Influence of CuO on temperature dependent H$_2$S gas sensing performance of ZrO$_2$ thick film resistor

Sudhakar B. Deshmukh[1*] Gotan H.Jain[2] Ramesh H.Bari[3]

*1. Department of Physics ,Arts Science and commerce College , Manmad ,Nashik, M.S.,
   423104,India

2. Department of Physics, Material Science Lab., K. T. H. M. College, Nashik, M.S. 422202,India

3. Department of Physics, GMD Arts, KRN Commerce and MD Science College, Jamner, Jalgaon, M.S., 424206, India

* E-mail of the corresponding author: mesudhakar_deshmukh@rediffmail.com

Abstract

Popular   screen printed   ZrO$_2$ thick film resistor was formulated for characterization. These films were surface modified by dipping them in 0.1 M CuCl$_2$ aqueous solution for the time intervals of 5,10,20, 30 and 40 minutes. Surface morphology and elemental composition were studied using scanning electron microscopy coupled with energy dispersive spectroscopy. It was observed that Cu converted into CuO at 200°C during sintering of the films and this p-type oxide plays role with n- type ZrO$_2$ for H$_2$S gas sensing. X-diffraction confirmed the polycrystalline nature of pure ZrO$_2$ powder and influence of copper on film surface disappear the polymorphs and only strong crystalline peak was observed. It was good indication for gas sensing. Bandwidth reduction was observed by characterizing film with UV spectroscopy techniques. Pure ZrO$_2$ film sample was shown wide bandwidth than sintered and modified film. The gas sensing performances of various gases were tested previously and it is reported for Ammonia except oxygen. Negative temperature coefficient of the CuO activated film shift response to H$_2$S gas at elevated temperature between 300°C to 450 ^{o}C. Maximum Gas sensing response was observed at operating temperature 450°c for 100ppm concentration. It was observed temperature, thickness and concentration dependent. Quick response time and fast recovery were recorded.

Keywords*: thick film , CuO activated, H$_2$S gas sensor, bandwidth reduction, quick response and fast recovery

1 Introduction

Thick and thin film technique have been used to produce metal oxide gas sensors.   These sensors are classified according to different principle as metal oxide, solid electrolyte   potentiometric and coductometric, capacitive, calorimetric, gravimetric and optical gas sensors .Among these resistive gas sensors are mostly applicable and popular because of easy fabrication. Role of chemical reaction mechanism is important, generally any gas sensor must possess three basic functions receptor, transducer and work function on the basis of adsorption-desorption surface reaction. Mechanism consists of adsorbed oxygen, Schottkeybarrier mechanism, grain size effects, porosity, rate of diffusion, film thickness, operating temperature, nature of oxide material whether n-type or p- type conductivity, homo and heterojunction, electrode contacts, sensor size, life cycle are the considerable parameters during studying to design fabrication gas sensors (M. Kleitz et al 1991 N. Yamazoe et al 2005, P.T.Mosely et al 1983, Pavel Shuk et al 2008). The principle of operation of metal oxide sensors is based on the change in conductance of the oxide on interaction with a target gas and the change is proportional to the concentration of the gas. Some oxides changes characteristics after doping and mixing as composite and play the effective role for gas sensing mechanism. Surface modification and doping are the techniques used to improve the parameters of gas sensors. Ionic conductivity , activation energy, band gap, electron negativity and barrier height also factor. ZrO$_2$ is best ionic conductor.   When ZrO$_2$ is doped with aliovalent oxides such as Y$_2$O$_3$, CeO, MgO , it acquires ionic conduction for oxygen ion over a wide range of temperature and partial pressures of oxygen, pure zirconia undergoes two structural transformation upon heating, Monoclinic $\leftrightarrow$(1170 ^{o}C) Tetragonal $\leftrightarrow$(2340 ^{o}C) $\leftrightarrow$ Cubic with melting finally occurring at approximately 2680 ^{o} C. (J. Riegel et al 2002, Ali Ataiwai et al 2009) The cubic phase has fluorite structure and lattice is face centered cubic (fcc) with four formula unit cells and with each Zirconium ion being surrounded by eight oxygen ions. It has need modification to achieved good electrical conductivity and thermal stability. Density of ZrO$_2$ material is 5.83 g/cm^3, 6.10 g/cm^3 and 6.09 g/cm^3 for monoclinic, tetragonal and cubic structures respectively.(Andress Dubbee et.al.2003) Now a days nano gas sensor have great importance because of high surface energy and maxium surface to volume ratio. Sensors are necessary part of daily life and usable in industrial , home appliances, food processes systems, in hospital, fire and safety, security alarms to alert after detection of toxic and hazardous gas leakages.(K .T. Jacob et al 1990,G.Reyana Garacia et al 2003, K .Zakarzawaka et al 2001) These are the number of applications for environmental monitoring.(Jinhual Liu et al 2003, P. T. Mosley et al 1991) In present work it has been extensively studied with CuO

modification.

2 Experimental

2.1 ZrO$_2$ thick film formulation

Zirconium dioxide was prepared by using Analytical grade Zirconyl (IV) Chloride octohydrate (ZrOCl$_2$.8H$_2$O) [Aldrich] explained previously as reported in literature elsewhere and it was dried, grinded for formation of small grains and calcinated at 1000 ^{o} C in muffle furnace for few hours. Glass Substrate   used were ultrasonically cleaned with acetone and thereafter deionized water and stored in hot oven at 40 to 60 degree temperature for few minutes to remove volatile and moisture impurities.   Thixotropic Paste was formulated by mixing dried ZrO$_2$ powder with   ethyl cellulose(temporary binder) 10 mass%, butyl carbitol acetate (organic solvents)95 mass% and alpha   terpineol (95 mass%) depending on mixture proportion .Permanent binder glass frit was not used since glass substrate utilized for present study. Inorganic to organic compound ratio maintained with 75:25 percentage to achieved desired viscosity and rheology of the paste. This thixotropic paste was kept in bowel for few minutes to good settlement. The screen printed thick films were dried in IR light source and sintered at 550 ^{o} C to burn organic binder to produce desired porosity. Thickness was maintained by squeegee strokes and optimized films were used for gas sensing performance. The films then kept in IR light source for drying and fired at 550^{0}C to burn organic binder and reduce porosity.(Deshmukh S.B.et al 2011 John Spirig et al 2007,G.H.Jain et al 2008)

2.2 Thickness Measurement

The thicknesses of the films was measured using the Taylor Hobson (Talystep, UK system). It was observed in the range from 35-55 μm. The Various thicknesses of the films were possible by controlling number of squeeze strokes. It was achieved considering substrate and functional material cracking limit at working   temperature   and shear stress.(G .H. Jain et al 2008, K.M. Garkar et al 2009)

2.3 Temperature Coefficient of the thick film

The temperature coefficient of the films was determined using following formula and it was observed NTC. It was observed in the range 0.00338 to 0.006632 /^{o}K.

$$TCR = \frac{\Delta R}{R(\Delta T)}/(^0K)$$

2.4 Modification of the ZrO$_2$ Thick Films

The surface modified ZrO$_2$ thick films were obtained by dipping them in 0.1M and 0.01M aqueous solution of cupric chloride (CuCl$_2$) for different intervals of time: 5, 10, 20, 30 and 40 min. These films were dried in IR light source, followed by firing at 550°C for 30 min. The films so prepared are termed as 'surface modified ZrO$_2$ films'. (M.S. Wagh et al 2006)

3 Characterization

3.1 Structural and Morphological Analysis of ZrO$_2$ Particles

Fig. 1 shows the XRD Pattern of Pure calcinated ZrO$_2$ powder, Sintered film, CuO influenced ZrO$_2$ films within range 20 to 80^0 X-ray diffractogram of the material was confirmed the polycrystalline structures of the ZrO$_2$. It is determined 2θ values and hkl planes corresponding to monoclinic at 35.2^0 (200), 63,08^0 (222) and tetragonal at 30.2^0 (111), 50.4^0 (220), 60.2^0(311),74.7^0 (400).The strongest peaks for the tetragonal phase was observed. Inspection of X-ray pattern shows that no cubical phase transformation. The observed peaks in the XRD pattern are matching with the standard recorded data (JCPDS 36-020) and (JCPDS 17-0923) After modification by dipping technique Cu is converted into CuO oxide during sintering temperature above 200 ^{o}C. Electronegativity (1.75) and ionic radius (0.73Å) of Cu^{2+} play important role and because of CuO activated surface of the film the polymorphs nature of ZrO$_2$ would be disappeared and only strong peaks was observed along with small exististance noise peak of Cu influenced in film. Reduction in peak intensity was observed after modification it is good for sensing ability

The average particle grain size of ZrO$_2$ powder was determined by using Scherrer formula and was estimated to be 82 nm.

$$D = \frac{0.9\,\lambda}{\beta COS\theta}$$

Where λ-wavelength of X-Ray in Å (1.542 Å) and β is the peak FWHM in radian.(V. A. Chaudhari et al 1999) It could be calculated from Warren's formula

$$\beta = \sqrt{\beta m^2 + \beta s^2}$$

where β_m is measured peak width in radian at half peak height and β_s corresponding width of the standard material.

3.2 **Surface** Morphology of the Films

SEM images were observed by JEOL-JSM 6360(LA), JAPAN coupled with EDAX analysis.fig.2 (a) and (b) depicts the SEM images unmodified (pure ZrO_2) and modified ZrO_2 thick films (20 min dipped). From these surface morphology observation it is seen that an unmodified film consists of larger grains distributed randomly. The Cu-modified film(with dipping time 20 Min.)Consists of smaller particles associated with larger ones, as in fig.2 (b).These particles could be attributed to CuO Particles. CuO grains may reside in the intergranular regions of ZrO_2 thick film. Effective sensing surface area was expected to be increased. Average particle size of the ZrO_2 is observed to be 119nm to 138 nm by SEM and matched with calculated value 82 nm having uniform bulk appearance on film

3.3 Elemental Composition Analysis of the Thick Films

The quantitative elemental compositions of the film were analyzed using an energy dispersive spectrometer,

and mass % values surface modified films are presented in table 1. Stochiometrically (theoretically) expected wt % of cations (Zr) and anions (O) are 66.67 and 33.33 respectively. The wt % of constituent cations and anions in the pure ZrO_2 and surface modified ZrO_2 were not as per the stoichiometric proportion and all samples were observed to be oxygen deficient, leading to semiconducting nature of material. It is clear from table 1 that the weight percentage of Cu went on increasing with dipping time. The film with dipping time of 20 min is observed to be more oxygen deficient (25.57wt %). The deficiency of oxygen reduces the resistance of the film. This oxygen deficiency would promote the adsorption of relatively larger amount of oxygen species favorable for higher gas response.CuO % ,ZrO_2% and elemental % of modified film accordingly dipping time is stated in table no.1. CuO is p- type and ZrO_2 on glass substrate act n-type oxide . (S. A. Patil et al 2006)

3.4 Electrical properties

3.4.1 I-V Characteristics

Fig.3 depicts the I-V characteristics of pure and modified ZrO_2 , the symmetrical nature of the I-V characteristics for particular samples shows that the contact are ohmic in nature .It is observed from fig.3 that the conductivity of pure ZrO_2 film is larger than that of modified film in air because basically zirconia is a ionic conductor, it is famous for oxygen gas response and modified film have less conductivity in air but by exposure of reducing gas modified film responsnd sudden decrease in resistance resulting increase in conductivity at optimal temperature .This increase in current depends on oxygen species and reaction mechanism. The conductivity of the film dipped for 20 minutes is least among all. This could be attributed to an increase in the amount of ZrO_2-CuO intergrain boundaries and hence intergranular potential barriers. CuO modified ZrO_2 film consists of large number of smaller particles of Cu species distributed around the larger particles on the surface of the ZrO_2 film. CuO grains may reside in the intergranular regions of ZrO_2, resulting in developing of intergrain boundaries and intergranular potential barriers.(1.1 eV to 2 eV)

3.4.2 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 ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$). The adsorption chemistry of CuO-modified ZrO_2 film surface would be different from the pure ZrO_2 thick film surface. The CuO misfits on the surface would be adsorb more oxygen species than the pure ZrO_2 thick film surface

3.4.3 Optical Properties of the film

Absorption spectra as a function of surface modification is shown in figure 5.The absorption spectra characteristics were observe using JASCO V-670, spectrophotometer. The adsorption at higher wavelength in the range 320-380 nm at intense absorption can be seen. Further absorption increases as film modified. Absorption coefficient decreases after modification. The band gap of the film were calculated using formula

$$Eg = \left(\frac{12400}{\lambda (A^0)} \ eV \right)$$

It was observed band gap reduces after sintering and modification of the ZrO_2 film. The values determined are 4.8eV, 4.2 eV, 3.2 eV for sintered, pure and modified films respectively.

4 Results and discussion

4.1 *Gas sensing performance*

The temperature dependence of the specific conductivity is given by following equation

$$\sigma_{ion} = \kappa T^{-1} \exp^{(-\Delta E_a / KT)}$$

Where K is a material constant . T the absolute temperature, k the Boltzmann constant, and ΔE_a is the activation energy. From this equation and nature of substrate and its shear stress optimal film thickness and temperature can be calculated for maximum conductivity at film cracking limit. Activation energies of typical solid electrolytes are in the range 01-1.0 eV and for resistive film would be in the range up to 2 eV.

Gas sensing performance is based on the principle of change in conductance by exposure of the target gas. The conductance should be increased by rise in temperature and gas concentration and it is stated by following equation

$$G = G_0 \exp^{(-qV / KT)}$$

Where G_o is a factor that includes the intragranular conductivity in the 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 .Gas sensors may present a constant resistance in the air at this time reducing gas form oxidation reaction with the oxygen adsorbed on the surface of semiconductor, isolation effect of gas molecules results in the change of surface potential, consequently the resistance of sensor may change. For reducing gas resistance reduces and conductivity increases while for oxidizing gas, resistance increases and conductivity decreases. Also conductivity increases by increasing in gas concentration.

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

$$S = \frac{G_g - G_a}{G_a}$$

Where G_a is the conductance of sensor in air medium, whereas G_g is the conductance of sensors in gaseous medium (Deshmukh S.B.et al 2011, Gotan Jain et al 2008)

4.2 *Sensing Characteristics of modified ZrO_2 film*

Fig. 6. Shows the variation of gas response of the modified ZrO_2 films (fired at 550^0C) to various gases (100 ppm) with Operating temperature ranging from 150 to 500^0C. For H_2S, the response goes on increasing with operating temperature, attains its maximum (14.58) at 450^0C and then decreases with a further increase in operating temperature. From the figure, it is clear

4.3 *Selectivity of H_2S gas*

Selectivity of a sensor is defined as the ability of a sensor to respond to a certain gas in the presence of other gases. (G .H. Jain. et al 2006)as response of different gases was tested at different temperature and it is selective for H_2S gas at operating temperature 450 ^{o}C as shown in fig.7

4.4 *Gas sensing mechanism*

Gas sensing mechanism is based on the amount of oxygen adsorbed (O_2^- , O^- , O^{2-}) on the sensor surface and is a function of temperature. At the operating temperature, in the absence of a target gas, oxygen gets adsorbed on the surface of the sensor and it extracts electrons from the conduction band of the sensor material , which can be explained by the following reactions(Wu Yuanda et.al.2001, Arijit Chowdhari et al 2001)

$$O_2 \text{ (gas) } \leftrightarrow O_2 \text{ (ads)} \qquad\qquad (1)$$

$$O_2 \text{ (ads) } + e^- \text{ (CB) } \rightarrow O_2^- \text{(ads)} \qquad\qquad (2)$$

$$O_2^- \text{(ads) } + e^- \text{(CB) } \rightarrow 2O^- \text{ (ads)} \qquad\qquad (3)$$

$$O^- \text{ (ads) } + e^- \text{ (CB) } \rightarrow O^{2-} \text{ (ads)} \qquad\qquad (4)$$
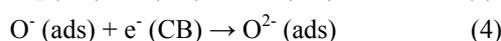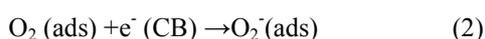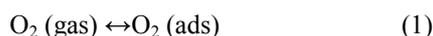
By exposure of target gas the chemical reactions responsible to enhance conductivity of the modified film could be represented as

$$ZrO_2 \text{ (Thick film) } + Cu^{2+} + O^{2-}\text{(ads) } + e^{2-} \text{ (CB)}$$

$$\leftrightarrow CuO + H_2S \downarrow \leftrightarrow CuS + H_2O \text{ (gas) } \uparrow \qquad\qquad (5)$$
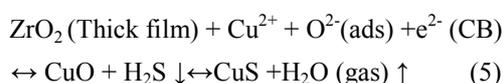
CuS is known to be metallic and conducting in nature. Due to the reduction of oxides into sulfides, the film resistance

would decrease suddenly .When H_2S turn off, upon subsequent exposure of sensor to air ambient at elevated temperature; sulfides got oxidized and could be recovered back to oxides as

$$2CuS+ 3O_2 \rightarrow 2CuO+2SO_2 \qquad (6)$$

This mechanism explain the decrease in resistance on exposure of CuO/ZrO_2 sensor element to reducing gases like H_2S and increase in resistance back to CuO when heated in air at operating temperature of about 200^oC and returns to its normal state, which is shown in equation (6) and hence, the reduced potential barrier appears again as previous.(G .H .Jain et al 2005, K .M. Garkar et al 2009)

The reaction of H_2S with the adsorbed oxygen ions can be represented as

$$2H_2S + 3O_2\text{-} \rightarrow 2H_2O + 2SO_2 + 6e^- \qquad (7)$$
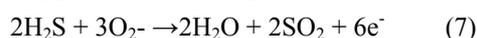
4.5 Response and recovery time

The time taken for the sensor to attain 80% of maximum change in resistance upon exposure to gas is response time (G.H. Jain et al 2008) .it was observed 2 s. and the time taken by the sensor to get back 80% to the original resistance is the recovery time .It was recorded40s.

Conclusion

Following conclusion can be drawn from the experimental results:

1. Surface modification process was employed to modify only surface of the film and portion of the base material.
2. The cupricated ZrO_2 film was observed to semiconducting in nature and showed a negative temperature coefficient of resistance.
3. The mechanism of the surface modified ZrO_2 film was the surface-controlled mechanism(adsorption/desorption).
4. The oxidation of sulfides (CuS) and the reduction of oxides (CuO) have also boosted the gas response and selectivity.
5. Cupric oxide would form larger number of misfits on the surface region therefore larger number of oxygen ions adsorbed on the surface, leading to high resistance.
6. The surface cuprication facilitated adsorption of a large number of oxygen ions on the surface, which could immediately oxidize the exposed H_2S gas, leading to faster response of the sensor.
7. The fast recovery of the sensor could be attributed to the larger oxygen deficiency would enable CuO modified ZrO_2 to adsorb more oxygen ions helping the sensor to recover fast.

Acknowledgement

Reference

Ali H. Ataiwi, Alaa A. Abdul – Hamead (2009) , "Study some of the Structural properties of ZrO_2 : ceramic coats prepared by spray Pyrolysis method, Eng. And Tech., Journal, Vol.27(160),pp.2918- 2930.

Andreas Dubbe (2003), Fundamentals of solid state ionic micro gas sensors, Sensors and Actuators B 88 ,138-148.

Arijit Chowdhari, Parmanand Sharma, Vinay Gupta, and K. Sreenivas (200), H_2S gas sensing mechanism of SnO_2 films with ultrathin CuO dotted islands, Journal of Applied Physics, ,Vol. 92, No.4,pp. 2172-2180.

Deshmukh S. B., Bari R.H., Jain G. H., Patil L.A.,(2011) Studies on gas sensing performance of pure and surface modified ZrO_2 thick film resistor ,IEEE conference publication,,pp.278-285,DOI;10.1109/ICSensT.2011.6136981

G. Reyna Garacia, M. Garacia - Hipolito, J. Guzman - Mendoza, M. Aguilar - Frutis, C. Falcony (2004), "Electrical, optical and structural chacterization of high - k dielectric ZrO_2 thin films deposited by the pyrosol technique", Journal of Material Science: Materials in Electronics 15, pp. 439-446.

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,(2008) Surface Modified $BaTiO_3$ thick film resistors as H_2S gas ,sensors and

Tranducers,Vol.90,Special issue,pp.160-173,.

G. H. Jain, L. A. Patil, (August 2006) Gas sensing properties of Cu and Cr activated BST thick films ,Bull. Mater. Sci. Vol. 29.4 , pp. 403-411.

J. Riegel, H. Neumann, H. M. Wiedenmann(2002), "Exhaust gas sensors for automotive emission control", Solid state Ionics, Vol. 152 -153, pp. 783-80

Jinhual Liu, Xingjiu Huang, Gang Ye, Wei Liu, Zheng Jiau, Wanglian Chan, Zhonghai Zhou and Zengliang Yu,"(2003)H_2S detection sensing characterstics of CuO/SnO2 sensor,,110-118.

John V. Spirig, Ramasamy Ramamoorthy, Sheikh A. Akbar, Routbort, Dileep Singh, Prabir K. Dutta(2007), "High temperature Zirconia Oxygen sensor with sealed metal/metal oxide internal reference, Sensor and Actuators B 124 ,pp.192-201..

JCPDS(36-020) (17-0923) data.

K. Zakrzewska (2001), Mixed oxides as gas sensors ,Thin solid films (39 1)29-238.

K. M. Garakar, B. S. Shirke, Y. B. Pati and D. R. Patil,(NOV. 2009) " Nanostructured ZrO_2 Thick film resistors operable at room temperature , Sensors and Tranducers ,Vol. 110, Issue 11,PP.17-25..

K. T. Jacob and Tom Mathews(1990), "Solid state electrochemical sensors in process control", Indian Journal of Technology, Vol. 28, pp. 413-425.

M. S. Wagh, G. H. Jain, D. R. Patil, S. A. Patil ,L .A .Patil(2006),' Modified Zinc oxide thick film resistors as NH_3 gas sensors, Sensors and Actuators B 115pp.128-133.

 M. Kleitz, E. Siebert, P. Fabry, J. Fouletier,(1991) "Solid state electrochemical sensors, in Sensors a comprehensive survey," Eds. W. G_ Pel, J. Hesse, J.N. Zemel.VCH New York, Vol. 2, pp. 341-428.

N. Yamazoe ,(2005) "Toward innovations of gas sensors technology (Review)", Sensors and Actuators,108, pp. 2-14.

N.Y amazoe , Y. Kurokawa, T. Seiyama(1983)," Effect of additives on semiconductor gas sensors', Sens and Actuators B,,p.283

P. T. Mosely, Material (1992), selection for semiconductor gas sensors, Sens and Actuators B,PP.,149-156.

P. T. Mosely (1991) Sensors new trends and future prospects of thick and thin fillm gas sensors, Sensors and Actuators,B,3,PP.162.

Pavel Shuk, Ed Bailey, Ulrich Guth(Special issue April 2008), "Zirconia Oxygen Sensor for the Process Application", Stae- of-the Art, Sensors and Tranducers, Vol. 90, pp. 174-184.

Ralf Riedel and I. Wei Chen,(2010) Ceramic material Classes, Properties Ceramic Science and Technology, WILEY, V C H, Verlag GmbH & Co. K Ga A Wienhein,Vol.2,pp.27-41.

V. A. Chaudhari, I. S. Mulla, K. Vijay Mohan(1999), "Selective hydrogen properties of surface functionalized Tinoxide", Sensors and Actuators, B 55 , pp. 154-160.
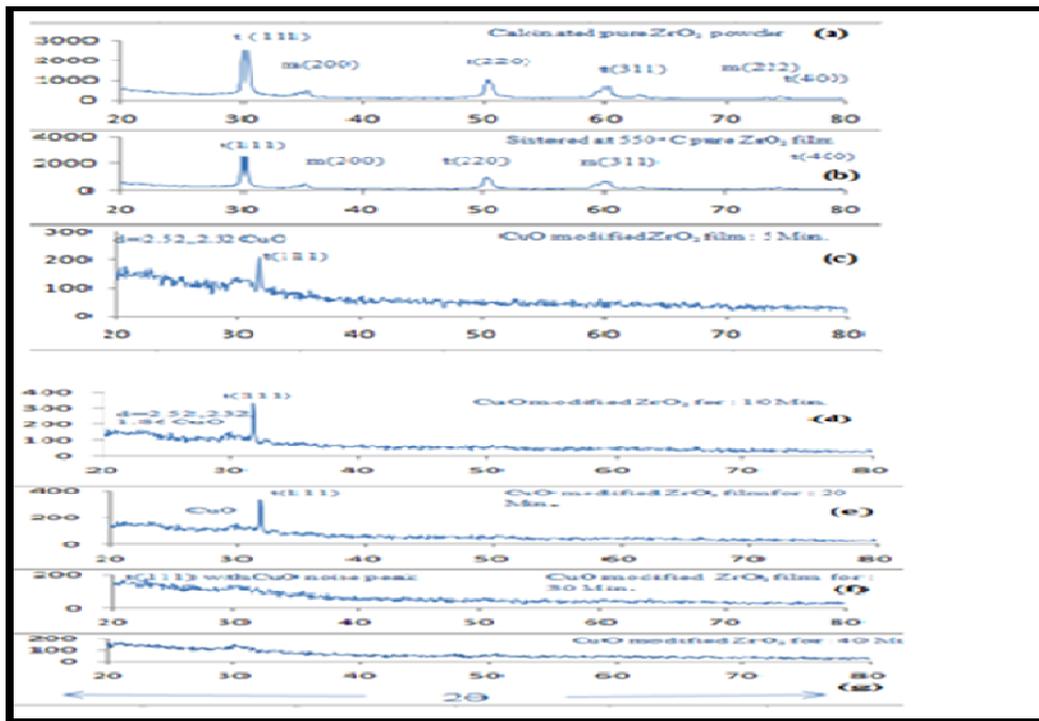
Figure 1.　　　　　XRD pattern of pure ZrO$_2$ and surface modified ZrO$_2$ thick films
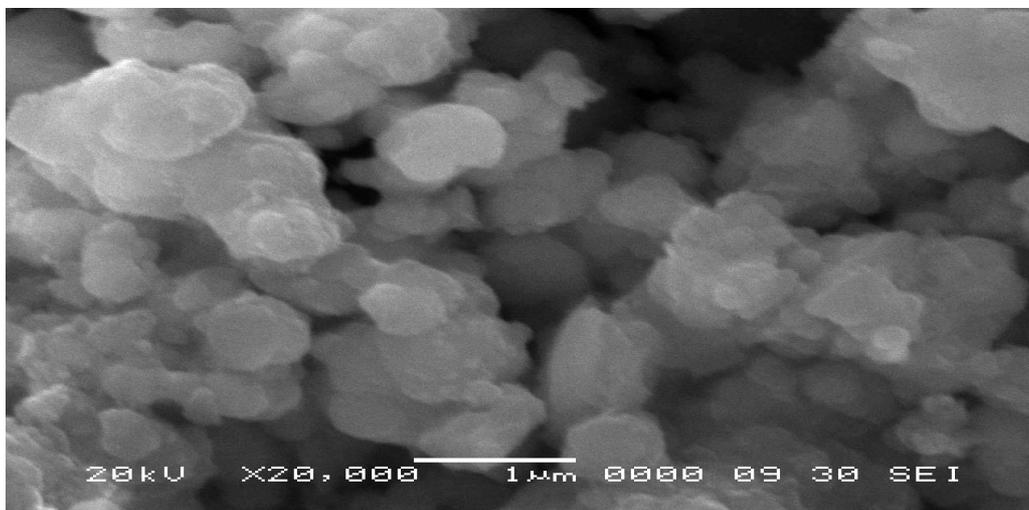
Figure 2.　　　　　(a) SEM image of pure ZrO$_2$ films
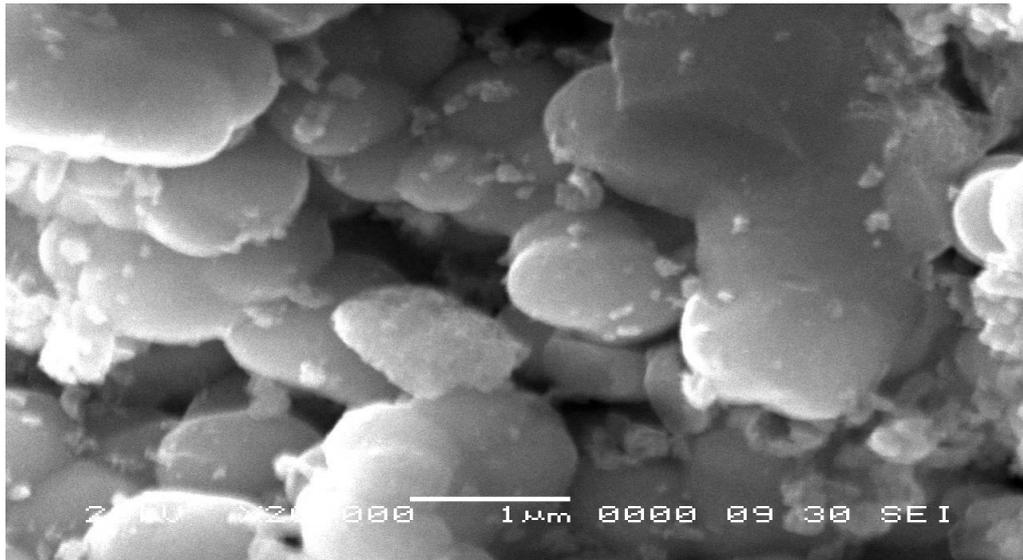
Figure 2.. (b) SEM image of modified ZrO$_2$ films
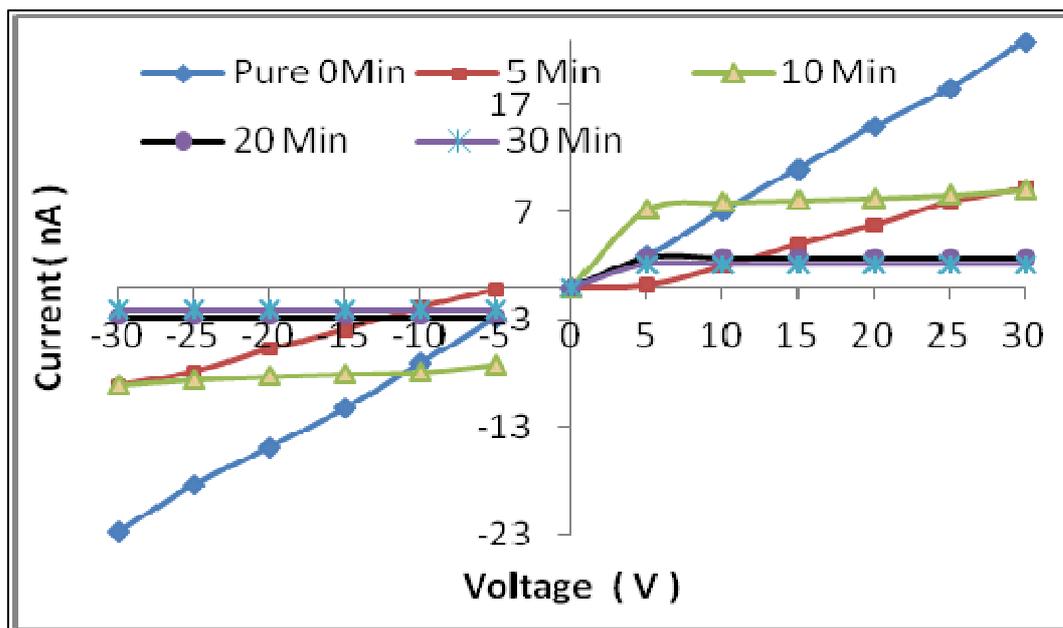
Figure 3.　　　　　I-V Characteristics of pure ZrO$_2$ and modified ZrO$_3$ films
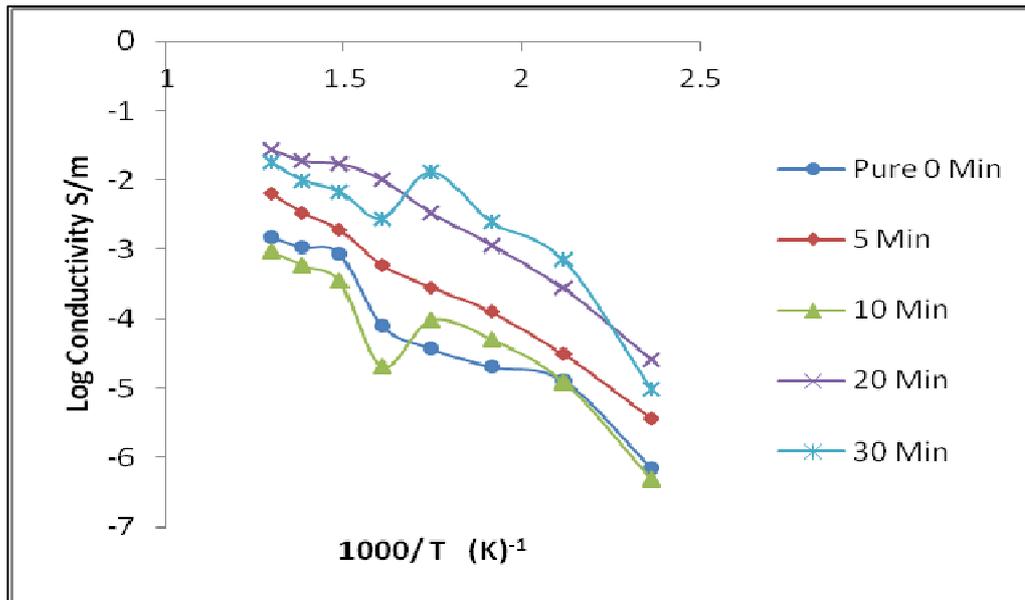
Figure 4.   Variation of Log conductivity in air of pure and modified films
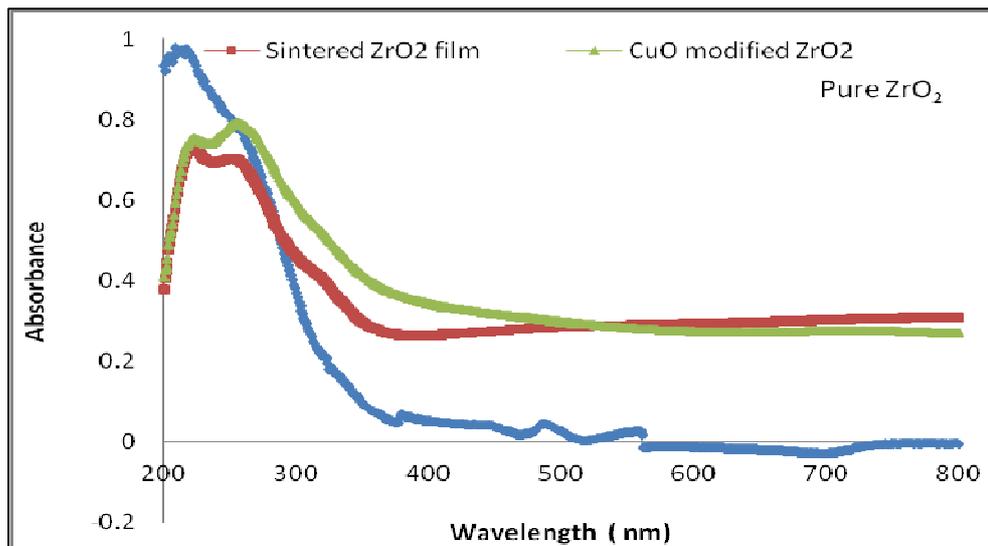
Figure 5.   Absorption spectra of pure and modified films
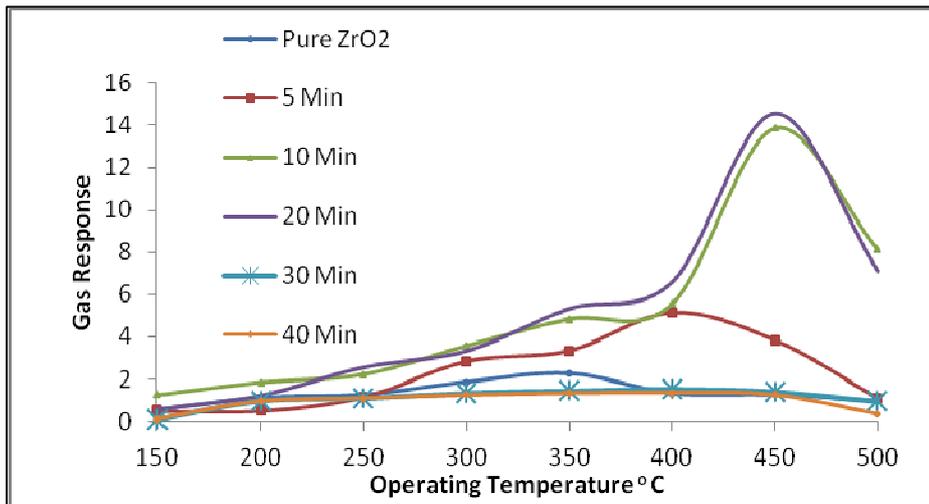
Figure 6.   Gas response of H_2S at different operating temperature for 100 ppm
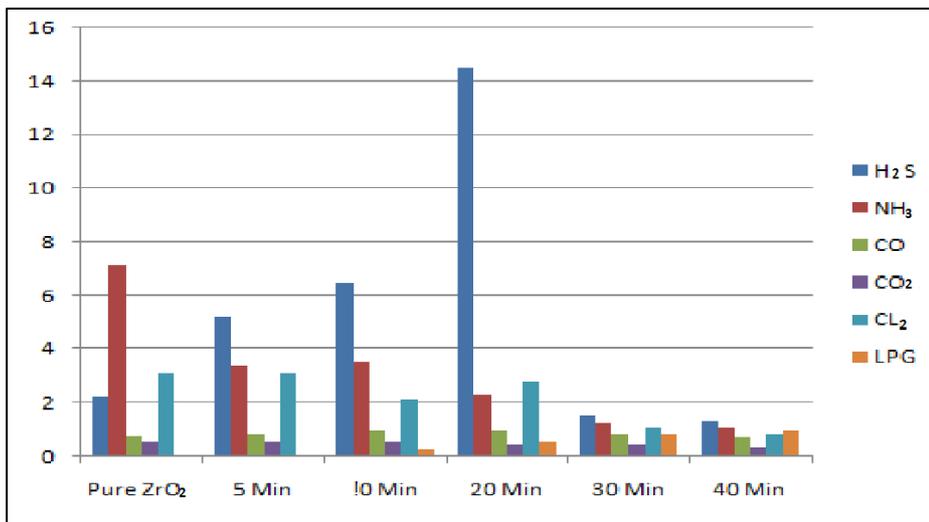
Figure 7.   Selectivity of H_2S gas among all tested gases
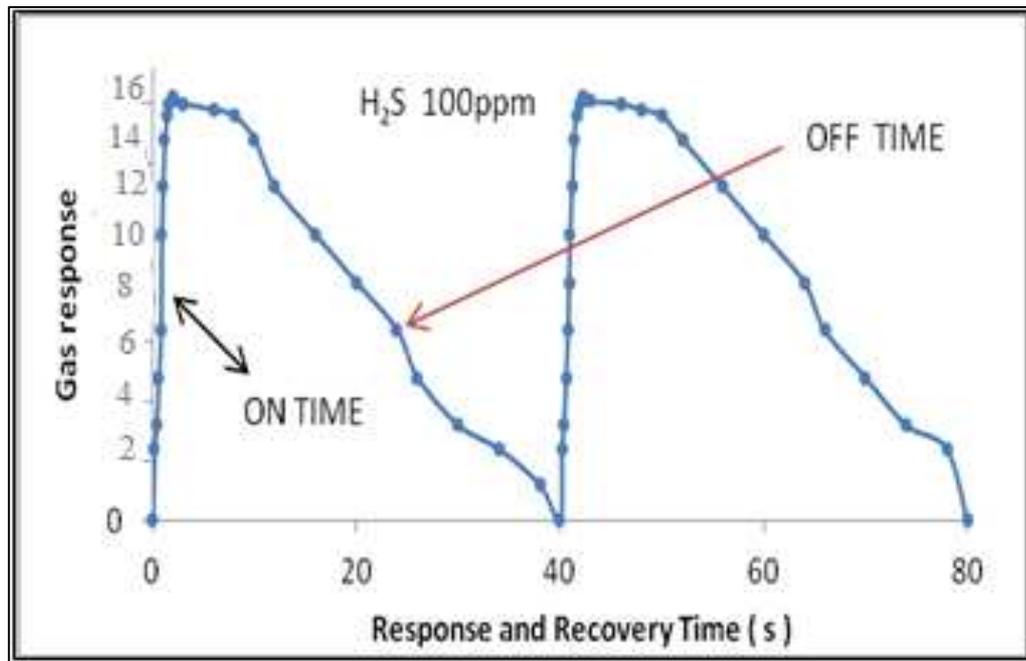
Figure 8.   Response and recovery time of H_2S gas sensor

Table 1 Elemental analysis of pure and modified ZrO_2 thick films

Type of the film	Zr Wt%	O Wт %	Cu Wt %	CuO Wt %	ZrO_2 Wt %	Total CuO-ZrO_2 Wt %
ZrO_2 Pure	33.33	66.66	0	0	100	-
Surface modified : 5 Min	73.96	25.96	0.07	0.09	99.91	100
:10 Min	73.27	25.91	0.82	1.03	98.97	100
: 20 Min	69.03	25.57	5.40	6.76	93.24	100
: 30 Min	73.61	25.94	0.45	0.56	99.44	100
: 40 Min	73.56	25.93	73.56	0.64	99.36	100