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H_2S gas sensing Performance of ZnO thin films prepared by spray CVD technique.

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Abstract : Hydrogen sulfide (H_2S) is a corrosive, malodorous toxic and flammable gas. It is normally generated from mines, sewage, gasoline, petroleum fields, natural gas production etc. It is tremendously dangerous to both environment and human beings. Therefore monitoring and controlling of H2S is very vital for the safety of human being and atmosphere. In nanotechnology era more attention is given to develop nanostructures metal-oxide semiconductors for various applications in day to day life. In that more importance is given to shape and morphology of particle. However it is not easy to control morphology as compared to particle size. Which required development of novel synthesis method or process to achieve the same and used for gas sensing. Practically it should be simple and cost effective method. On these considerations chemical methods are more suitable than physical process. Zinc oxide (ZnO) is a very fascinating material due to its versatile application generated by various properties like wide band gap (3.37 eV), high excitation binding energy (60 meV) and hexagonal wurtzite structure. 0.075M intrinsic ZnO thin film prepared at 330 ˚C core temperature and low substrate temperature (220˚C) by using modified spray CVD technique to sense H_2S gas. The structural investigation is done using XRD. The film surface and three dimensional morphology are studied with FESEM and AFM respectively. Pure ZnO thin film shows sensitivity S≈20% (S=Ra-Rg/Ra) to 10 ppm of H_2S gas at 300 ˚C operating temperature with fast response and recovery time.
Keywords: ZnO, Thin film, Spray CVD, H_2S sensing.

Introduction

Hydrogen sulfide (H_2S) is a corrosive, malodorous toxic and flammable gas. It is normally generated from mines, sewage, gasoline, petroleum fields, natural gas production etc. It is tremendously dangerous to environment and human beings. The human nose can sense H_2S gas level up to 0.02 ppm, generally there maximum sensitivity is approximately up to 5 ppm. The additional exposure to the gas influences the nervous system of human and even death can happen at very low concentration[1,2,3,4,5,6]. Therefore monitoring and controlling of H_2S is very vital for the safety of human being[7]. It is a need to have H_2S sensor with good response, sensitivity, repeatability, low cost, low detection limit and easy fabrication process. Metal oxide semiconductor materials such as ZnO. SnO2, WO3, In2O3, CeO2, Fe2O3, composite etc based gas sensor are generally used for monitoring in environmental and industrial applications[8,9,10,11,12].

Zinc oxide is a very fascinating material due to its versatile application generated by the particular properties. The different keystone properties are wide band gap (3.37 eV), high excitation binding energy (60 meV), hexagonal wurtzite structure[13]. Various methods are used for synthesis of ZnO thin film. Epitaxy method was used to developed hexagonal ZnO nanostructure[14], PVD method[15], MOCVD epitaxial method[16] for the fabrication of vertical nanorods of zinc oxide at 400^{o}C. Z. Solid state pyrolytic reaction[17]. RF magnetron sputtering[18] and CVD[19] technique for wide range at room temperature to 330 ˚C. The effect of post annealing treatment with RF sputtering is reported[20]. Spin coated sol-gel method is also reported[21]. In 2000 spray pyrolysis technique for ZnO thin film deposition is used[22].

The present paper describes the deposition of Zinc oxide film from pure zinc acetate. The ZnO films were fabricated by using Spray CVD technique. The structural investigations were done using XRD. The film surface and three dimensional morphology are studied with FESEM and AFM respectively. Pure ZnO thin film shows sensitivity of S≈20% (S=Ra-Rg/Ra) to 10 ppm of H2S gas at 300^{O}C operating temperature with fast response and recovery time.

Experimental Techniques

Synthesis

A 0.075M solution of pure zinc acetate [Zn(CH3COO) 2.2H2O] (Thomas Baker, India) in methanol was used to prepared ZnO thin film by spray CVD method. The substrates were cleaned in the laboratory by using the standard procedure to obtain good quality films. The distance between substrate and spray nozzle was 38 cm. The compressed air the spray rate of 6 ml/min was maintained constant. Before synthesis of ZnO thin film the TG-DTA analysis was done to obtain the decomposition temperature and it was found to be 330^{o}C. The difference preparation parameters were optimized to obtain the good quality thin film of zinc oxide. The effect of variation in reaction chamber temperature or core temperature was studied. The core temperature was varied from 300˚C to 360˚C in step of 30˚C and four samples were prepared at constant substrate temperature (220˚C). In second part substrate temperature was varied from 190˚C to 250˚C in steps of 30˚C keeping core temperature constant at 330˚C. The temperature was controlled by electronic temperature controllers. It is to be noted that each film is deposited for 3 times and the results obtained confirmed that films are reproducible.

Structural and Morphological analysis

The crystal structure of film was studied by brukar AXS X-ray diffractometer. The film thickness and roughness was measured by Ambios XP-1 profilometer. The surface morphology was investigated by the field emission scanning electron micrograph (FESEM). The electrical properties such as conductivity, resistivity, carrier concentration, mobility and sheet resistance were obtained by Vander Pauw method and Hall Effect setup. For ohmic contact silver paste was used. Three dimensional morphology of the film was investigated by atomic force microscopy (AFM) by using Nanoscope instruments USA in contact mode with V shape silicon nitrate cantilever of length 100 µm and 0.58 N/m spring constant.

Gas response measurements

The gas sensing unit assembly is designed in the laboratory to test hazardous gases are shown in the Fig. 1. It consists of hot plate which is inserted enclosed in airtight SS housing. The gas is inserted into the chamber from septum with a rubber gasket at lower part of spring pressure contact is made up with film under test. A Rigol DM 3062 Digital multimeter is used to measure the resistance connected through external leads, with and without revealing the H_2S gas. The film is placed on the heater block, the heater temperature is monitored and controlled by using PID controller and its resistance is monitored with computer interfaced multimeter. The desired gas ppm concentration is taken from the canister, containing pressurized gas approximately 20 Kg/cm² at 1000 ppm, by using syringe and injected into SS housing. The response and recovery time of H_2S gas is also measured by using Rigol digital multimeter as a function of time.

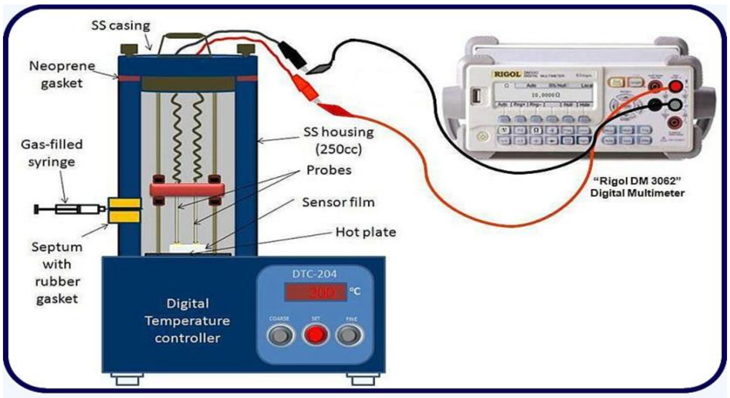

Fig. 1 Schematic diagram of the Gas sensor unit

3. Result and discussion

During the deposition zinc acetate droplets arrived in reaction chamber, where they get thermally decomposed and converted into fine particles of zinc oxide and other byproducts. These fine particles were pushed upwards by air pressure and arrive at preheated substrate. Pre-heated substrate initiates the nucleation centers for the growth of film and provides average kinetic energy for the uniform deposition. Therefore deposition occurs in two steps i) requisite chemical pyrolysis ii) nucleation process. The substrate temperature, air pressure, distance between nozzle and substrate decide the large area and crack free deposition on the substrate.

To obtain a good quality ZnO thin film, it is essential to optimize some preparative parameters such as core temperature, spray rate, substrate temperature etc. The following sections explain the optimization of the crucial parameters.

Characterization and electric property due to variation in core temperature

X-ray diffraction studies

Figure 2 shows the X-ray diffraction pattern for the ZnO thin film prepared at different core temperature varied from 300 to 360˚C in steps of 30˚C. It shows that ZnO films are polycrystalline, with hexagonal close packed structure. ZnO films exhibits the preferential orientation along (002) plane. These results are similar to the results reported[23]. Some other minor diffraction planes are observed along (100), (101) (102), (110), (103), (200) and (112) planes. The d values observed are in good agreement with the standard values reported in PDF for ZnO thin film (JCPDS card file no. 80-0075, a=3.2498 and c=5.2066 Å) which confirms the polycrystalline wrutize structure of ZnO. The film deposited at 330˚C core temperature shows highly oriented films as compare to film at other temperature. It is also observed that crystalline size is optimum at 330˚C core temperature (22 nm).

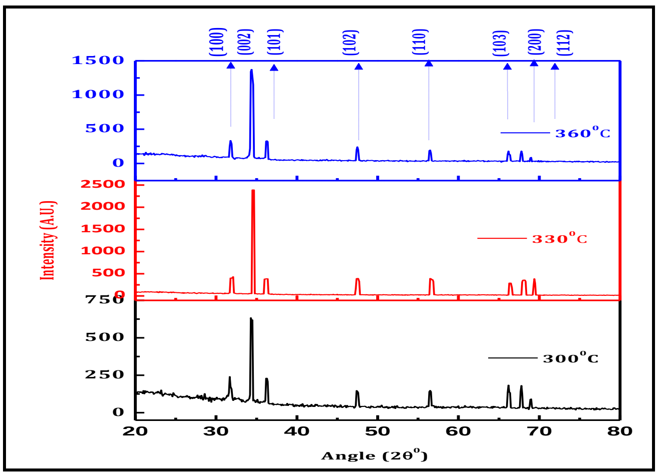

Fig. 2 XRD patterns for core temperature variation of ZnO thin films

Surface morphology

The surface morphology of undoped ZnO nanocrystals shows interesting dependency on the core temperature. From FESEM shown in Fig.3, it is observed that films are cracks free with good uniformity and all samples exhibits polycrystalline morphology. The film developed at 330 ˚C core temperature is more compact and grain size is maximum. Fig. 4 shows the atomic force micrograph (AFM) of ZnO film developed at 330 ˚C core temperature. Film is uniform, dense and well packed. The surface thickness and roughness is also analyzed by using AFM as shown in Fig. 5. It is seen that due to pyramidal shape grains the roughness of film increases.

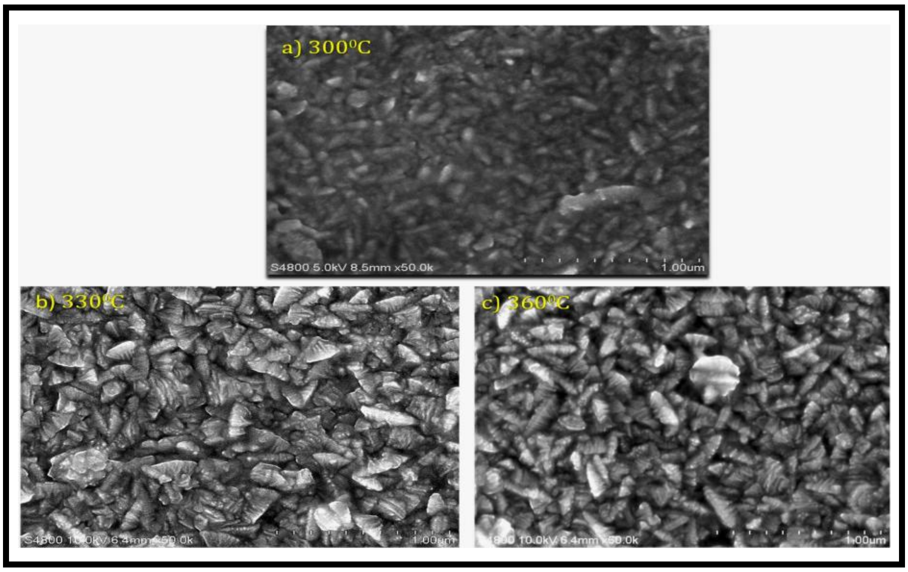

Fig. 3 Plain view FESEM micrographs for ZnO films prepared at various core temperatures

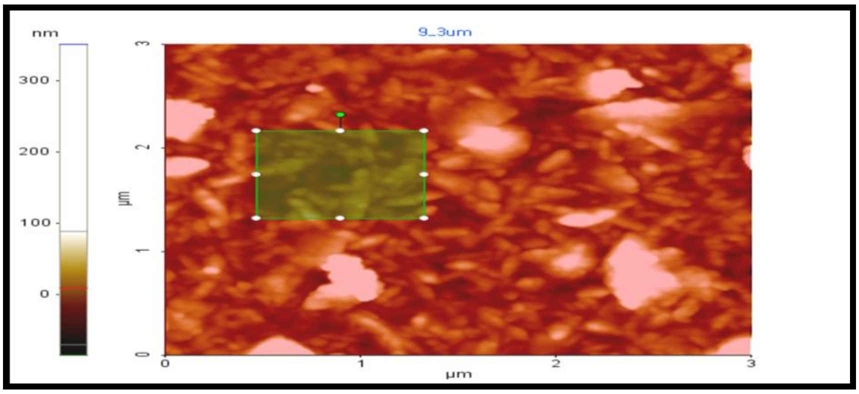

Figure. 4 AFM micrograph of a typical undoped ZnO at 330^{0}C

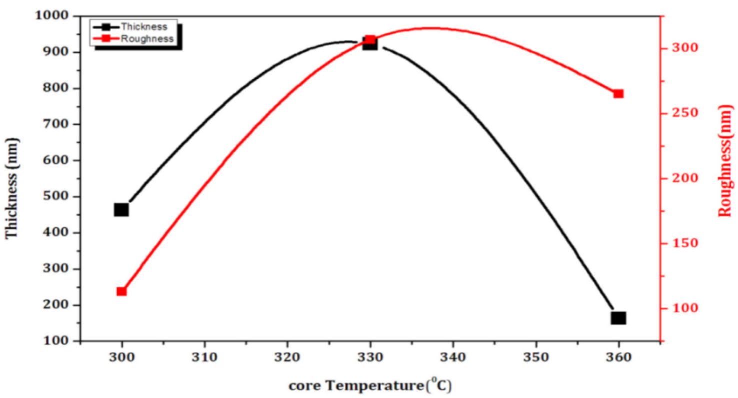

Fig. 5 Variation thickness and roughness of ZnO thin film with core

Electrical Resistivity

Fig.6 shows plot of ln(σ) versus 1000/T for the ZnO thin film deposited by spray CVD method at different core temperature. It shows semiconducting properties, at room temperature resistivity was in the range of 10^{-2} Ω-cm for the sample developed at 330 ˚C core temperature. The activation energies are observed between 0.08 to 0.27 eV, are calculated from the slope of graph. For polycrystalline structure with lower carrier density (<10^{20}), resistivity is mostly due to grain boundary electron trapping[24,25]. Resistivity is minimum for the sample prepared at 330 ˚C core temperature, which indicates that film has good crystalline size.

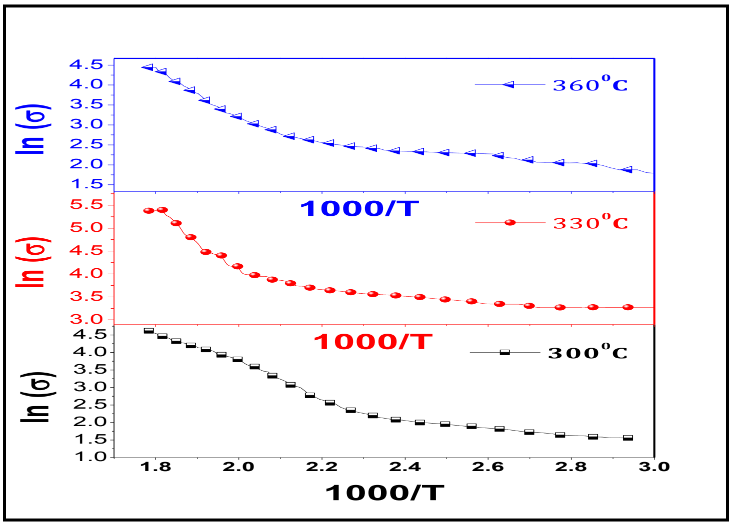

Fig.6 Variation of ln(σ) with (1000/T) for ZnO thin film.

Characterization and electric property due to variation in substrate temperature

The XRD diffraction pattern for the ZnO thin film deposited at various substrate temperatures are shown in Fig.7 and are deposited at 190˚C to 250˚C in steps of 30˚C. It has three well defined peaks, (100), (002) and (101) which specify ZnO has a polycrystalline wurzite structure. All samples show dominants intensities for the (002) peak, which are oriented along c-axis normal to the substrate[26]. It is observed that among all films, the film prepared at 220˚C substrate temperature shows high preferential orientation along c-axis. Therefore this is optimized substrate temperature[27].

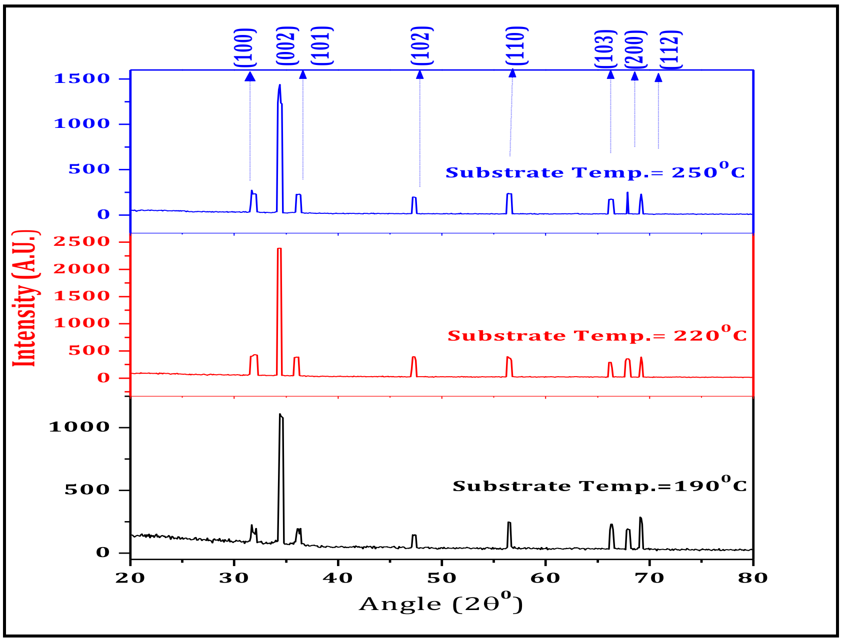

Fig.7 XRD patterns of ZnO thin films with substrate temperature variation

Surface morphology

The plain view FESEM of ZnO thin film obtained at various substrate temperatures. In general for all films no cracks are observed on large scan area. The more irregular growth is observed at low substrate temperature (190 ˚C) and high (250 ˚C) substrate temperature, slightly regular growth is examined at 220˚C substrate temperature. Fig.8 shows the 3D topography of the ZnO obtained at 220˚C substrate temperature. It supports the results obtained from FESEM and XRD. The 3D topography shows large height of triangular shaped pyramids which prove the growth along c-axis normal to substrate as observed in XRD. Fig.9 shows roughness variation and thickness recorded by the XP-1 surface profiler for all samples. The shape of grain increases the roughness for samples of 220˚C substrate temperature as compared to other samples.

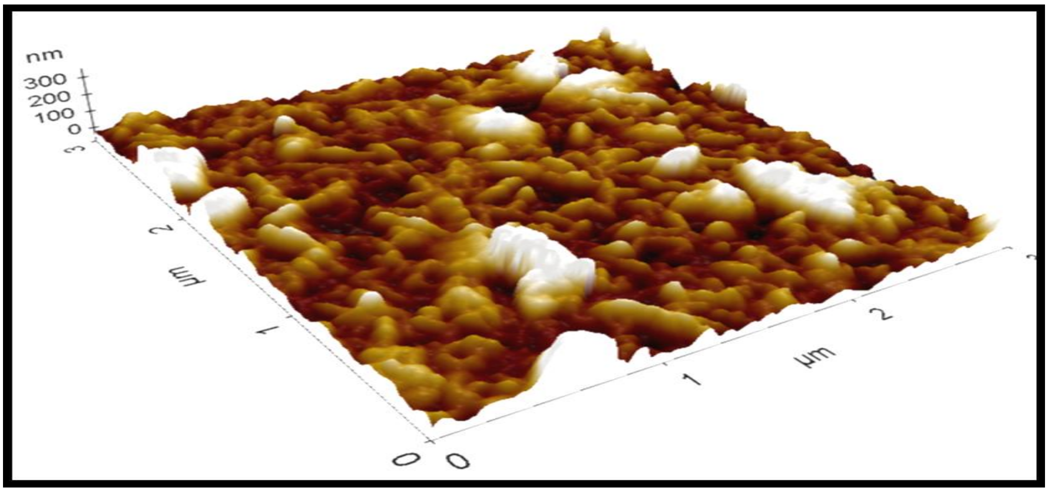

Fig. 8 (3D) Topography for a typical 220^{0}C substrate temperature

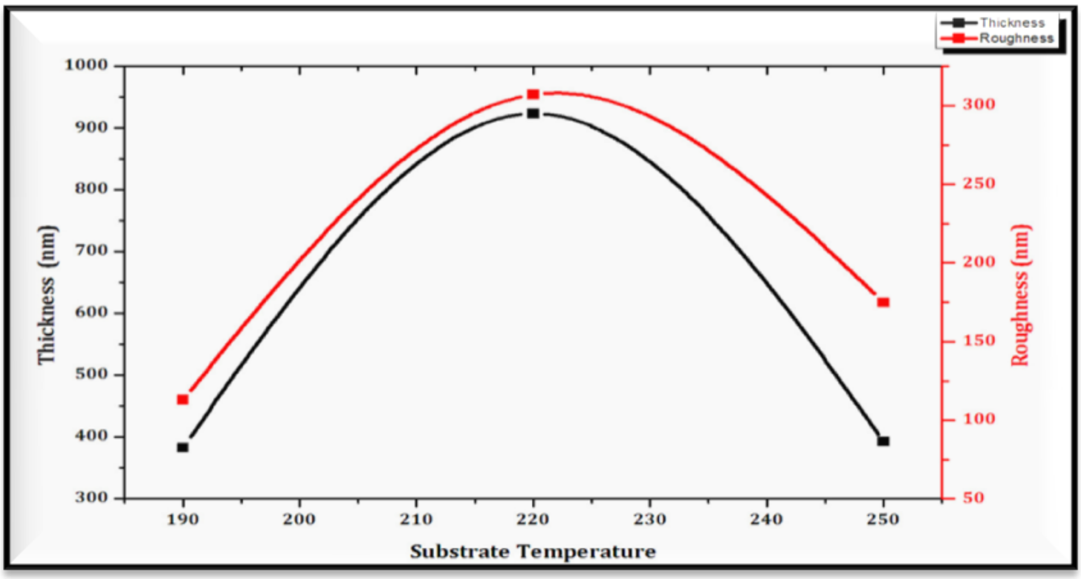

Fig. 9 Variation of Thickness and Roughness with substrate temperature

Electrical resistivity

Fig.10 shows the plot of ln(σ) version 1000/T for the ZnO thin film obtained at various substrate temperatures. It shows semiconducting properties of ZnO thin film. In low temperature region of conduction, the conductivity increases due to increases in mobility. Therefore small energy is required for conduction process. In high temperature region, the conductivity increases may be due to adsorbed oxygen molecules from the surface, which decreases the potential barrier at grains boundaries. The activation energy in the low temperature region is always less than high temperature region and high activation energy is called intrinsic conduction[28,29]. As compared to other samples activation energy is low in both regions for sample obtained at 220 ˚C substrate temperature.

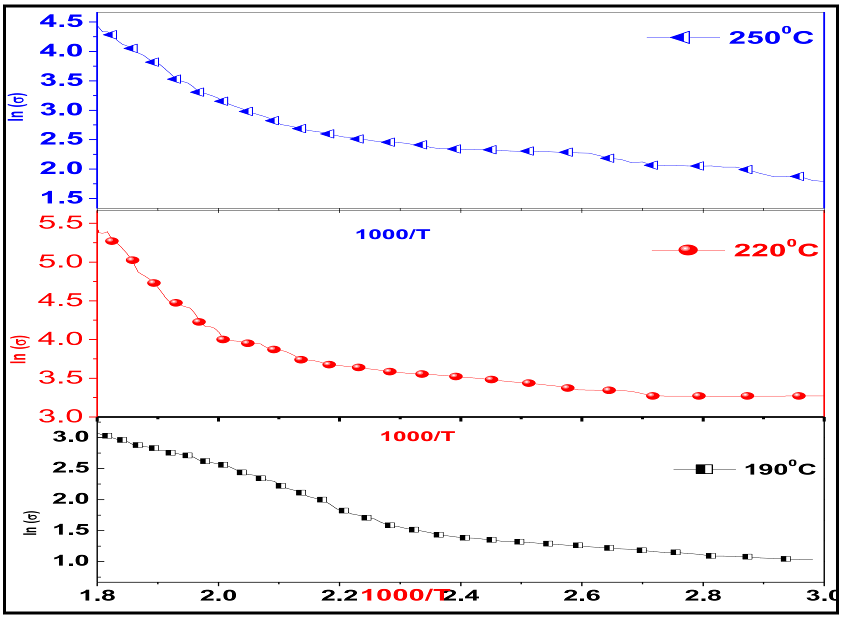

Fig.10 Variation of ln (σ) Vs 1000/T with substrate temperature

H2S sensing studies

As discussed in section two ZnO thin films are prepared at optimize preparative parameters by modified spray CVD technique. Out of these pure 0.075M ZnO thin film prepared at 330˚C core temperature and 220˚C substrate temperatures are used for the H2S gas sensing.

Resistance Stabilization

Fig.11 shows variation of resistance with time; initially the resistance was decrease rapidly up to 50 seconds at 300˚C operating temperature and afterwards it remains constant. Before exposing the films to H2S gas the films are allowed to stabilized inside the chamber nearly for 10 minutes and stabilized resistance were taken as *Ra*. The stabilization is faster when operating temperature is high. Therefore pre heating of sensor is required.

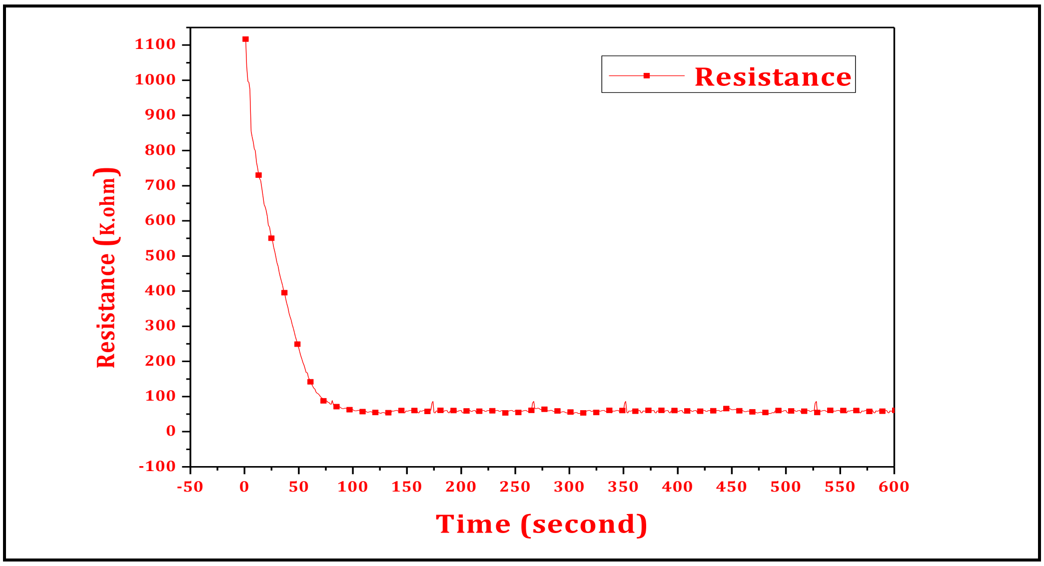

Fig.11 Stabilization curve for ZnO thin film at 300°C operating temperature.

Variation in operating temperature

It is well known that sensitivity of gas sensor is mainly dependent on the operating temperature in order to obtained the optimum operating temperature, response of ZnO thin film at 10 ppm of H_2S at operating temperatures ranges from 250˚C to 325˚C in steps of 25˚C were examined. The samples are named as A, B, C and D for operating temperature 250°C, 275°C, 300°C, and 325°C respectively. The variation of resistance as a function of time is used to calculate the sensitivity of sensor. It can be given as,

$$S = \frac{(Ra - Rg)}{Ra} \times 100 \qquad (1)$$

Where 'R_a' is the resistance of sensor ambient environment while 'R_g' is the resistance measured in test gas environment. Out off all samples the sample 'C ' shows fast response and recovery time with maximum sensitivity of 20% at 300˚C operating temperature as shown in Fig.12 and 13 respectively. From these figures, it clear that operating temperature plays a very important role in achieving the maximum response to a gas of interest. When the sensor is exposed to reducing gas at a particular operating temperature the oxygen adsorbents are removed by reduction reaction mechanism. Therefore the steady state coverage of adsorbents is decreases and hence operating temperature plays an important role[30-32]. At the optimal operating temperature, H2S reacts to the sensor surface to inject the electron into conduction band, because of that electron concentration increases. This decreases the resistance. On the other hand the higher operating temperature causes to increases the carrier concentration, which reduces the Debye length and this might be one of the reason for decreased in gas response at higher operating temperature as in case of sample 'D' shown in Fig.14. This also shows 300 ˚C is the optimized operating temperature to sense H_2S gas by ZnO sensor. Similar results are reported for CO gas with Al doped ZnO sensor[33]. At low operating temperature the respective sensitivity is also low because H_2S gas molecules doesn't has sufficient thermal energy to react with oxygen species at the surface.

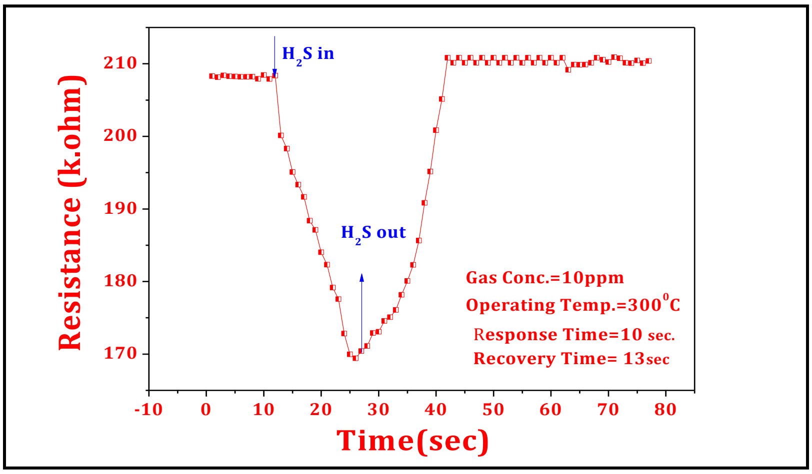

Fig.12 H_2S gas response of ZnO thin films for 300˚C operating temperature.

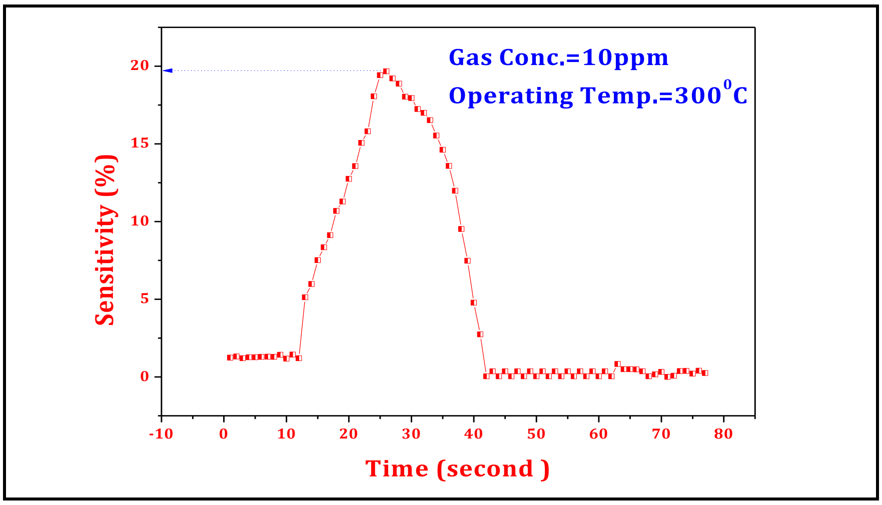

Fig.13 Typical H_2S gas Sensitivity at 300^{0}C operating temperature for ZnO thin film.

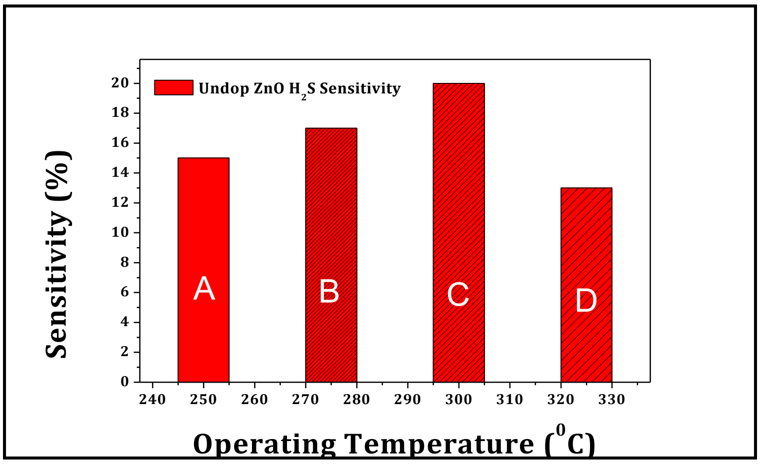

Fig.14 H_2S gas Sensitivity of ZnO thin film as a function of operating temperature

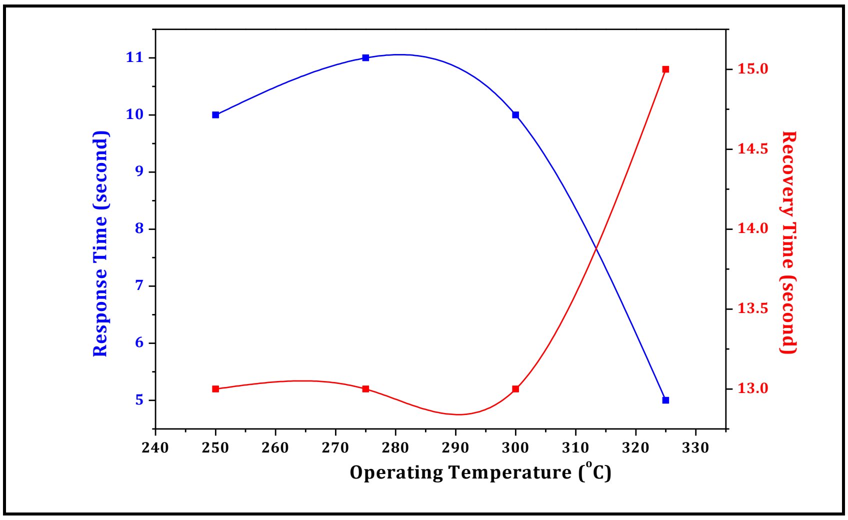

Fig.15 Transient response of H_2S gas w. r. t. operating temperature.

When the operating temperature increases to 300˚C, the adsorbed oxygen gets converted from $O2^-$ to O^- by which thermal energy created was high to overcome energy barrier. Response and recovery time are the essential parameters of gas sensor. These are generally defined as the amount of time required to reach to 90% of the desired final resistance for the sensor. The average response time of 10 second is observed for full operating temperature range except for sample 'D' as shown in Fig.12. The effect of both response and recovery time with change in operating temperature for all samples are shown in Fig.15. This indicates the fast response to H2S gas with rise in operating temperature but small delay to recover in environment.

Conclusions

In summary, ZnO thin film sensor can be prepared by modified spray CVD technique. The effect of variation in core and substrate temperature on the structural and electrical properties has been studied. The ZnO thin film is prepared at 330˚C core temperature and 220˚C substrate temperature, used for H2S gas sensing. Among all the samples tested, the sample tested at operating temperature 300˚C exhibits highest response (S≈20%) and easily detects the low concentration (10 ppm of H2S).

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