

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 ZrO₂ film

From the figure 7 shows the variation of gas response of the pure ZrO₂ films (fired at 550 °C) to various gases (100 ppm) with Operating temperature ranging from 150 to 450 °C. For NH₃, 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 NH₃ (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 ZrO₂ depends on the surface of states produced by chemisorptions of oxygen and other gaseous molecules, resulting in space charge and electron barriers. NH₃ 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 ZrO₂.

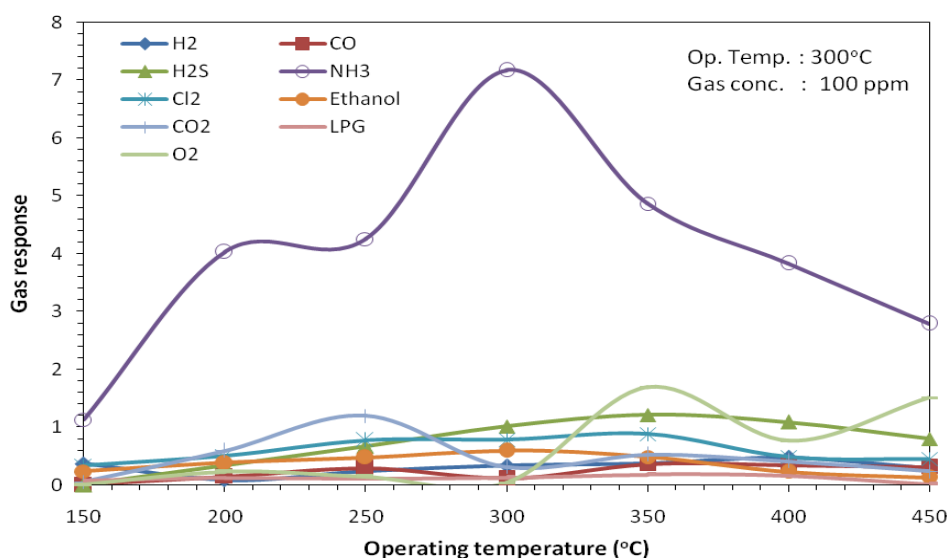


Figure 7(a). Gas response to different gases at different operating temperature

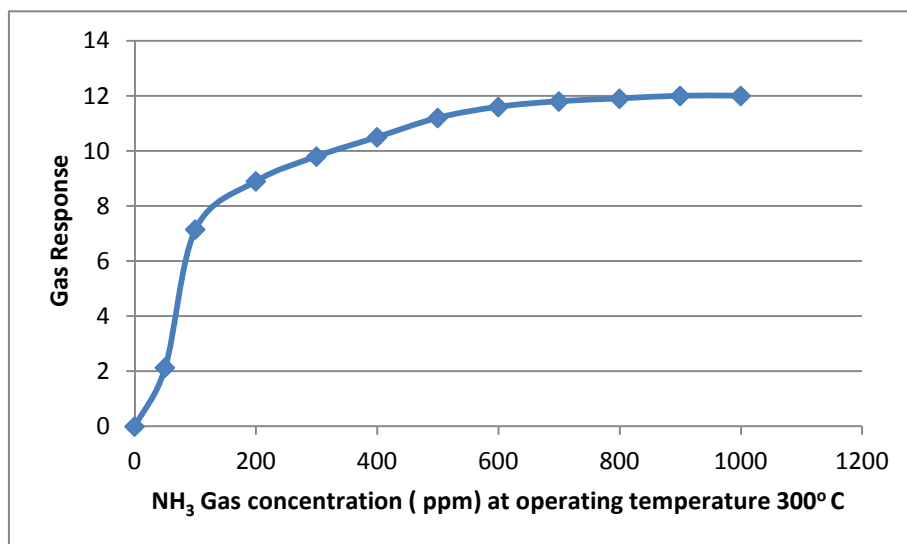


Figure 7 (b) Variation of gas response according to concentration at optimal operating temperature

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

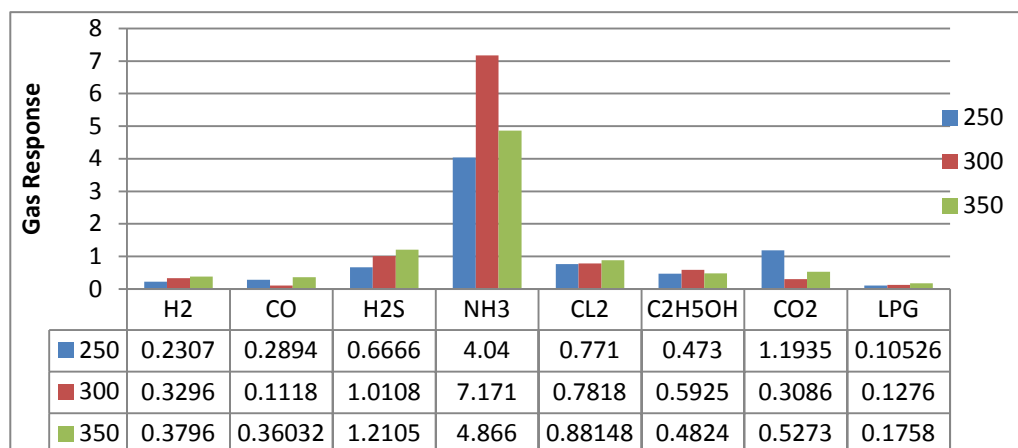
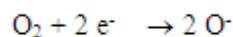


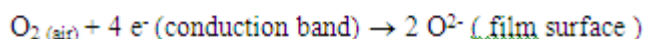
Figure 8. Selectivity of NH₃ among various target gases at operating temperature

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

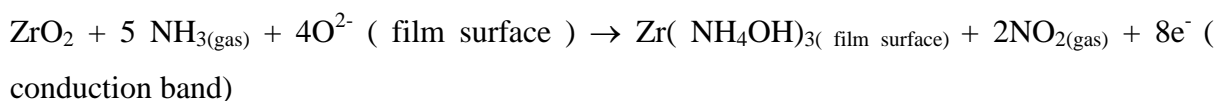


At higher temperature electrons capture from conduction band as



Gas sensing mechanism is generally explained in terms of conductance either by adsorption 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]

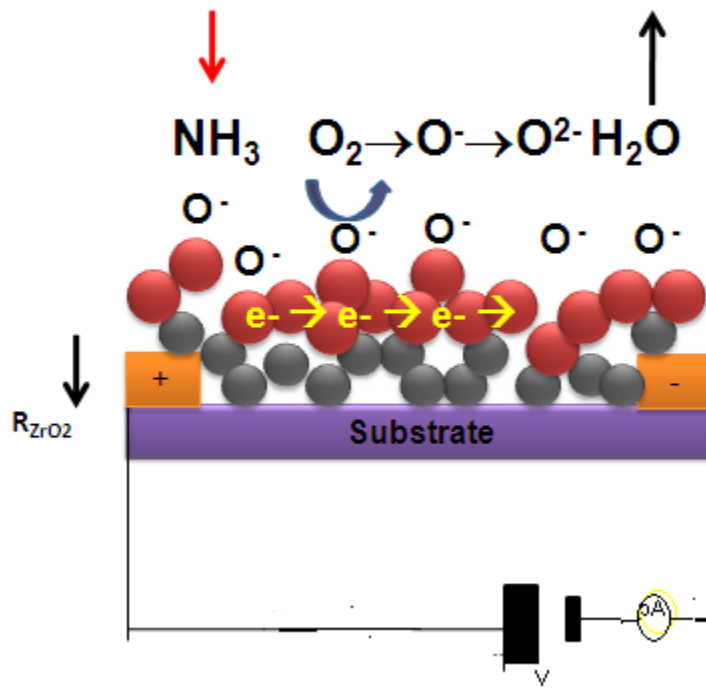


Figure 9. Representation of oxygen species adsorption on film surface

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 ZrO₂ thick film while fast recovery time(8 s) was recorded at 300⁰C

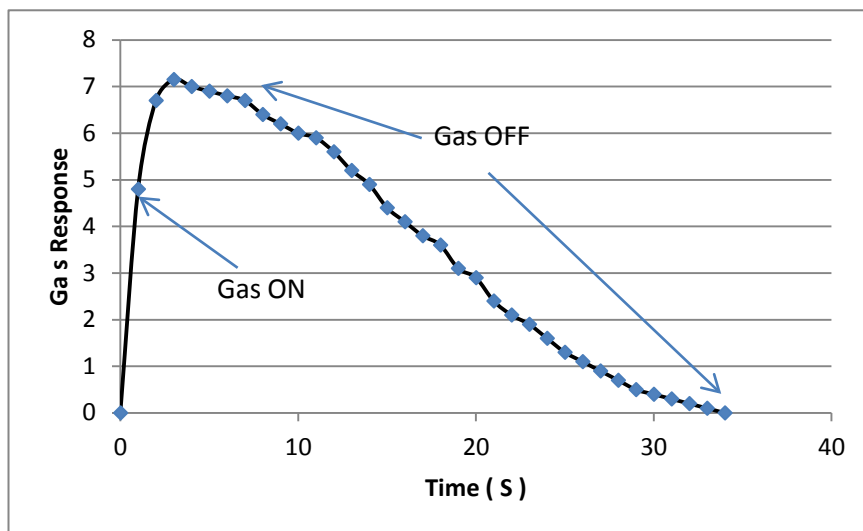


Figure 10. Gas response and recovery time in second

VI. CONCLUSION

In this paper Structural, electrical, optical and gas sensing properties of ZrO₂ thick film were studied. ZrO₂ 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 4.2eV. 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 In₂O₃ thick film: A low temperature H₂S 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 SnO₂ 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. Massalstki, Structure of metals, Pergamon Press, Oxford, 1980.
- [6] Francismenil, Helene Debeda, Claude lucat, Screen printed thickfilms: from functional material to functional devices, Jpurnal 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 TiO₂-ZrO₂ 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 ZrO₂ 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 α -Fe₂O₃, with SnO₂, ZrO₂, TiO₂ 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 sputerring, 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 Tranducers, 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 Tranducers, 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.