Studying the Effect of Seed-layers of Zinc Oxide Nanostructured Thin Film for Liquefied Petroleum Gas Sensor Application

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Abstract

Gas sensors are devices that can convert the concentration of an analyte gas into an electronic signal. Zinc oxide (ZnO) is one of the most important n-type metal oxide semiconductor which has been utilized as gas sensor for many years. In this work, ZnO nanostructured films were synthesized by a hydrothermal growth from ZnO seeds and used as a liquefied petroleum gas (LPG) sensor. At first ZnO seed layers were deposited on glass substrates by using spin coating method, then ZnO nanostructured were grown on these substrates by using hydrothermal growth method. The effect of seed layers of ZnO nanostructured on its structural, optical, and electrical properties was studied. These nanostructures were characterized by scanning electron microscopy, X-ray diffraction, optical spectroscopy, and sheet resistance measurement unit. The sensing performances of the synthetic ZnO nanostructures were investigated for LPG. XRD showed that all the ZnO nanostructures were hexagonal crystal structure. ZnO nanostructured thin film showed high sensitivity towards LPG gas. The sensitivity of the film is observed to increase with increase in number of seed layers. The sensitivity of the film was investigated by measured change in sheet resistance under with LPG gas.

Keywords: Thin film; Gas sensor; Nanostructure; Hydrothermal growth.

Introduction

To monitoring the air quality in city areas has become a priority due to the great amounts of pollutants released in the atmosphere which have a harmful effect on the human and animal's health and also on the vegetation [1]. Gas sensors are devices that can convert the concentration of an analyte gas into an electronic signal, and are an important component of devices commonly known as electric noses [2].

To detect pollutant gases different kinds of gas sensor have been developed. In the past eighty years, scientists have developed various gas sensors such as electrochemical sensors, catalytic combustion sensors, infrared sensors, and diffusion fuel cell sensors [2]. These sensors have large amount of application in chemical engineering, medical,

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agriculture, architecture and other fields. These are electrolyte-based potentiometric sensors for automobile exhaust monitoring and another important type of commercial sensor is the metal oxide semiconductor gas sensor, e.g. SnO_2, which uses changes in resistance of the metal oxide to detect the low concentration of gases [2].
In this thesis work, we have developed and characterized the ZnO nanostructured thin film on glass substrate by hydrothermal method and used for LPG gas sensor application. For this work, at first we have deposited ZnO thin film on glass substrates and synthesized ZnO nanostructured thin film for different seeds layers. Then this sample is characterized by using different instruments.

Methodology

Zinc acetate dehydrate was first dissolved in mixture of ethanol and di-ethanolamine (DEA) solution at room temperature. The molar ratio of DEA to Zinc acetate was maintained nearly 1.0 and the concentration of Zinc acetate was 0.6M. The solution was stirred at 60^0C for 2 hours to get a clear and homogeneous solution which served as precursor. This solution was filtered through Whatman filter paper [4].The prepared Zinc acetate precursor was dripped on to spin coated substrate. The spinning velocity of the substrate was more than 2500 rpm initially and then 3000 rpm for 40 seconds in order to spread the colloid on to the glass with uniform thin layer. The deposited film is heated at 400^0C for 10 min. After that the same coating process is repeated for different 2 layers, 3 layers, 5 layers, and 8 layers to get uniform, transparent and conducting thin film of ZnO.

For nanostructure growth solution, Zinc nitrate hexahydrate [Zn (NO3)2].6H2O, hexamethylene-tetramine (C6H12N4) (A.R. grade) and DI water were used as starting materials and solvent respectively. Zinc nitrate hexahydrate and hexamethylenetetramine was first dissolved in DI water at room temperature. The concentration of Zinc nitrate hexahydrate and hexamethylenetetramine was 0.3M. The solution was stirred at 60^0C for 2 hours to yield a clear and homogeneous solution which served as precursor. The precursor solution was filtered through Whatman filter paper [6].

Now, for hydrothermal growth, the prepared ZnO solution was taken into an air tight glass bottle. Then the ZnO seeds layer deposited substrates was immersed in precursor solution, which solution was taken into air tight glass bottle. Then that glass bottle was immersed into a preheated water bath at 70℃ for different time duration such as 2hrs, 4hrs, 6hrs, 8hrs, and up to10hrs. After cooling, the ZnO film were washed with de-ionized water several times, and then dried in air. The crystallinity of the ZnO films was determined by X- ray diffractometer. Optical transmittance was obtained using USB 2000 photonics spectrometer. The electrical properties were determined from

sheet resistance measurement. Morphology and dimension of the ZnO nanostructures thin film was studied by scanning electron microscopy (SEM). The LPG sensing properties were studied in a gas sensor assembly comprising a temperature controller, a chromel-alumel thermocouple, an electrical heating plate, a gas chamber, and a LPG volume measurement unit.

Results and discussion

Here we study the structural properties of ZnO seed layers and ZnO nanostructured thin film on glass substrates. Typical XRD patterns of 8 coated ZnO seed layers are shown in Fig.1. From Table 1, we find that, the crystalline peaks with 2θvalues can be exactly indexed to the hexagonal wurtzite structured ZnO (JCPDS card no 03-0891). The sharp diffraction peaks indicate the good polycrystallinity of the prepared films and no peaks for other zinc compounds are detected in the different pattern.

Table.1. JCPDS d-values, observed d-values, intensity measured for (hkl) plane ($I_{(hkl)}$), intensity of (hkl) plane taken from the JCPDS card ($I_{0(hkl)}$), and observed 2θvalue of ZnO seed layers.

JCPDS(card no 03-0891)d-values (A^0)	Observed d-values (A^0)	$I_{0(hkl)}$	$I_{(hkl)}$	Observed 2θvalue
2.8000	2.8010	90	66	32
2.6000	2.5979	60	100	34.5
2.4600	2.4662	100	89	36.4
1.9000	1.9473	80	20	47.6
1.6300	1.6274	100	19	56.5
1.4800	1.4743	90	23	63
1.3800	1.3775	100	15	68
1.3600	1.3599	70	10	69

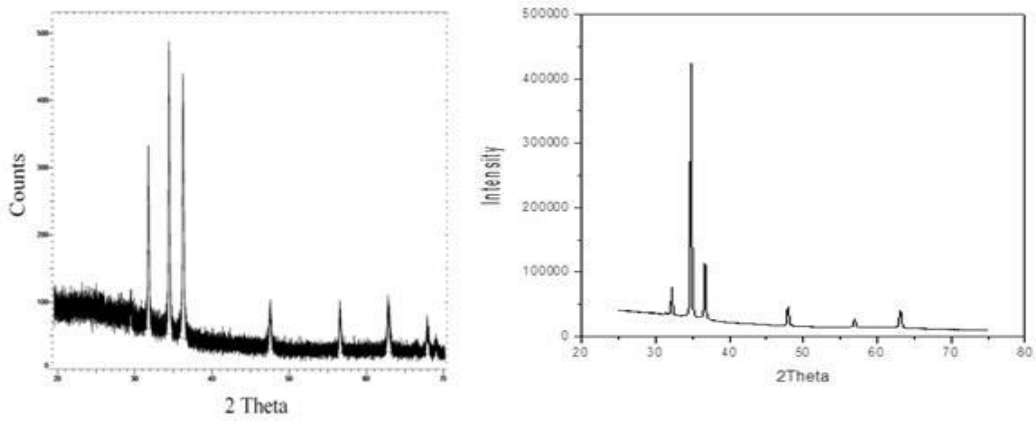

Fig.1. Observed XRD pattern of ZnO seed layers and nanostructured thin film (Hydrothermal growth for 10 hours).

Table.2. FWHM value (β), grain size (D), intensity measured for (hkl) plane ($I_{(hkl)}$), intensity of (hkl) plane taken from the JCPDS card ($I_{0\,(hkl)}$), dislocation density(δ), d-values and texture coefficient ($T_{c\,(hkl)}$) of ZnO nanostructured thin film.

JCPDS (card no 03-0752) **d-values** (A^0)	**Obser-ved d-values** (A^0)	**Obse-rved 2θ-valu-es**	**FWHM**	**D(nm)**	$I_{(hkl)}$	$I_{0(hkl)}$	$T_{c(hkl)}$	δ/nm^2 $\times10^{-5}$
–	2.85	31.3	2.3	37	1.43	–	–	0.0073
2.7800	2.7781	32.19	0.169	511	11	100	0.40	0.382
2.5800	2.57624	34.79	0.1534	567	100	80	4.59	0.311
2.4400	2.44897	36.66	0.1761	496	27	100	0.99	0.406
1.8900	1.89792	47.88	0.2288	397	11	100	0.40	0.634
1.600	1.61675	56.90	0.205	460	5	100	0.18	0.472
1.4700	1.47342	63.09	0.2645	363	12	100	0.44	0.758

Texture coefficients of crystalline materials are calculated from the XRD result by using the relation [7],

$$T_{c(hkl)} = \frac{I_{(hkl)} / I_{0(hkl)}}{\frac{1}{n}\sum_n I_{(hkl)} / I_{0(hkl)}}$$

Where $T_{c(hkl)}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity measured for (hkl)plane, $I_{0(hkl)}$ is the intensity of (hkl) plane taken from the JCPDS card (card no. 03-0752) fitting in the X-ray diffraction pattern material, n is the number of diffraction peak. The calculated texture coefficient values of ZnO nanostructures thin film for different (hkl) planes are shown in Table 2.

Further investigations on the dimension of the nanostructures, grown by hydrothermal synthesis were investigated by scanning electron microscopy (SEM).

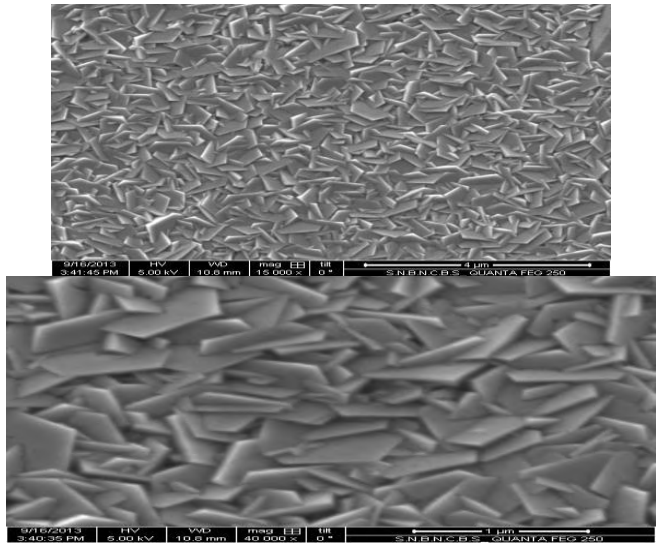

Fig.2. SEM images of (8 coating) ZnOnanosheet synthesized by hydrothermal route for 2hours at different resolution (a) 4µm (b) 1µm resolution.

Fig.2. shows SEM image of ZnO film synthesized by hydrothermal route for 2 hours and Fig. 3 shows the SEM image of ZnO film synthesized for 10 hours. From this figure we find that nano sheet like structures were formed in both cases. The average dimensions of the nanostructures were measured based on the image. From figure the average thickness of plate like nanostructures was about 10 nm, which is slightly lower than the result of Shao et al. [8] and Li et al. [9]. From this image the average length and width of nanostructures is observed to be about 550 nm and 220 nm, respectively, which is also slightly lower than the values observed by different research group [10].

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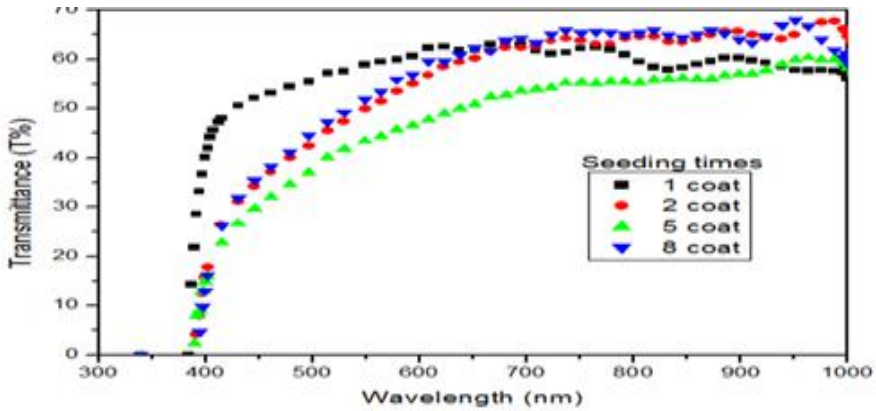

Fig. 3. Optical transmittance spectra of ZnO nanostructured films fabricated at 70℃ for different seed layers.

Fig. 3.shows the transmittance of the ZnO nanostructured thin film fabricated at 70℃ for different seed layers. From Fig.4.10 we have calculated the average transmittance of the film, in the wavelength ranging from 300-1000 nm. The average transmittance was observed to be different for different coat. The average transmittance of the film for 1, 2, 5 and 8 coats of seed layer is observed to be nearly about 60%, 65%, 50% and 65% respectively. From the Fig. 8, it is clearly observed that in all case the average transmittance is observed to be less than 65% in the wavelength range 300-1000 nm, regardless the seeding layer. When the deposition condition like substrate temperature and other chemicals are kept fixed the value of transmittance changes according to change in the seeding time. From the graph it is observed that transmittance starts to decrease rapidly at lower range of wavelength.

Fig. 4. below depicts the variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) film prepared at same growth time, but have different seed layers of ZnO nanostructured thin film. From the figure we see that the allowed direct band gap decrease from 3.175 eV to 3.092 eV with the increase the seed layers. The band gap is observed to be 3.175 eV for one coated sample, but for 2, 5 and 8 coated
Sample have nearly about 3.092 eV.

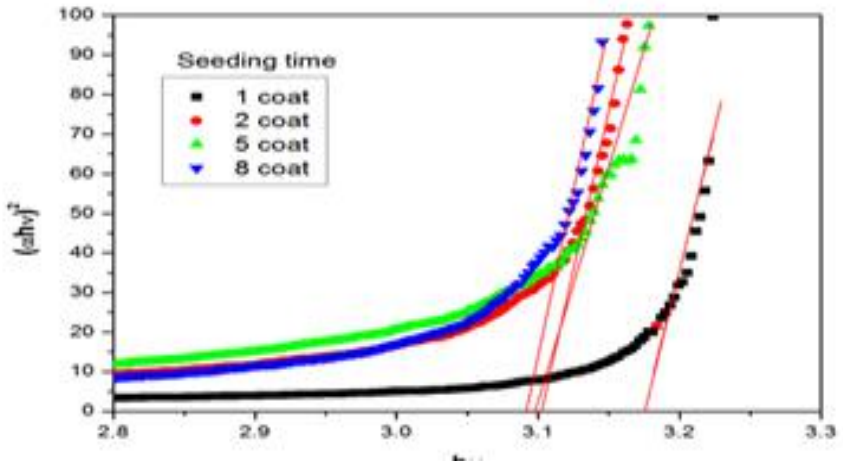

Fig. 4. $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for the ZnO nanostructured thin film at 70℃ for different layers of coating.

From the figure the band gap is observed to decreases slightly with increase in seed layers. Although many factors influence the variation of energy band gap, in our case the energy band gap decreased with increase of coating times of seed layers may be due to the increased in thickness of nanostructured film. For higher number of coating times of seed layers, the thickness of the film may be increased, due to this band gab may be decreased.

We have measured sheet resistance in air as well as in presence of LPG gas by using four-point probe methods operating at temperature of 300℃. Fig. 5.shows the sheet resistance of ZnO nanostructured thin film versus with different layers of seeding in air and LPG flow condition.

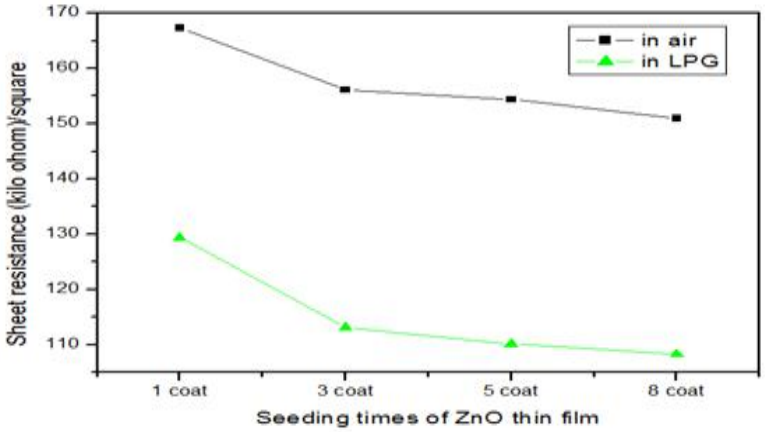

Fig.5. The sheet resistance of ZnO nanostructured thin film at different number of coats of seed layers in air and in LPG flow condition.

The continuous gas flow rate was 16.66 ml/sec for each sample. In both case the sheet resistance of the film is observed to be decreases rapidly with seeding time up to 3 coats. Beyond this the sheet resistance decreases slightly up to 8 coats. The sheet resistance of the film in air for 1, 3, 5, and 8 coats (for hydrothermal growth at 8 hours) is found to be 167, 156, 154, and 151 kilo ohom/squre, respectively. Similarly, the sheet resistance of the film in LPG flow condition is observed to be 129, 121, 114, and 108 kilo ohom/square respectively. There are many factors that influence the decreases in sheet resistance with increase the number of coating of seed layers. In our case the decrease of sheet resistance may be related to the number of metal centers increased. Because with increase the number of coating of seed layers the number of nuclei of metal centers increased, and the film formed become denser and compact as number of coating increases. For small number of coating, the connection between grains may be loose and thus film appears to be porous. With the increased number of coating, the films become denser. So that sheet resistance decreased with increase in seeding times. This decreases value of sheet resistance with increased number of coating is applicable to observed high sensitivity.

Fig. 6.shows the sensitivity versus number of coating of seed layer of ZnO thin film at temperature 300℃ obtained by hydrothermal growth for 8hrs.

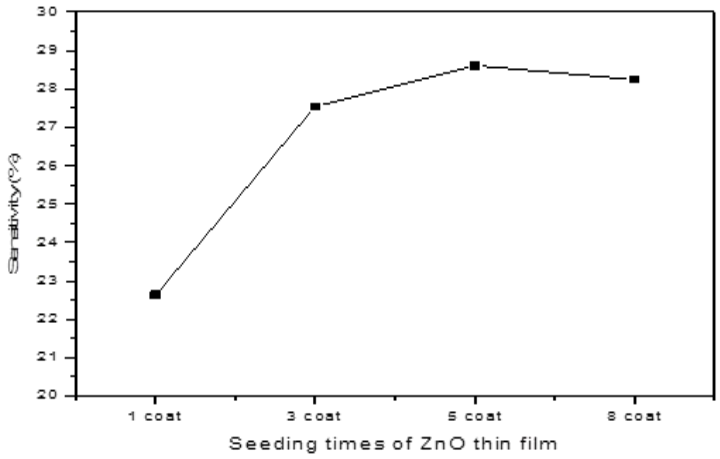

Fig. 6. Sensitivity versus different number of coating of ZnO thin film.

From the figure we see that sensitivity of the film increases rapidly with increasing the number of coating of seed layer thin film up to 3 coats, beyond this the sensitivity increases in slow rate. This is because for small number of coating, the connection between grains is poor and thus the resistivity is high. The sensitivity of ZnO nanostructures thin film fabricated at temperature 70℃ for 1, 3, 5, and 8 coats (having same growth times) are found to be 22.63%, 27.54%, 28.61%, and 28.24%, respectively. The Fig.11.reveals that the response range of sensor is from 22.63% to 28.24% for the different coat of ZnOthin film at gas flow rate 16.66 ml/sec, with continuous flow of LPG gas. In our case sensitivity increased with seeding time may be due to larger surface area of nanostructures. For small number of coating, the connection between grains is loose and thus film appears to be porous. With the increased number of coating, number of grains increase thus increasing the surface area of film. So it is obvious that for the greater surface area, the interaction between the adsorbed gases and the sensor surface are stronger. So that sensitivity is increased with increasing number of coating of seed layers. On increasing the coatings further, the grains tend to overlap on others thus not contributing much in increasing the surface area. So we obtain a less steep curve for the 5 coated ZnO seed layer. The decrease in sensitivity for the 8 coated ZnO seed layer can be attributed to the same reason that the overlapping of more grains with increased number of coatings tend to decrease surface area significantly. From our observation we observed maximum sensitivity for 5 coated seed layers of ZnO.

Conclusion

In this work, ZnO nanostructures were synthesized by a hydrothermal route from ZnO seed layers. The effect of the different seed layers of ZnO nanostructured thin film were studied. XRD showed that all the ZnO nanostructures were hexagonal wurtzite structure. SEM reviled that the length and width of ZnO nanostructure increased with increase in growth time. Band gap for ZnO nanostructured thin film decreased from 3.175 eV to 3.092 eV for the increasing seed layers while the sensitivity for the same samples increased. The sensing performance of the ZnO nanostructures was observed with LPG in air. The sensitivity of ZnO nanostructures was observed to be 22% to 28% with different seed layers.

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