Journal of Nanotechnology & Advanced Materials
An International Journal

http://dx.doi.org/10.12785/jnam/030203

Gas Sensing Properties of Nanostructured ZnS Thin Films

M. S. Shinde [1,], Smt. Swapna Samanta[2], M. S. Sonawane[4], P. B.Ahirrao[3] and R. S. Patil[4,*]*

[1]Dept. of Physics, M.J.M. Arts, Commerce & Science College Karanjali (Peth),Dist-Nashik - 422 208 (M. S.) India.
[2]Dept. of Physics, Gokhale Education Societys HPT Arts and RYK Science College, Nashik – 422 005, India.
[3]Dept. of Physics, S.V.S.'s DadasahebRawal College Dondaicha. Dist. – Dhule, India.
[4]Dept. of Physics, P. S. G. V. P. M'S Arts, Science & Commerce College Shahada,Dist- Nandurbar - 425 409, India.

Received: 19 Apr. 2015, Revised: 22 Jun. 2015, Accepted: 25 Jun. 2015.
Published online: 1 Jul. 2015.

Abstract: Nanostructured semiconducting Zinc Sulphide (ZnS) thin films were deposited on glass substrate by relatively simple, quick and cost effective modified chemical bath deposition (MCBD) method. The characterization of as deposited thin films was carried out for the structural, compositional, surface morphological and gas sensing properties using X-ray diffraction (XRD), E-DAX, scanning electron microscopy (SEM) and gas sensing static unit. The mechanism of hydrogen sensing by the ZnS thin film is attributed to the reaction on the material surface or removal of chemisorbed oxygen from the film surface by testing gas. The sensor gave optimum responses to different gases at different operating temperatures. The surface misfits operating temperature can affect the microstructure and gas sensing performance of the sensor. The resistance responses of the nanocrystallineZnS thin films were measured by exposing as deposited film to different gases namely ammonia (NH_3), carbon dioxide (CO_2), ethanol (C_2H_5OH), hydrogen sulphide (H_2S), liquid petroleum gas (LPG), hydrogen (H_2) and chlorine (Cl_2). It was found that the sensors exhibited various sensing responses to these gases at different operating temperature. The results demonstrated that nanocrystallineZnS thin film can be used as a new type of gas sensing material which has a high sensitivity and good selectivity to Chlorine (Cl_2) gas for 500 ppm at room temperature.

Keywords: Nanostructure,MCBD, ZnS, gas sensing, sensitivity.

1 Introduction

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade. The concept of nanotechnology has been started about for the last half century ago and it has already been established its potentiality in various industrial applications. Nanotechnology deals with process that takes place on nanometer scale (<100 nm). Nanotechnology forms bridge that links single element with single crystal bulk structure. Usually large scale structures are made of polyatomic or molecular assemblies of matter, where the multiplicity of such unit blocks, whether ordered or statistically distributed. Due to this microscale properties effectively extended down to the microscale, traditional manufacturing techniques have been miniaturized for fabrication of microstructure as in microelectronics, in a top down approach atom by atom manufacturing synthesis. Nanoparticles, therefore with their oligo-atomic or molecular composition comprising a countable number of such units, represent a scale of matter where radically different phenomena are manifested and dominated its behavior.

Nowadays nano based zinc sulphide thin films evoked much attention due to their vast potential in various fields. It is used as key material for solar control coatings, antireflection coating for heterojunction solar cells, for light emitting diode and other optoelectronic devices such as blue light emitting diode, electro luminescence devices and photovoltaic cells which enable wide application in the field of displays, sensors and lasers. There are several techniques such as thermal evaporation[1], spray pyrolysis[2], molecular beam epitaxy[3], RF reactive sputtering[4], chemical bath deposition[5-6], modified chemical bath deposition[7], photo chemical deposition[8], atomic layer deposition[9], screen printing[10] have been used for the deposition of zinc sulphide thin films. Y. G. Liu (2007) et al. [11] have reported room-temperature oxygen sensing from individual ZnSnanobelts. It was found that Under UV illumination the current

*Corresponding author e-mail: mahen3569@rediffmail.com, rspatil_shahada@yahoo.co.in

through ZnSnanobelt increase from 0.265 to 2.26 nA as the oxygen pressure decrease from 1×10^{5} to 3×10^{-3} Pa. The conductance of ZnSnanobelt exhibits a logarithmic dependence on oxygen pressure, which was supported to theoretical prediction. The sensing mechanism was explained on the basis of enhanced modulation of ZnSnanobelts conductance by adsorbed oxygen underillumination.

Zhi-Gang Chen (2008)et al. [12] have grown oriented ZnSnanobeltson Si substrate using hydrogen-assisted thermal evaporation method under moist gas conditions.

It was found that these ZnSnanobelts had a single crystal hexagonal wurtzite structure growing along the [0 0 1] direction. They had a rectangular cross section with lengths of up to tens of micrometres, a typical width of 50–150 nm, and a thickness of ~40 nm. A silicon-induced vapour–liquid–solid process was proposed for the formation of the ZnSnanobelts and their assembly. These oriented nanobelts have much faster response time to hydrogen gas than that of pure ZnO and Pd-sensitized ZnO, showing excellent hydrogen sensing properties. SalihOkur (2010)et al. [13] have synthesized ZnS nanowires by the vapor–liquid–solid (VLS) method and humidity sensing properties of obtained ZnS nanowires were investigated by quartz crystal microbalance (QCM) method and electrical measurements. The synthesized nanowires were exposed to relative humidity (RH) between 22% and 97% under controlled environment. This showed ZnS nanowires have a great potential for humidity sensing. N Uzar (2011) et al. [14] have synthesized Zinc sulfide (ZnS) nanostructures by vapor–liquid–solid (VLS) method which is based on thermal evaporation. After suitable characterization it was found that ZnS nanowires have wurtzite structures with diameters in range of 50–400 nm. The humidity sensing was investigated by quartz crystal microbalance (QCM) and electrical resistance measurement techniques at different relative humidity (RH) conditions between 33% and 100% RH at room temperature. QCM results showed that the oscillating frequency of ZnS nanowires loaded on QCM crystal decreases in range of 33–84% RH, but increases at 90% and 100% RH. The sensitivity of ZnS nanowires-based sensor (R_{Air}/R_{RH}) increases over 1000 times from 33% to 100% RH. These experimental results showed that ZnS nanowires have a great potential for humidity sensing applications at room temperature. Xu L (2011)et al. [15] have reported a novel ethanol gas sensor based on organic-inorganic ZnS/cyclohexylamine (CHA) nanowires via a solvothermal route. The sensor exhibited significantly better performance with response time of approximately 0.6 sec. and recovery time of approximately 10 sec. even under a low ethanol concentration and the high surface area, small nanofiber diameter, and hybrid nature made the ZnS/CHA nanowires gas sensor have high sensitivity to ethanol gas at a lower operating current of 160 mA. Moreover, the gas sensing mechanism was explained on the basis of the two simultaneous steps for the adsorbing process due to the hybrid nature. This work indicates that the ZnS/CHA hybrid can be a novel candidate for the ethanol gas sensor with high performance. M. Hafeez (2011) et al.[16] have reported the effect of dimensionality of ZnS nanostructures on hydrogen gas sensing characteristics. Vapor-Liquid-Solid (VLS) growth mode was employed to synthesize ZnS nanostructures with different dimensions by controlling the growth parameters, i.e. variation in the substrate temperature and the carrier gas flow rate. The growth was explained by using the chemical tension model and the saturation conditions were determined for each growth. A variety of these nanostructures were tested for hydrogen gas sensing. The rapid response time was obtained for nanowires in few hundred millisecond's range with a sensitivity of 8, which was due to its high aspect ratio as compared to the other nanostructures.

In present paper the gas sensing properties of as deposited nanostructured ZnS films were studied for different gases like ammonia, hydrogen, carbon dioxide, chlorine, ethanol, hydrogen sulphide and L.P.G. at different operating temperatures keeping fixed gas concentration and finally selectivity of different tested gases is compared with each other.

2 Experimental details

The deposition of nanocrystalline ZnS thin films includes substrate cleaning, solution preparation and preparative parameter optimization. The as deposited MCBD ZnS thin films were characterized using various techniques in order to get information about the structural, surface morphological, electrical and optical properties.

2.1 Nanocrystalline ZnS thin film formation

All the reagents used for the preparation of ZnS thin film are of analytical grade (Loba chemicals) and used as it is without further purification. The modified chemical method is mainly based on immersion of the substrate into separate cation and anion precursor solutions and rinsing between every immersion with ion exchange water to avoid homogeneous precipitation. The cationic precursor for ZnS thin film deposition was zinc sulphate [$ZnSO_4.H_2O$], solution complexed with mixture ammonia [NH_3] and hydrazine hydrate [$H_2NNH_2.H_2O$]. The pH of this solution was adjusted to ~ 8.5. The anionic precursor was thiourea[$SC(NH_2)_2$] solution with pH ~ 6.3. The concentration of thiourea solution was 0.1 mol L^{-1} throughout the experiment. For rinsing purpose, highly purified deionised water was used. For the deposition of ZnS thin films, glass substrate was immersed in cationic precursor solution of zinc sulphate for 25sec. In which zinc ions are

adsorbed on the surface of the substrate. The substrate was rinsed with ion exchange water for 15 sec. To remove loosely bounded ions. The substrate was then immersed in an anionic precursor of thiourea for 25 sec. In which sulphur ions are reacted with pre-adsorbed zinc ions on the glass substrate. This was followed by rinsing again in ion exchange water for 15 sec. to remove unreacted sulphur ions. This completes one deposition cycle for the deposition of ZnS thin films. By repeating such deposition cycles for 65 times, a ZnS thin film on glass substrate was obtained. The deposition was carried out at room temperature.

2.2 Characterization Techniques

The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuKα radiation (α= 1.5404°A) in 2θ range from 20^0-80^0. The surface morphological study of ZnS films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360 A. Gas sensing performance was measured by homemade static gas sensing unit.

3 Result and Discussion

3.1 Structural Studies

The XRD pattern of as deposited ZnS thin film onto glass substrate is shown in **fig.1**. The X-ray diffraction studies shows that ZnS film is nanocrystalline in nature with hexagonal crystal structure. The central broad hump is due to the amorphous glass substrate. The short intense peaks at 2θ = 27.332 (d = 3.2603Å), 2θ = 28.571 (d=3.1217 Å), 2θ = 30.533 (d = 2.9254Å) and 2θ = 47.529 (d = 1.9115Å) corresponding to the (1 0 1), (0 0 6), (1 0 3) and (1 0 8) planesof ZnS with hexagonal crystal phase. The crystallite size was estimated by using the well-known Scherrer's formula,

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where λ = 1.5406 Å for CuKα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle.

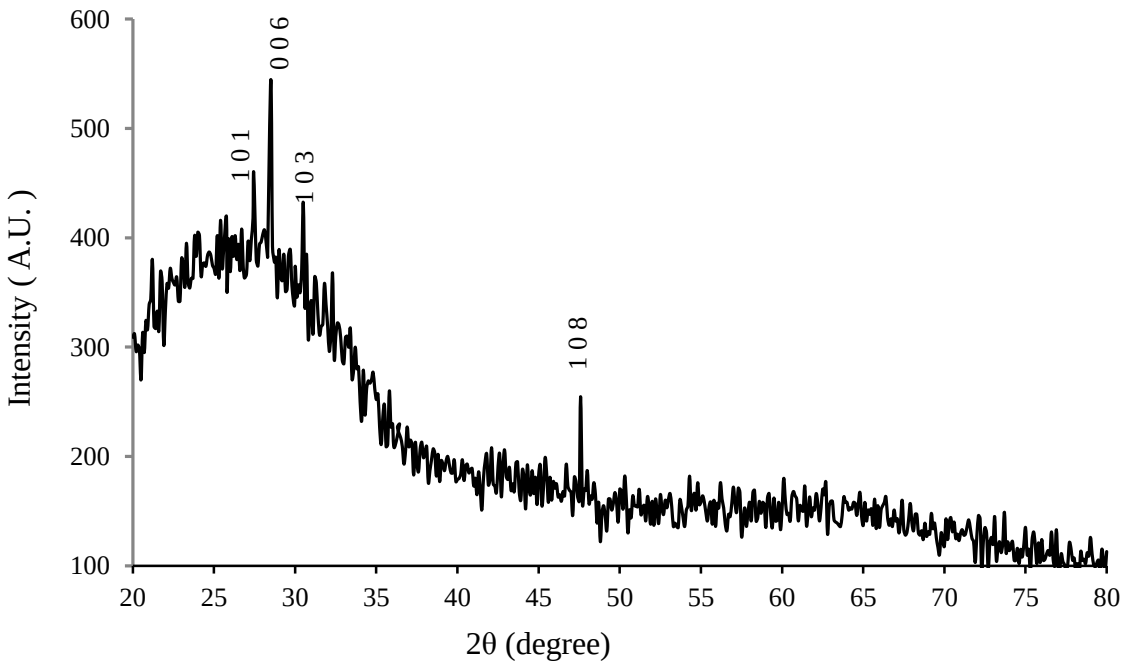

Fig. 1: The X-ray diffraction pattern of as-deposited ZnS on glass substrate at room temperature.

The sample of as-deposited ZnS thin film resulted in an average crystallite size of 50 nm.

3.2 Surface morphological studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The ZnS thin film with 410nm thickness was used to study the surface morphology using a scanning electron microscopy. **Fig. 2** shows a scanning electron microscope of ZnS thin film at X 10,000 magnification the scale bar length is 1µm. The average grain size of ZnS thin film was estimated using Cotrells methods [17]. The estimated average grain size is 50 nm of ZnS thin film, same as found from XRD pattern.

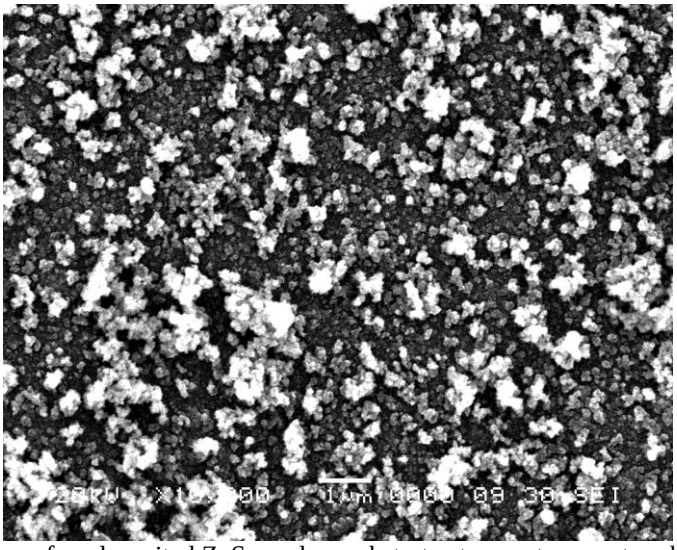

Fig. 2: The surface morphology of as-deposited ZnS on glass substrate at room temperature by scanning electron microscopy studies.

The as-deposited film shows spherical shape grains. It is observed that the film is uniform whitish and well substrate covered.

3.3Energy dispersive X-ray analysis

The energy dispersive x-ray analysis (EDAX) technique is used to determine quantitative composition of ZnS films deposited on glass substrate. The composition ratio was 1:1of atomic mass percent for Zn and S respectively as shown in **fig.3.** The EDAX analysis shows the presence of zinc (Zn), sulphar (S) elements from the glass substrate. Two major peaks correspond to Zn and S. From XRD and EDAX results, we conclude that the films are composed of pure zinc sulphide.

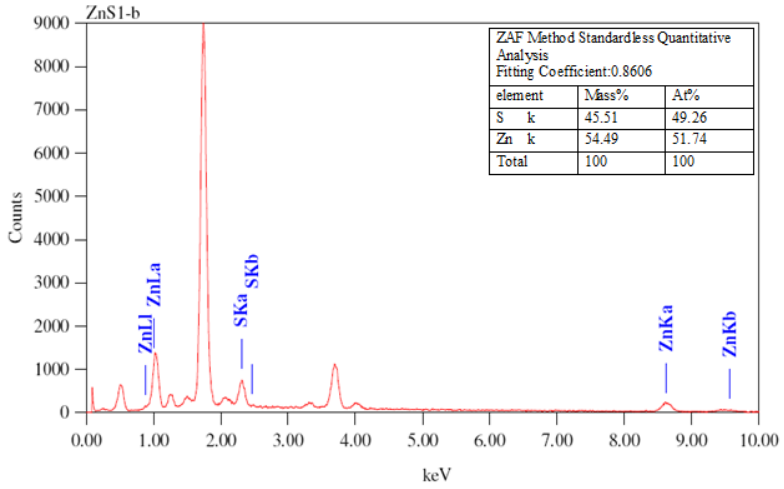

Fig. 3: The energy dispersive X-ray analysis of as-deposited ZnS film on glass substrate.

3.4 Sensing Performance

3.4.1 Gas sensing properties of nanocrystalline ZnS thin films

The gas-sensing properties of ZnS thin films to different gases, namely ammonia (NH_3), carbon dioxide (CO_2), ethanol (C_2H_5OH), hydrogen sulphide (H_2S), liquid petroleum gas (LPG), hydrogen (H_2) and chlorine (Cl_2) were studied. Sensitivity (S)or Gas response is measured as the ratio of change in resistance of the sensor on exposure of the target gas to

the original resistance in air medium using relation

$$\text{Sensitivity S (\%)} = \frac{Ra - Rg}{Ra} \text{ x } 100 \quad (2)$$

Where Ra is the stabilized resistance of sensor in air medium and Rg is the resistance in the presence of target gas andselectivity or specificity is measured, as the ability of a sensor to respond to certain gas in the presence of more gases. Selectivity of one gas over other is defined as, the ratio of the maximum response of other gas to the maximum response of the target gas at optimum temperature.

$$\text{Selectivity} = S_{gas} / S_{target\ gas} \quad (3)$$

3.4.2 Stabilization of Sensor

For the initial studies on gas sensing properties of M-CBD deposited ZnS thin films, the thermal run was carried out for the stabilization of sensor in ambient air prior to exposure of any gas. This thermal run is very important process because it ensures stable zero level for gas sensing application.

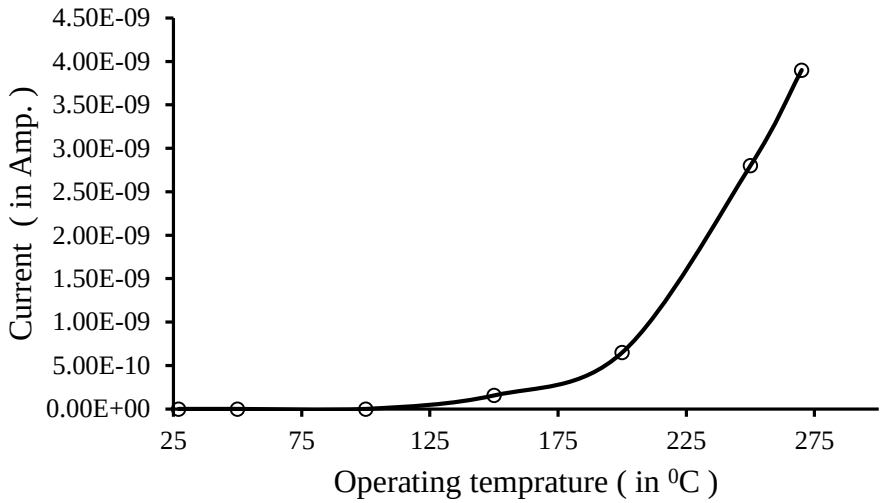

Fig 4: The typical initial stabilization curve of current of ZnS thin films sample at different temperatures (R.T. to 270 ^{0}C).

Fig.4showsthe typical initial stabilization curve of current of ZnS thin films sample at different operating temperatures (R.T. to 270 ^{0}C). Similar to CBD ZnS thin films, every time for each sample, prior to exposing the any gas on the ZnS film sensor, it was allowed to equilibrate inside the gas chamber for thermal run. In thermal run thin film was heated with interval of 20 ^{0}C and brings to room temperature this process was carried out upto 270^{0}C.

3.4.3 Effect of temperature

Fig. 5 depicts the variation gas responses as function of operating temperature of nanocrystalline ZnS thin films for different gases with 500 ppm concentration. From **fig. 6** it is observed that nanocrystalline MCBD ZnS thin film sensor

shows high sensitivity at 85^{0}C for Chlorine, H_2S and CO_2 gas.

The highest responses of MCBD deposited nanocrystallineZnS thin film for gases like LPG, H_2, NH_3, Cl_2, C_2H_5OH, H_2S and CO_2 were found to be 2.17%, 6.51%, 1.42%, 14.61%, 1.37%, 8.34% and 7.91% respectively. The sensitivity for LPG, H_2, Cl_2, H_2S and CO_2 was observed to increase with increase in temperature but in case of ammonia and ethanol the behavior of thin film sensor is quite different. For ethanol it is observed that gas response was starts from 250^{0}C and remains up to 270^{0}C. ZnS sensor shows highest sensitivity at 250^{0}C for ammonia and at 200^{0}Cfor chlorine.

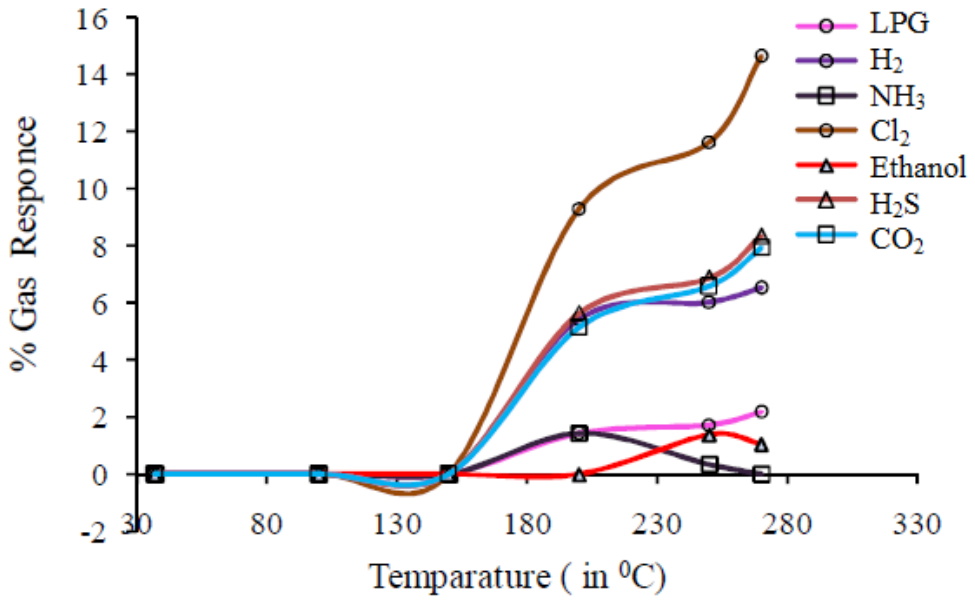

Fig. 5: Variation of gas response as function of operating temperature.

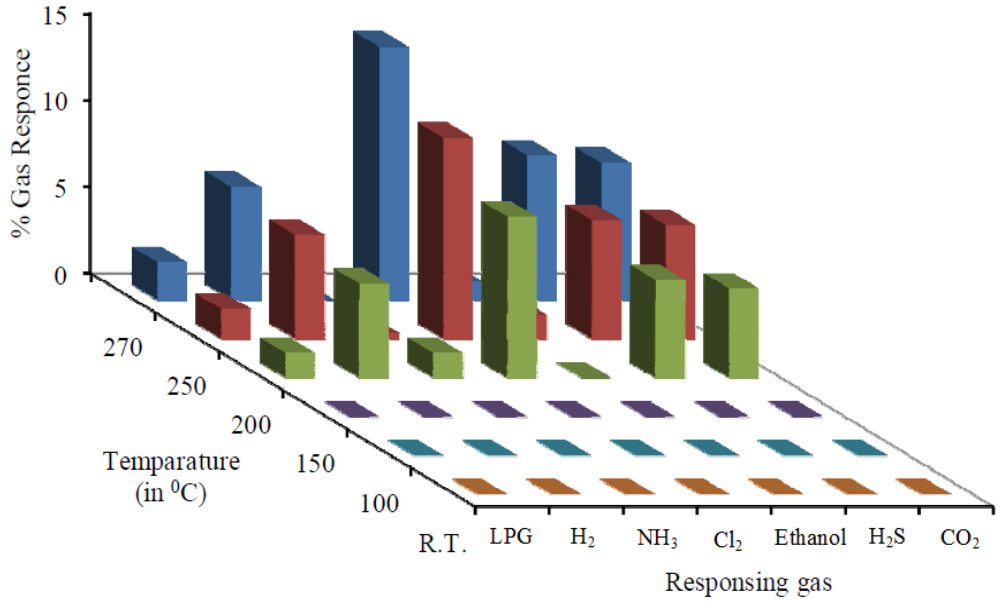

Fig. 6: Variation of gas response with operating temperature forZnS thin film gas sensor for different gases.

3.4.4 Selectivity of ZnS thin films for various gases

The gas response of MCBD deposited nanocrystalline ZnS thin film sensor was tested for ammonia (NH_3), carbon dioxide (CO_2), ethanol (C_2H_5OH), hydrogen sulphide (H_2S), liquid petroleum gas (LPG), hydrogen (H_2) and chlorine (Cl_2).

It is observed from **fig. 7** that the nanocrystalline ZnS sensor gives maximum response to Cl_2 gas at 270^0C. The nanocrystallineZnS thin film sensor showed highest selectivity for Cl_2 among all other tested gases.

In n type of semiconductors when any reducing gases comes in contact with the film surface its resistivity get decreases and for oxidizing gases its resistivity increases. In zinc sulphide thin films the gas sensing activity is by a change in electrical conductivity due to the interaction between the surface complexes such as O^-,O^{2-}, reactive chemical species (S^{2-}), and gas molecules to be detected[18]. When nanocrystallineZnS thin films are exposed to air, the oxygen molecules are adsorbed on the thin film surface as negatively charged ions by capturing free electrons from the semiconductor ZnS, thereby creating a depletion layer with a low conductivity near the nanorods surface.

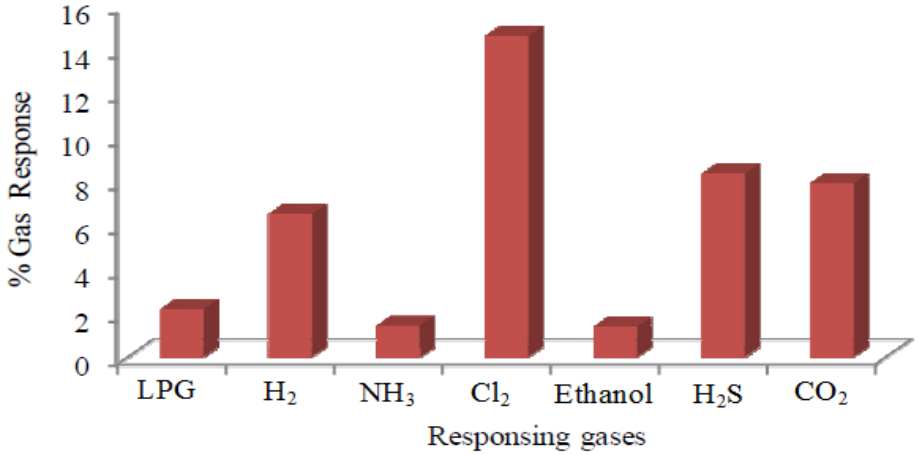

Fig.7: Selectivity of ZnS thin films for various gases at 500 ppm gas concentration.

Since the ZnSnanorods are very thin, they create a significant amount of surface acceptor states, leading to a high resistance in the normal state without any testing gas. The reason for the enhancement in conductance or resistance of our ZnSnanorods is due to the reaction on the material surface or removal of chemisorbed oxygen from the surface by testing gas. The Oxygen in air can be adsorbed on the surface of the semiconducting thin film sensor and following reactions were carried out, and hence different species of oxygen (O^2, O^{2-}, and O^-) capture the electrons [19, 20].

$$O_{2(gas)} \leftrightarrow O_{2(ads)} \quad \text{.....(A)}$$

$$O_{2(ads)} + e^- \leftrightarrow O_2^-{}_{(ads)} \quad \text{.....(B)}$$

$$O_2^-{}_{(ads)} + e^- \leftrightarrow 2O^-{}_{(ads)} \quad \text{.....(C)}$$

Reducing gases react with chemical species like S^{2-} and O^- resulting in a consequent increase in the conductance and oxidizing gases decrease the conductance. The semiconducting ZnS thin film gas sensor consists of ZnS semiconductor grains and have an electron or hole conductivity. The external effect of any gas influences the conductivity. It can change the conductivity of the bulk or the grain surface and the height on the grain boundary potential barriers. The gas molecules are active particles in semiconductor sulphides and create donor or acceptor states of the grain surface or in their bulk.

4 Conclusion

Here we observed that MCBD ZnS thin film sensor shows increase in conductivity for gases like like LPG, H_2, Cl_2, H_2S and CO_2 and decrease in conductivity for gases like NH_3, C_2H_5OH at 270^0C i.e. surface chemistry of nanocrystalline ZnS thin film sensor is suitable for gas sensing of various gases.

References

[1] V. Dimitrova, J. Tate, *Thin Solid films*, **365**, 134, (2000).

[2] M. C. Lopez, J. P. Espinos, F. Martin, D. Leinen, J.R. Ramos-Barrado, *J.of Cryst Growth.***285**, 66, (2005).

[3] M. Yoneta, M. Ohishi, H. Saito, *J. of Cryst.Growth*, 127, 314, (1993).

[4] I.O. Oldaji, L. Chow,*Thin Solid Films*, **339**, 148, (1999).

[5] U.Baishya and D.Sarkar. *Indian Journal of Pure and Applied Physics*, Vol.**49**, PP.186-189, (March2011).

[6] F.Gode, C.Gumus,M.Zor, *Journal of Crystal Growth*,299, 136-141, (2007).

[7] M. S. Shinde, P. B. Ahirrao, I. J. Patil and R. S. Patil, *Indian Journal of Pure & Applied Physics*, Vol.**49**, 765-768, November (2011).

[8] M. Gunasekaran, R, Gopala Krishnan, P. Ramasamy. *Mat.Lett*, 58, 67, (2003).

[9] Y.S. Kim, S.J. Yun, *Appl. Surf. Sci.*, **229**, 105, (2004).

[10] Y.S. Seol, H.B. *ImJ. of Mater.Sci.***22**, 3533, (1987).

[11] Y. G. Liu, P. Feng, X. Y. Xue, S. L. Shi, X. Q. Fu, C. Wang,Y. G. Wang and T. H. Wang,*Applied Physics Letters*, Volume **90** Issue 4, pages 42109-11, (2007).

[12] Zhi-gang Chen,Jin Zou, Gang Liu, Hao Feng Lu,FengLi,GaoQing and Hui Ming Cheng Silicon-induced oriented ZnSnanobelts for hydrogen sensitivity,*Nanotechnlogy***19**, 055710 (5 pages), (2008).

[13] SalihOkur, NeslihanUzar, NesliTekgüzel,AyseErol and M. Cetin Arikan, *Physica E: Low-dimensional Systems and Nanostructures*, Volume **44**, issue 6, p. 1103-1107, (March, 2012).

[14] N Uzar, S Okur and MC ArikanSens Actuators A Phys**167(2),** 188-193, (2011).

[15] Xu L, Song H, Zhang T, Fan H, Fan L, Wang Y, Dong B, Bai**11(3)**, 2121-5, (2011).

[16] M. Hafeez, U. Manzoor and A. S. Bhatti,*Journal of Materials Science: Materials in Electronics*, Volume **22**, Number 12, 1772-1777, (2011).

[17] A. Cottrell, Intorduction to Mettallurgy, Arnold, Londan, P.173, (1975).

[18] Zhi-gang Chen, Jin Zou, Gang Liu, Hao Feng Lu, Feng Li, Gao Qing and Hui Ming Cheng *Nanotechnlogy*,**19**, 055710 (5 pages), (2008).

[19] V. R. Shinde, T. P. Gujar, C. D. Lokhande, R. S. Mane, Sung-Hwan Han, *Materials Science and Engineering B-advanced Functional Solid-state Materials*, vol. **137**, no. 1, pp. 119-125, (2007).

[20] V. R. Shinde, T. P. Gujar, C. D. Lokhande, R. S. Mane, Sung-Hwan Han, Sensor Actuator B-Chem , vol. **123**, no. 2, pp. 882-887, (2007).