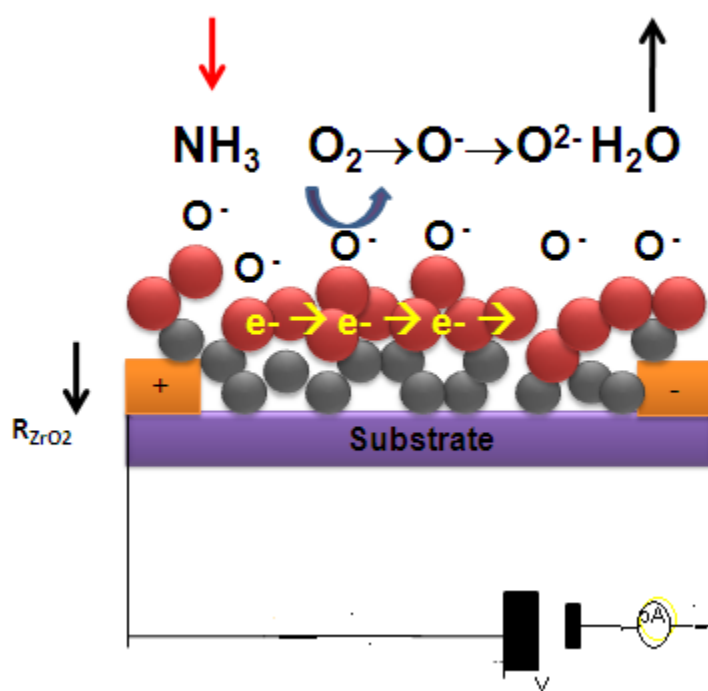


Figure 9. Representation of oxygen spices adsorption on film surface

d. Response and Recovery Time

Response time (RST) is defined as the time required for a sensor to attain the 90% of the maximum increase in conductance after the exposure of test gas on the film surface, while recovery time (RCT) is defined as the time taken to get back 90% of the maximum conductance in air. The quick response time (4s) was observed for ammonia to pure ZrO_2 thick film while fast recovery time (8 s) was recorded at 300°C .

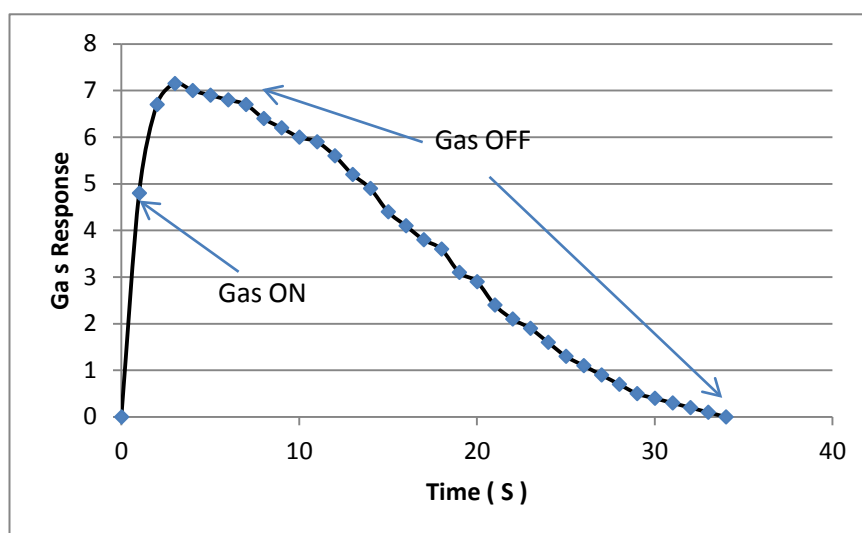


Figure 10. Gas response and recovery time in second

VI. CONCLUSION

In this paper Structural, electrical, optical and gas sensing properties of ZrO_2 thick film were studied. ZrO_2 thick film shown response to ammonia gas at optimal temperature 300°C . The film was resistive and gas sensing depends on film geometry, surface morphology, grain size and growth. For reducing type gas resistance decreases and film showed negative temperature coefficient. Texture coefficient calculation predicts crystalline nature and optical band gap was found to be 4.2 eV. quick response and fast recovery time was recorded. It was observed 4 s and 30 s. Small size, low consumption, inexpensive, easy construction, no wastage, good surface area are advantages of the sensor.

REFERENCES

- [1] M. Kleitz, E. Siebert, P. Fabry, J. Fouletier, "Solid state electrochemical sensors, in Sensors a comprehensive survey," Eds. W. Gopel, J. Hesse, J. N. Zemel, VCH New York, Vol. 2, pp. 341-428, 1991.
- [2] D. N. Chavan, V. B. Gaikwad, D. D. Kajale, Ganesh E. Patil, G. H. Jain, "Nano Ag-doped In_2O_3 thick film: A low temperature H_2S gas sensor", Journal of Sensors, Vol. 2011, Article ID 824215, 8 pages doi:10.1155/2011/824215.
- [3] J. E. Sundeen, R. C. Buchanan, Electrical properties of nickel-Zirconia cermets films for temperature and flow sensors application, Sensors and Actuators A, Vol. 63, No. 1, 1997, pp. 33-40.
- [4] G. E. Patil, D. D. Kajale, P. T. Ahire, D. N. Chavan, N. K. Pawar, S. D. Shinde, V. B. Gaikwad and G. H. Jain, "Synthesis, characterization and gas sensing performance of SnO_2 thin films prepared by spray pyrolysis", Bulletin of Material Science. Vol. 34, No. 1, February 2011, pp. 1-9.
- [5] C. S. Barret, T. B. Massalski, Structure of metals, Pergamon Press, Oxford, 1980.
- [6] Francismenil, Helene Debeda, Claude lucat, Screen printed thickfilms: from functional material to functional devices, Journal of the European Ceramic Society, 25 (2005) 2105-2113.
- [7] Ganesh E. Patil, D. D. Kajale, V. B. Gaikwad, N. K. Pawar and G. H. Jain, "Properties and Gas Sensing Mechanism Study of CTO Thin Films as Ethanol Sensor", Sensors & Transducers Journal, Vol. 137, Issue 2, February 2012, pp. 47-58.

- [8] Pavel Shuk, Ed Bailey, Ulrich Guth, "Zirconia Oxygen Sensor for the Process Application", State-of-the Art, Sensors and Transducers, Vol. 90, Special issue, April 2008, pp. 174-184.
- [9] J. Riegel, H. Neumann, H. M. Wiedenmann, "Exhaust gas sensors for automotive emission control", Solid state Ionics, Vol. 152 -153, 2002, pp. 783-800.
- [10] S. Meriani, Advances in Zirconia Science and Technology (Elsevier, New York,1989).
- [11] Zirconia Engineering ceramics , edited by E. H. Kisi (Trans.Tech,Uticon-zurich,1998).
- [12] M. E. Manriquez, T. Lopez, R. Gomez, "Preparation of $\text{TiO}_2\text{-ZrO}_2$ mixed oxides with controlled acid-base properties", J. Molecular Catalysis A: Chemical, Vol. 220, 2004, pp.229-237.
- [13] Sung Ho Lee and Tae Yung Song, "Kinetics of gas phase oxygen control system and oxygen concentration measurement in liquid Pb and LBE", J. Ind. Eng. Chem., Vol. 13, No. 4, 2007, pp. 602-607.
- [14] P. T. Mosely, Material selection for semiconductor gas sensors, Sens. and Actuators B, 1992, pp. 149-156.
- [15] P. Peshev, Stambolova, S. Vassilev, P. Stefanov, V. Blaskov, K. Starbova, N. Starbov, "Spray pyrolysis deposition of nanostructured zirconia thin films", Material Science and Engineering B, Vol. 97, 2003, pp. 106 -110.
- [16] K. T. Jacob and Tom Mathews, "Solid state electrochemical sensors in process control", Indian Journal of Technology, Vol. 28, pp. 413-427, 1990.
- [17] N. Yamazoe, "Toward innovations of gas sensors technology", Sensors and Actuators, Vol. 108, 2005pp. 2-14.
- [18] G. Reyna Garacia, M. Garacia - Hipolito, J. Guzman - Mendoza, M.Aguilar - Frutis, C. Falcony, "Electrical, optical and structural characterization of high - k dielectric ZrO_2 thin films deposited by the pyrosol technique", Journal of Material Science: Materials in Electronics 15, pp. 439-446, 2004
- [19] N. Yamazoe, Y. Kurokawa, T. Seiyama, "Effect of additives on semiconductor gas sensors', Sens and Actuators B, Vol. 8, 1983, p.283
- [20] O. K. Tan, W. Cao, W. Zhu, J. W. Chai, J. S. Pan, Ethanol Sensors based on nanosized $\alpha\text{-Fe}_2\text{O}_3$, with SnO_2 , ZrO_2 , TiO_2 Solid solution, Sensors and Actuators B, Vol. 93, 2003, pp. 396-401.
- [21] P. T. Mosely, New trends and future prospects of thick and thin film gas sensors, Sensors and Actuators B, Vol. 3, 1991, pp.162.

- [22] D. H. Aguilar, L. C. Torres-Gonzalez, and L. M. Torres-Martines, Study of the crystallization of ZrO_2 in sol-Gel system: ZrO_2-SiO_2 , Journal Solid Chemistry, Vol. 5, pp. 349-57, 2000.
- [23] JCPDS Data Card(17-0923).
- [24] T. G. Nenov, S. P. Yordanov, Ceramic sensors, technology and application, Technomic Publication, Lancasten, Vol. 1, 1996, pp. 137-138.
- [25] Ali H. Ataiwi, Alaa A. Abdul - Hamead, "Study some of the structure properties of ZrO_2 ceramic coats prepared by spray pyrolysis method", Eng. and Tech. Journal, Vol. 27, No. 16, pp. 2918-2930, 2009.
- [26] S. Takada, Relation between optical property and crystallinity of ZrO_2 thick films prepared by R.F. Magnetron sputtering, J. Applied Phy., Vol.73, No. 10, 1993, pp. 4739.
- [27] John V. Spirig, Ramasamy Ramamoorthy, Sheikh A. Akbar, Jules L. Routbort, Dileep Singh, Prabir K. Dutta, "High temperature Zirconia oxygen sensor with sealed metal/metal oxide internal reference", Sensors and Actuators B, Vol. 124, 2007, pp. 192-201.
- [28] G. H. Jain, V. B. Gaikwad, D. D. Kajale, R. M. Chaudhari, R. L. Patil, N. K. Pawar, M. K. Deore, S. D. Shinde and L. A. Patil, "Surface modified $BaTiO_3$ thick film resistors as H_2S gas," Sensors and Transducers, Vol. 90, Special issue, April 2008, pp. 160-173.
- [29] K. M. Garakar, B. S. Shirke, Y. B. Pati and D. R. Patil, "Nanostructured ZrO_2 thick film resistors as H_2 gas sensors operable at room temperature", Sensors and Transducers, Vol. 110, Issue 11, pp. 17-25, Nov..2009.
- [30] S. S. Sunu, E. Prabhu, V. Jayaraman, K. I. Gnanasekar, T. K. Seshagiri, T. Gnanasekaram, Electrical conductivity and gas sensing properties of MoO_3 , Sens. Actuators B, Vol. 101, 2004, pp.161-174.
- [31] C. P. Chen, T. K. Tesena, S. C. Tsai, C. K. Lin, H. M. Lin, Effect of precursor characteristics on zirconia and ceria particle morphology in spray pyrolysis, Ceramic International, Vol.3, 2006, pp.8.
- [32] V. A. Chaudhari, I. S. Mulla, K. Vijay Mohan, "Selective hydrogen sensing properties of surface functionalized Tin oxide", Sensors and Actuators, B, Vol. 55, pp. 154-160, 1999.
- [33] S. D. Shinde, G. E. Patil, D. D. Kajale, V. B. Gaikwad and G. H. Jain, "Synthesis of ZnO nanorods by spray pyrolysis for H_2S gas sensor", Journal of Alloys and Compounds, Vol. 528, 2012, pp. 109-114.

- [34] M. Caglao, T. Caglar, S. Ilican, The determination of the thicknesses and optical constants of the ZnO Crystalline thin film by using envelope method, *Journal of optoelectronics and advanced materials*, Vol. 8, No.4, August 2006 ,pp.1410-1413
- [35] S. D. Shinde, G. E. Patil, D. D. Kajale, V. B. Gaikwad and G. H. Jain, “Synthesis of ZnO nanorods for gas sensor applications”, *International Journal on Smart Sensing and Intelligent System*, Vol. 5, No. 1, March 2012, pp. 57-70.
- [36] Yan Wang, Yanmei Wang, Jian Liang Cao, Fanhong Kong, Baolin Zhu, Shuihua Wu, “Low temperature H₂S sensors based on Ag doped Fe₂O₃ snanoparticles”, *Sensors and Actuators, B*, Vol. 131, 2008, pp. 183-189
- [37] S. C. Gadkari, Manmeet Kaur, V. R. Katti, V. B. handarkar, K. P. Mutha and S. K. Gupta, “Solid State Sensors for toxic gases”, *Founders day special issue, BARC*, 2005, pp. 49-60,
- [38] G. Sberveglier, G. Groppelli, and P. Nelli,”Highly sensitive and selective Nox and NO₂ sensors based on Cd-Doped SnO₂ thin film, *Sens. Actuators B.*, Vol.4, pp.457-460, 1991.
- [39] X. Liu, Z. Xu, Y. Liu and Y. Sherr, A novel high performance ethanol gas sensors based on CdO.Fe₂O₃ semiconducting materials, *Sens. Actuators B*, Vol. 52, pp. 270-273, 1998.
- [40] J. A. Rodriguez, I. Jimenez, A. Cirera, J. Cerda, and J. R. Morante, Gas sensing properties of sprayed films of (CdO)_x(ZnO)_{1-x} mixed oxide, *IEEE sensors Journal*, Vol.5, No.1, Feb.2005.
- [41] Atsushi Satsuma, Ken-ichi Shimizu, Koichi Kashiwagi, Tadanori Endo, Tadashi Hattori, Horoyuki Nishiyama, Shiro Kakimoto, Satoshi Sugaya, Hitoshi Yokoi, “Structure and sensing Mechanism of Tungstated- Zirconia Thick Film Sensors for Urea-SCR”, *Proceedings of International Symposium on Eco Topia Science (ISET07)* 2007.
- [42] C. Xiang feng, L. Xingqin and M. Guangyao, Effects of CdO dopant on the gas sensitivity properties of ZnFe₂O₄ semiconductors, *Sens. Actuators B*, Vol. 65, 2000, pp. 64-67.