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Comparative studies and gas sensing performance of bulk ZrO_2 thick and nanostructured ZrO_2 thin films

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Abstract:

Zirconium dioxide was prepared using Zirconyl (IV) Chloride octohydrate ($ZrOCl_2.8H_2O$) and was calcinated at various temperatures. As prepared powder was used to formulate thixotrophic paste. The paste screen printed on glass substrate as ZrO_2 thick films and was fired at temperatures 550 ^{0}c. The same precursor of Zirconium oxychloride octohydrate of 0.05M aqueous solution was spray pyrolyzed on glass substrate as thin films. Thick films observed as bulk nature while thin films observed nanostructured. Both films were examined using different analytical treatment includes XRD, SEM, FESEM, EDAX analysis. Gas sensing performances of various gases were tested at various operating temperature. Maximum response was observed for ammonia. Ammonia response for thick film was 7.1 at 300 ^{o}C while 58.8 at 150 ^{o}C temperature for thin film. Responses for other gases were discussed. Comparative studies in all aspects were presented in this paper.

Keywords: *ZrO_2thick films, thin films, response.*

1. Introduction

Sensors in the form of thick and thin films are very attractive and have been widely used in gas sensing application [1]. The main advantages of thick and thin film sensors are simple construction, small size, good sensitivity, selectivity, quick response and fast recovery time, low operating temperature, high stability, good accuracy, easy processing, reproducibility, low Cost and low consumption. It is flexible and versatile technology wherein resistors and capacitors of various values, combinations can be fabricated with basic thick film functional materials with desired pattern on substrates [2-4].

In the present work, we have studied the preparation, characterization and gas sensing performance of pure ZrO_2 thick and thin films. Thick films and thin films were deposited using screen printing and spray pyrolysis techniques respectively. Comparative aspect was observed that the thick films deposited found to be bulk in nature and thin films deposited found to be nanostructured in nature. Both techniques have advantages and disadvantages, the similar advantages are low cost, simple and easily operate with large scale for uniform deposition. In between two technique, thin film technique superior than thick film technique because of formation of nanocrystalline structure, therefore it have high surface to volume ratio and high sensing surface area [5-8]. The other comparative points observed with respective to crystallite

size, grain size, particle size parameters were measured using different analytical technique (XRD, SEM/FESEM and TEM) and gas sensing performance with response and recovery time were discussed.

2. Preparation of ZrO_2 Powder

Zirconium dioxide was prepared by dissolving 25gm of Zirconyl (IV) Chloride octohydrate ($ZrOCl_2.8H_2O$) [Sigma-Aldrich] in 200ml deionized water. The solution was stirred at 98 ^oC for 2 h into which drop wise aqueous ammonia solution was added until a pH value of 9.3achieved after with subsequent filtration and washing to obtain $Zr(OH)_4$. This compound was dried at 100 ^oC for 24 h, heated at 1^0C/min up to 600 ^oC and calcinated for 3 h to produce ZrO_2 and it was dried, grinded for formation of small grains and calcinated at 800 ^oC , 900 ^oC and 1000 ^oC in muffle furnace for few hours.[9,10]

$$Zr(OH)_4 \xrightarrow{600^oC} ZrO_2 + 2H_2O\uparrow \text{----------(1)}$$

2.1 Preparation of thick films

2.1.1 Formulation of screen printing paste

The thixostropic pastes were formulated by mixing lab prepared zirconium oxide powder which was calcinated at 1000 ^oC with the ethyl cellulose (temporary binder) in mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineool. The ratio of inorganic to organic proportion was kept at 75:25 in formulating the paste. This thixotropic paste was kept in bowel for few minutes to good settlement.

2.2 Preparation of ZrO_2 thin films

2.2.1 Deposition of nanostructured ZrO_2 thin films

As prepared precursor solution of $ZrOCl_2.8H_2O$ (0.05M) was sprayed, through a glass nozzle of 0.1mm bore diameter on hot glass substrate at temperature 350 $^oC \pm 5$ ^oC at spray rate 5ml/min for different spray time 30min.The horizaonatal movement was kept uniform and compressor air pressure controlled between 3 to 8 kg/cm^2, this had been done to optimized viscosity and surface tesion and momentum of the droplet. Also substrate to nozzle distance played better role. It was kept 28cm.

3. Characterization

3.1 Structural analysis: X-ray diffraction

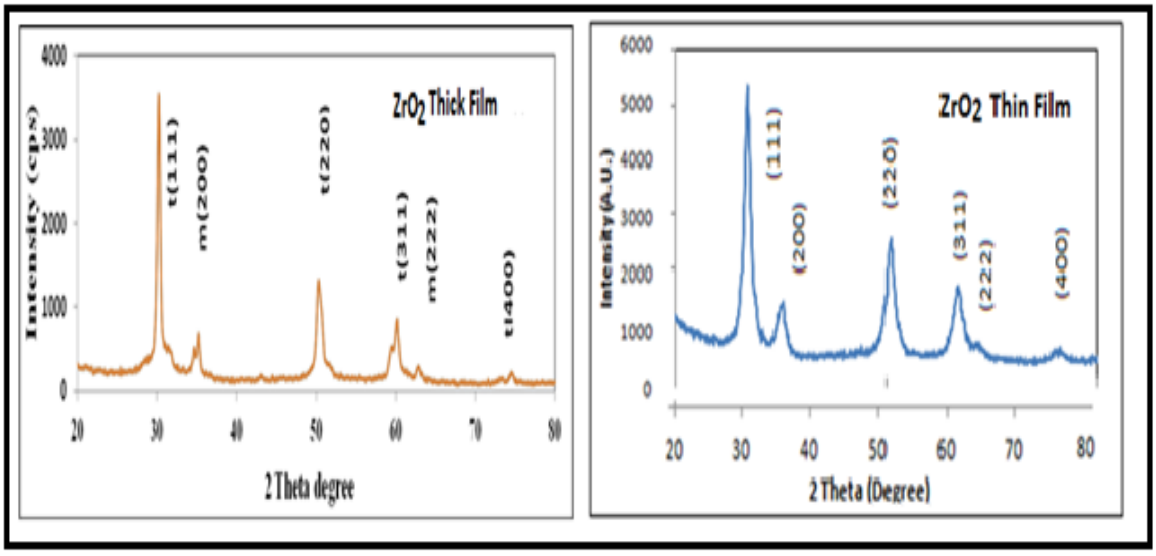

Figure 1 (a):XRD of ZrO_2 for Thick Films (b): XRD of ZrO_2 for Thin Films

Fig. 1(a-b) scanned in the 2θ range of 20-80ºC. Shows the XRD pattern of ZrO_2 thick and thin films. The 2$\boldsymbol{\theta}$ values corresponding to observed (h k l) plane for monoclinic and tetragonal phase at 35.2^0 (200), 63.08^0 (222) and 30.2^0 (111), 50.4^0 (220), $60.2^{\mathbf{0}}$(311), 74.70^0 (400) respectively are well matched with the standard reported data card (JCPDS: 36-020) and (JCPDS: 17-0923).

The average crystallite size of ZrO_2 prepared thick and thin films were determined using Debye- Scherrer's formula

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

Where, D = Average crystallite size

λ = X-ray wavelength (1·542 Å)

β = FWHM of the peak in radians

θ= Diffraction peak position.

It was found to be in the range of 25 nm and 7 nm for thick and thin film respectively.

3.2 Surface morphology: analysis using SEM images

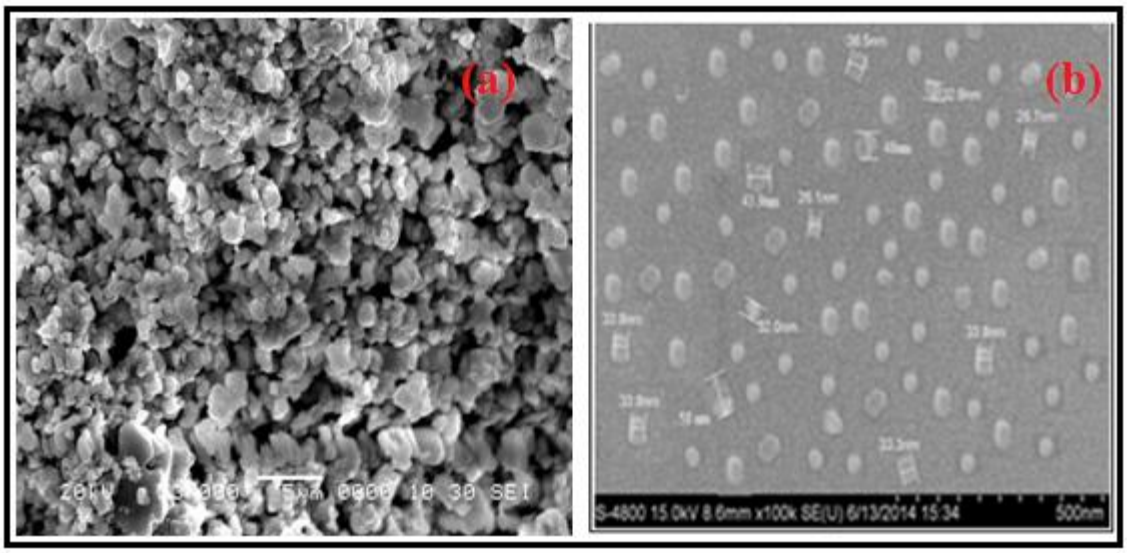

Figure 2: (a-b) SEM and FESEM micrographs of pure ZrO_2 thick and thin film

Fig. 2 (a-b) shows the SEM and FESEM images of pure ZrO_2 thick and thin films. It is clear that the grain seems to be bulk and nanocrystalline in nature and the grains are found to be spherical in nature, uniformerly distributed.

3.3 Elemental analysis using EDAX

Table 1 : Elemental compositional analysis of ZrO_2 thick film and ZrO_2 thin film.

Elemental composition	**Fired ZrO_2 thick films**		**Annealed ZrO_2 thin films**	
	mass %	**at %**	**mass %**	**at %**
Zr	74.33	66.45	71.00	33.04
O	25.7	33.55	29.00	66.96
ZrO_2	100	100	100	100

The quantitative elemental composition of Zr and O associated in thick and thin film element was carried out and it is represented in table. Atomic Wt% of cations (Zr) and anions (O) are 66.45 and 33.55 respectively. It is matched with theoretical expected wt% percentage. EDAX spectra of both thick and films are shown in Fig.3. From the table it was observed that ZrO_2 thick and thin film were observed to be nearly stoichiometric in nature.

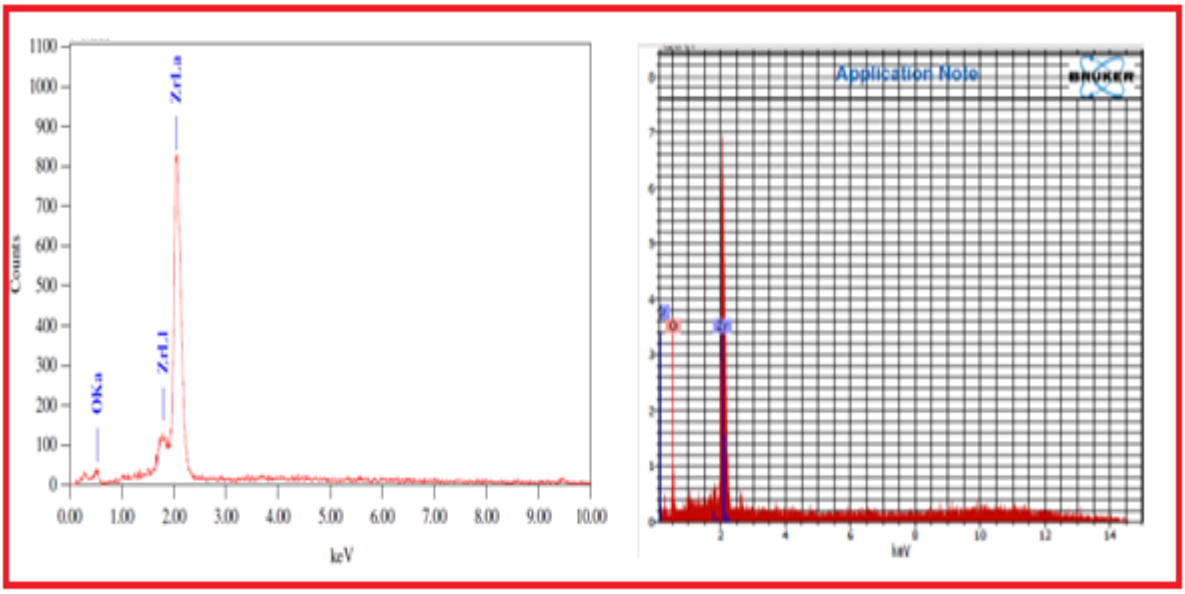

Figure 3 : EDAX Spectra of ZrO_2 Thick and thin films

4. Gas sensing performance.

4.1 Sensitivity for thick and thin films

Fig. 4(a) shows the gas response for different gases at different operating temperature for 100 ppm. The films showed maximum gas response (7.1) to NH_3 at temperature 300ºC. It is well known that the sensitivity of metal-oxide semiconductor sensors is mainly determined by the interactions between a target gas and the surface of the sensors [11].

Fig. 4(b) shows variation of gas response with operating temperature of samples on exposure of 500 ppm ammonia. It is clear from Fig. 4(b) that the ammonia response to sample P2 shows maximum gas response (P2 = 58.5) at 150 °C .

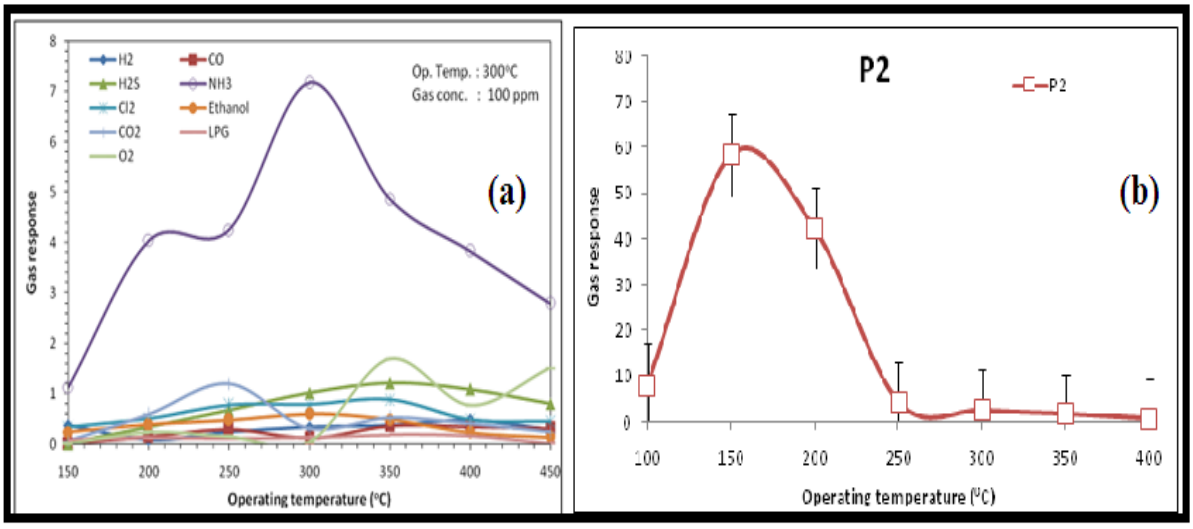

Figure 4 (a) and (b) Gas responses to different gases at 100 ppm concentration.

4.2 Selectivity for thick and thin films

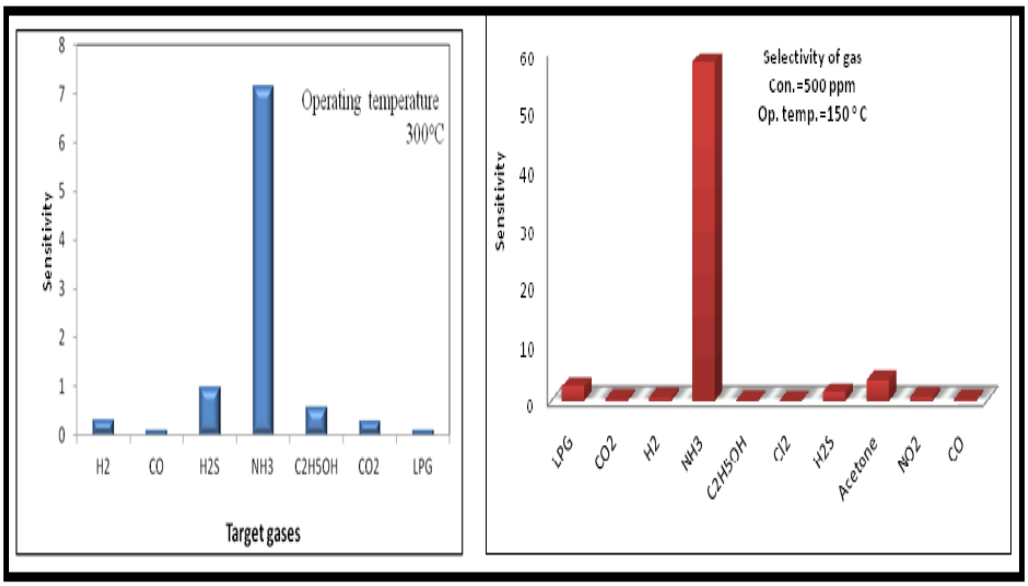

Figure 5 (a) and (b) Selectivity profile studies.

Fig.5 (a) and (b) shows the selectivity of gas respond and it shows highest sensitivity (7.1) to NH_3 gas (measured at 100 ppm) at 300ºC against all other tested gases: H_2, H_2S, Cl_2,C_2H_5OH, CO_2, LPG,CO.Fig.5(b) shows selectivity of ammonia against various gases at different operating temperature. It is clear from Fig. Fig.5 (a) and (b) that the responses of all samples to, H_2, C_2H_5OH, Cl_2, NO_2 and H_2S gases are lower as compared to ammonia.

4.3 Response and Recovery time for thick and thin films

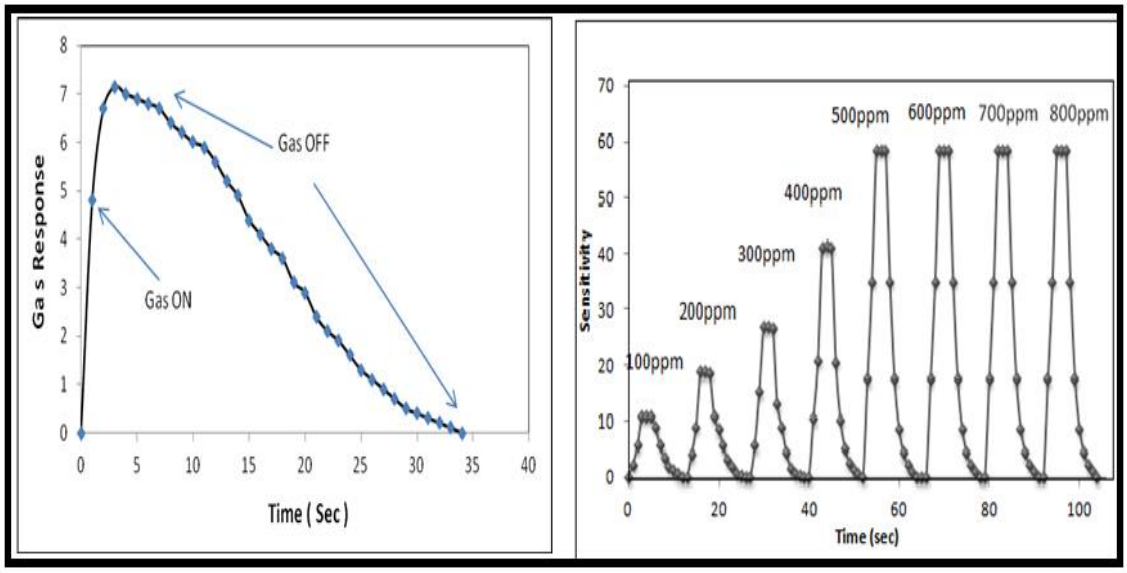

Figure 6: Gas response and recovery time in second

Fig. 6 (a) shows the response and recovery characteristics of ZrO_2 thick film sensor to 100 ppm. The response of ZrO_2 thick film sensor was found to be quick (~ 4S) to 100 ppm of NH_3, while the recovery was fast (~ 8 s). Fig. 6 (b) shows the response and recovery time of most sensitive sample of different concentration of gas. The sensor shows quick response (4 s) and fast recovery time (10 s). 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 [12].

5. Discussion

5.1 Gas sensing mechanism

It is well known that the electrical conductivity in ZrO_2 oxide is due to a non-stiochiometric composition as a result of oxygen deficiency [13]. The conductivity is n-type , when the sensor surface is placed in air ambient, the oxygen molecules are adsorbed at the surface resulting in the formation of O_2^- , O^- , O^{2-} ions, thus decreasing the concentration the number of charge carriers near the surface giving rise to a depletion region. When exposed to reducing gas ammonia mutual interaction between the reactant i.e. reducing gas and oxygen species, results in oxidation of reducing gas at the surface. This oxygen phenomenon helps in removal of oxygen ion from ZrO_2 resulting in decrease barrier height, thus increasing conductivity. During the chemisorptions at higher temperature 125^o C, oxygen is adsorbed in ionic form as shown in the following reactions.

$$O_2 + e^- \rightarrow O_2^- \quad (3)$$

$$O_2^- + e^- \rightarrow 2O^- \quad (4)$$

Above 175^{o}C, the reactivity of O^{2-} species is high. The formation of O^{2-} species is also possible as follows

$$O\ ads^- + e^- \rightarrow O^{2-} \quad (5)$$

O^{2-} is not adsorbed because these species are not stable and are usually trapped by oxygen vacanciesT(15-18). The adsorption and desorption mechanism is shown if Fig.7

Reducing gas like NH_3 reacts with adsorbed oxygen ions, surface adsorbed oxygen interact with NH_3 and release electron back to conduction band.The possible reaction is

$$2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + 3e^- \quad (6)$$

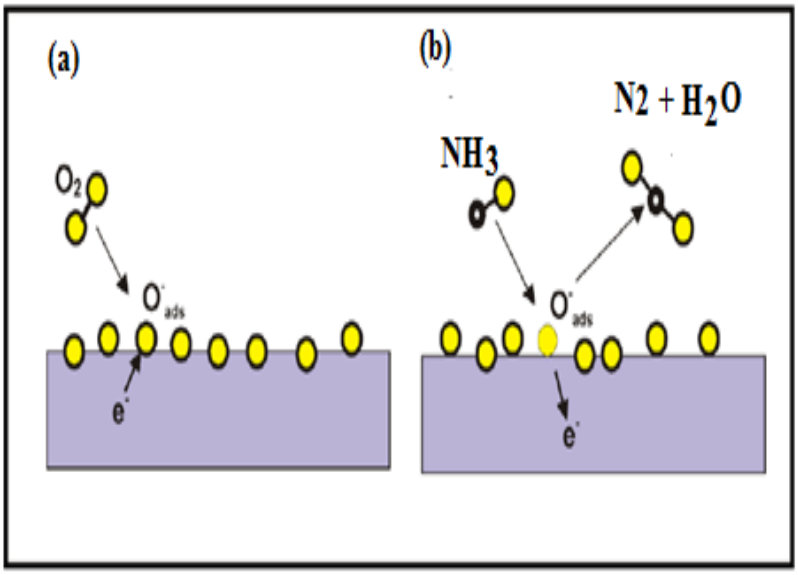

Figure 7: Schematic representation of oxygen adsorption-desorption.

. 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 takes place

$ZrO_2 + 5\ NH_{3(gas)} + 4O^{2-}$ (film surface) $\rightarrow Zr(\ NH_4OH)_{3(\text{ film surface})} + 2NO_{2(gas)} + 8e^-$ (conduction band) (7)

This shows n-type conduction mechanism, thus generated electron contribute to sudden increase in conductance of the thick film [14].

Comparative study of various analytical and conventional gas sensing properties

Table 2: Comparative study of structural, morphological and optical band gap property of pure ZrO_2 thick and thin film

Analytical technique	**Properties**	**Thick film**	**Thin film**
XRD	Average crystallite size	25 nm	5.8 nm
SEM/FESEM	Average Grain size	71 nm	37 nm
Nature of film	Structure	Polycrystalline(Bulk)	Nanocrystalline

Inspite of this other observed properties were estimated in respective chapter 3 and 5.

Table 3: Comparative study of ZrO_2 thick and thin film with respective to gas sensing performance

Performance criteria	**Sensor form**	
	ZrO_2 thick film	**ZrO_2 thin film**
	Gas	**Gas**
Most sensitive gas	NH_3	NH_3
Gas response	7.1	58.8
Concentration (ppm)	100	500
Operating temperature (^oC)	300	150
Response time (sec.)	4	4
Recovery time (sec.)	8	10

From table 3 and 4 we have conclude that thin films are suitable for gas sensing application since it provide large surface area for the reactivity of target gas. It has observed that both thick and thin films are sensitive to NH_3 at different operating temperature. Pure ZrO_2 thin film had shown maximum gas response at lower temperature than pure ZrO_2 thick films it may be change in microstrutured property.

Conclusions

XRD confirmed the identity of ZrO_2 thick and thin films Surface morphology study from SEM, FESEM analysis confirmed that grains are observed to be mixed shape of spherical nature. From EDAX spectra it is confirmed that initially ZrO_2 powder was non-stoichiometric and after firing it was found to be stoichiometric in nature. Pure ZrO_2 thick film is found sensitive (7.1)to ammonia gas at 300^{o}C temperature for 100ppm concentration respectively, The prepared sensor shows maximum gas response to NH_3 (58.8) at 150 ^{o}C for thin film. Quick response (4 s) and fast recovery (10s) are the main future of the sensor

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