

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 figure 8, 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.

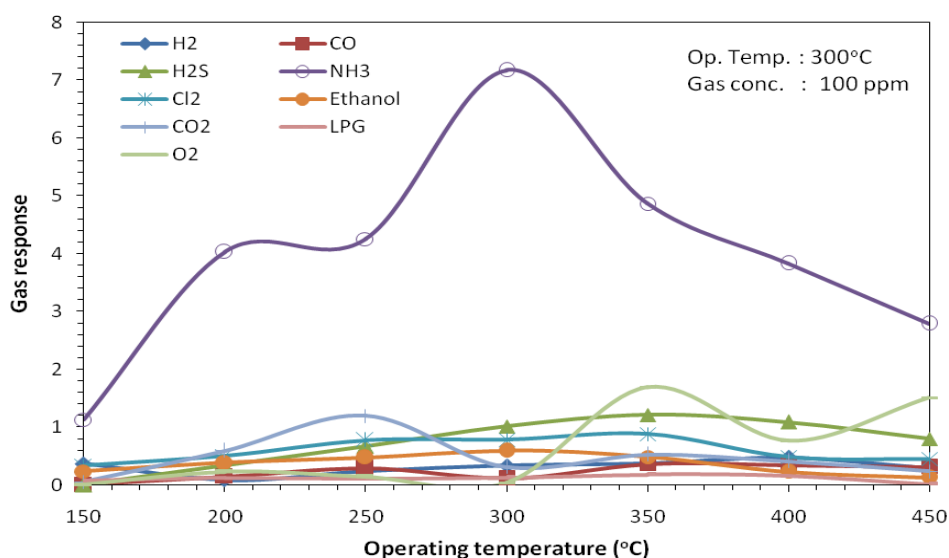


Figure 7(a). Gas response to different gases at different operating temperature

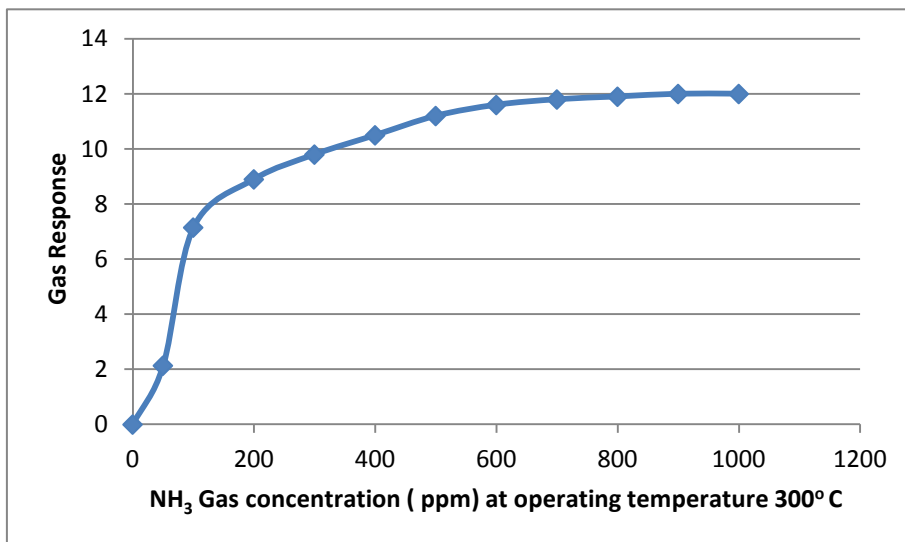


Figure 7 (b) Variation of gas response according to concentration at optimal operating temperature

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

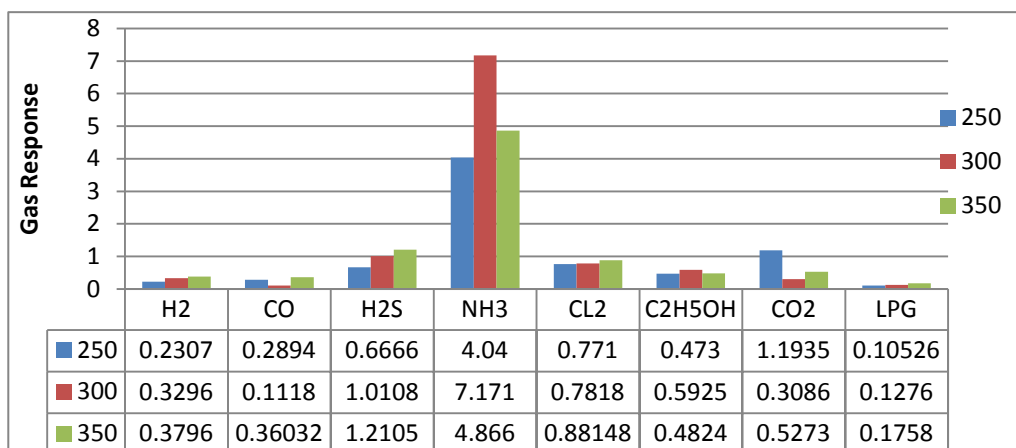
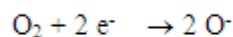


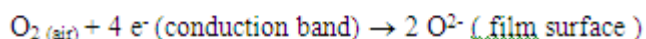
Figure 8. Selectivity of NH₃ among various target gases at operating temperature

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

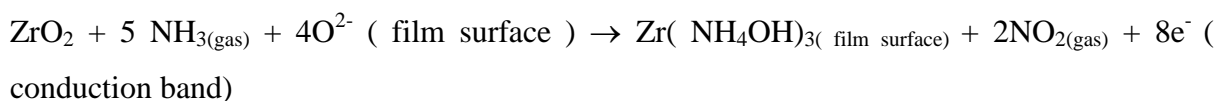


At higher temperature electrons capture from conduction band as



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]

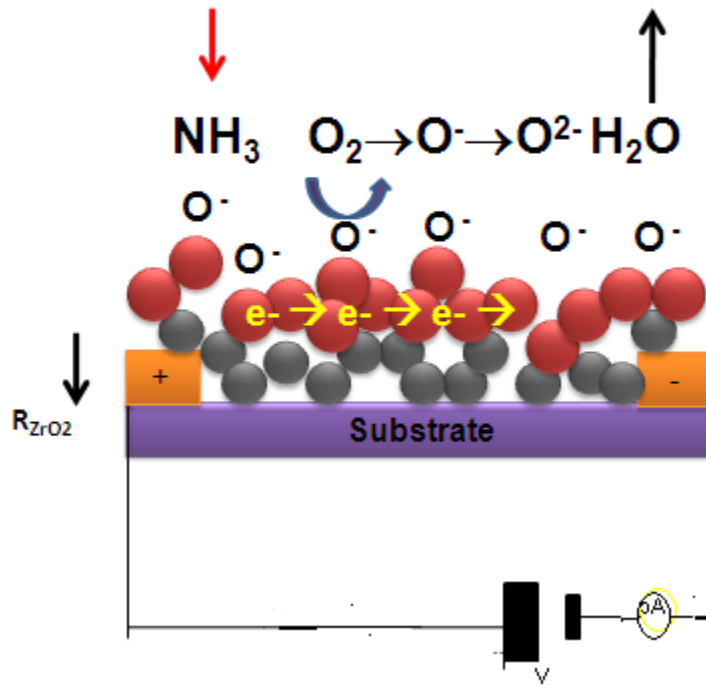


Figure 9. Representation of oxygen species adsorption on film surface

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

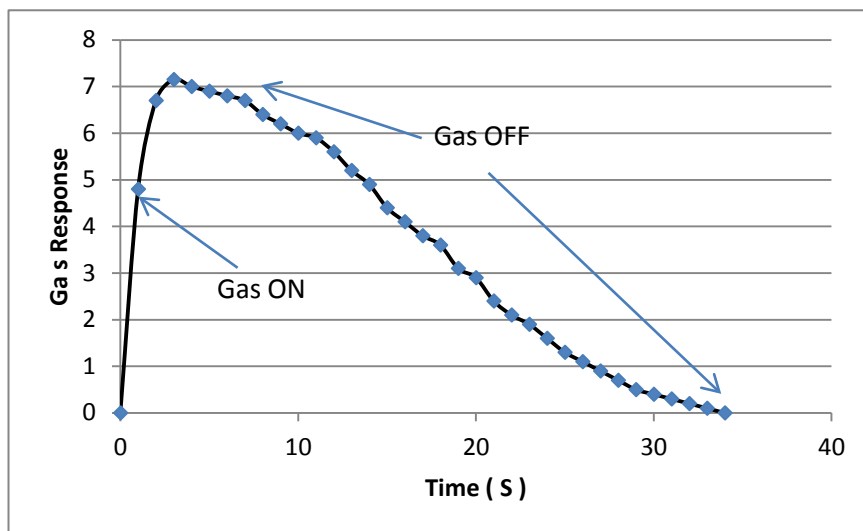


Figure 10. Gas response and recovery time in second

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.

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