Study on the effect of growth-time and seed-layers of Zinc Oxide nanostructured thin film prepared by the hydrothermal method for liquefied petroleum gas sensor application

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Abstract

Gas sensors are devices that can convert the concentration of an analytic gas into an electronic signal. Zinc oxide (ZnO) is an important n-type metal oxide semiconductor which has been utilized as gas sensor for several decades. In this work, ZnO nanostructured films were synthesized by a hydrothermal route 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 for different time duration. The effect of growth time and seed layers of ZnO nanostructured on its structural, optical, and electrical properties was studied. These nanostructures were characterized by X-ray diffraction, scanning electron microscopy, optical spectroscopy, and four probes 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 with preferential orientation. SEM reviled that the size of nanostructure increased with increase in growth time. Band gap and sheet resistance for ZnO nanostructured thin film decreased with increase in growth time. ZnO nanostructured thin film showed high sensitivity towards LPG gas. The sensitivity of the film is observed to increase with increase in no of seed layers as well as growth time. The dependence of the LPG sensing properties on the different growth time of ZnO nanostructured was investigated. The sensing performances of the film were investigated by measured change in sheet resistance under expose to LPG gas.

Keywords: Gas sensor; Nanostructure; Hydrothermal growth; Electric nose

1. Introduction

Monitoring the air quality especially in urban areas has become a priority due to the great amounts of pollutants released in the atmosphere which have a noxious 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.
The history of gas sensors can be traced to the last century. Miners are among the first groups that become aware of the importance of detecting hazardous gases in their working environment. In the early years, small animals, such as birds, were used as poor substitute for quantifiable method to measure this hazard [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 a broad range of application in chemical engineering, medical, agriculture, architecture and other fields. The first are electrolyte-based potentiometric sensors for automobile exhaust monitoring. 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 synthesized 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 growth time. Then this sample is characterized by using different instruments.

### 2. Experimental Set UP

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 approximately 1.0 and the concentration of Zinc acetate was 0.6M. The solution was stirred at 600°C for 2 hours to yield a clear and homogeneous solution which served as precursor. The precursor 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 2000 rpm initially and then 3000 rpm for 30 seconds in order to spread the colloid on to the glass with uniform thin layer. The deposited film is heated at 4200°C 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(NO$_3$)$_2$]. 6H$_2$O, hexamethylene-tetramine (C$_6$H$_{12}$N$_4$) (A.R. grade) and DI water were used as starting materials and solvent respectively. Zinc nitrate hexahydrate and hexamethylene-tetramine was first dissolved in DI water at room temperature. The concentration of Zinc nitrate hexahydrate and hexamethylene-tetramine was 0.3M. The solution was stirred at 600°C for 2 hours to yield a clear and homogeneous solution which served as precursor. The precursor solution was filtered through Whatman filter paper [6]. 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°C 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 home-made gas sensor assembly comprising a temperature controller, a chromel-alumel thermocouple, an electrical heating plate, a gas chamber, and a LPG volume measurement unit.

### 3. 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 2θ values 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_{0(hkl)}), intensity of (hkl) plane taken from the JCPDS card (I_{(hkl)}), and observed 2θ value of ZnO seed layers.

<table>
<thead>
<tr>
<th>JCPDS(card no 03-0891)d-values (Å^2)</th>
<th>Observed d-values (Å^2)</th>
<th>I_{0(hkl)}</th>
<th>I_{(hkl)}</th>
<th>Observed 2θ value</th>
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<td>1.3599</td>
<td>70</td>
<td>10</td>
<td>69</td>
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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.

<table>
<thead>
<tr>
<th>JCPDS(card no 03-0752)d-values (Å^2)</th>
<th>Observed d-values (Å^2)</th>
<th>Observed 2θ value (°)</th>
<th>FWHM</th>
<th>D(Å)</th>
<th>I_{0(hkl)}</th>
<th>I_{(hkl)}</th>
<th>T_{c(hkl)}</th>
<th>δ/mm²</th>
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<td>2.85</td>
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</table>

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

\[ T_{c(hkl)} = \frac{1}{n} \sum_{n} \frac{I_{(hkl)}}{I_{0(hkl)}} \]

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. 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].

From Fig. 3. the average thickness of the plate like nanostructures was observed to be nearly same as the thickness at low growth time but length and width of nanostructures was nearly about 1050 nm and 525 nm, respectively. Comparing the SEM image of ZnO for 2 hrs and for 10 hrs we find that with increase in growth time the dimension of area of nano sheet increased but thickness of the plate does not increase markedly. The reason for larger length in this case may be possibly due to longer growth time.

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

Fig. 3: SEM images of ZnOnanosheet synthesized by hydrothermal route for 10 hours at different resolution (a) 20µm and (b) 4µm.

Fig. 4 shows the transmittance and absorbance of ZnO nanostructured thin films fabricated at different growth time. From Fig. 4(a) we have calculated the average transmittance of the wavelength ranging from 300-1000 nm. The average transmittance is observed to decrease from 75% to 55% with increase the growth time. The decreases of transmittance of the film with growth time could be related to two factors. One is the thicker ZnO nanostructured thin films had larger hexagonal grain size and larger surface roughness. The other is the higher absorption effect for the thicker films. From the Fig. 4 (a) it is clearly observed that in all cases the transmittance is observed to be less than 75%, wavelength range 300-1000 nm, regardless the growth time. When the deposition condition like substrate temperature and other chemicals are kept fixed the value of transmittance is observed to decrease with increased in growth time.
From the graph it is observed that transmittance starts to decrease rapidly at 400 nm wavelength. From this figure we find that the absorption edges shift to high wavelength with increase in growth time. Fig. 4(b). Depicts the absorption spectra of the films obtained in the wavelength range of 300 to 1000 nm. The absorbance edge have been found broad and pronounced around 800 nm for all deposited films. From the graph it is clearly seen that the absorbance decreases sharply at wavelength range about 550 nm to 650 nm and then decreases gradually up to about 800 nm. Beyond 800 nm, the absorbance is very low and nearly constant for all deposited ZnO nanostructured thin films. From the graph it is clearly seen that as growth time increases absorption edge shift to higher wavelength value.

Depending on a band structure of the material both direct and indirect transitions occur in a case of crystalline or polycrystalline material. As discussed earlier nature of optical transition and the optical band gap of these films are obtained using the relation $(\alpha h\nu) = A(h\nu-E_g)^{n}$ where $n=\frac{1}{2}$, for direct allowed transition, $E_g$ is the energy band gap, $\alpha$ is the absorption coefficient. Direct and indirect optical band gap of these nanostructured thin films is obtained by extrapolating the linear portion of the plot on to $h\nu$-axis. The point where the linear part of $(\alpha h\nu)^{2}$ versus $h\nu$ curve intersects the $h\nu$ axis gives us the band gap value for allowed direct transitions; on the other hand, the point where linear part of $(\alpha h\nu)^{1/2}$ versus $h\nu$ curve intersects the $h\nu$ axis gives us the band gap value for allowed indirect transitions[5]. Fig.5. Depicts the variation of $(\alpha h\nu)^{2}$ versus photon energy $(h\nu)$ film prepared at different growth time of ZnO nanostructures thin film. From the figure we see that the allowed direct band gap decrease from 3.164 eV to 3.107 eV with the increase in growth time. These values are lower than that observed by the research group [48] for the ZnO nanostructures thin film growth by hydrothermal process. Wang et al [48], also observed that the peak position of free excitonic emission redshifted from 3.3 to 3.2 eV with increasing of grain size from 21 to 64 nm. However many factors (enhanced strain, enlarged grain size and more oxygen vacancies between atom and molecule etc) influence the variation of the energy band gap. Since from XRD analysis and SEM analysis we have observed that with increase in growth time grain size of the ZnOnano sheet increases. Thus in our case decreases of energy band gap with increase of growth time may be due to larger size of nanostructures.
We have measured sheet resistance in air as well as in presence of LPG gas by using four-point probe methods at operating temperature of 300°C. Fig. 6. shows the variation of sheet resistance of ZnO nanostructured thin film versus growth time in air and LPG flow condition. The sheet resistance of the film is observed to decreases rapidly with growth time up to 6 hrs. Beyond this time the decreases is rather slow. Although many factors influence the variation of the sheet resistance. In our case decreases of sheet resistance with increase of growth time may be related to the grain size. We have observed that size of nanostructures was increased with increase in growth time. The increase in size of nanostructures led to deposition of more dense and compact film. Also this led to decrease in grain boundaries which result in decrease in sheet resistance. The sheet resistance of the film for 2, 4, 6, 8, and 10 hours is observed to be 269, 244, 153, 151 and 139 kilo ohm/square, respectively.

The sheet resistance is observed to decreases with increase in the growth time of ZnO nanostructured thin film in similar way as in absence of LPG gas. The sheet resistance for growth time of 2, 4, 6, 8, and 10 hours is observed to be 204, 179, 111, 108, and 90 kilo ohm/square respectively. The value of sheet resistance in LPG gas is observed to be less than the value of sheet resistance in air. When the LPG gas is introduced in the gas chamber, CH₄, C₃H₈ and C₄H₁₀ molecules present in LPG react with pre-adsorbed oxygen species. As a result the surface oxygen concentration is reduced, and electrons that were initially trapped by oxygen anions are released back in to the ZnO solid, leading to an increase in the conductivity of the ZnO surface. So that sheet resistance decreases in presence of LPG [3].

In the work of Lokhande group [3] it is observed that for each film, the sensitivity increased with temperature up to 300°C and then decreased at 450°C. The sensitivity of all the films does not exhibit any significant difference at lower temperature. At a lower operation temperature, the low sensitivity can be expected because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species. At low temperatures the sensitivity is restricted by the speed of the chemical reaction, and at higher temperatures it is restricted by the speed of diffusion of gas molecules. At some intermediate temperature, the speed values of the two processes become equal, and at that point the sensitivity reaches its maximum. Thus in the present case the operating temperature of ZnO nanostructured thin films was takes as 300°C at which the ZnO sensor response attained its peak value.

Fig. 7 shows the sensitivity as a function of growth time measured at temperature 300°C for ZnO nanostructures thin film obtained by hydrothermal growth technique upon exposure to LPG. The sensitivity of ZnO nanostructures thin film for growth time of 2, 4, 6, 8 and 10hrs are observed to be 24%, 26%, 27%, 28%, and 35%, respectively. The sensitivity is increased with growth time may be due to formation of larger nano sheet which led the higher surface area.
The Fig. 7 reveals that the sensitivity increased from 24% to 35% as the growth time increased from 2 hrs to 10 hrs, for gas flow rate 16.66 ml/sec, with continuous flow of LPG gas. From our observation we conclude that better sensitivity was observed at 10 hours.

Fig. 8 shows the transmittance of the ZnO nanostructured thin film fabricated at 70°C 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. 9 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. 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 gap 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°C. Fig. 10 shows the sheet resistance of ZnO nanostructured thin film versus with different layers of seeding in air and 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 ohm/square, respectively. Similarly the sheet resistance of the film in LPG flow condition is observed to be 129, 121, 114, and 108 kilo ohm/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. 11: The sheet resistance of ZnO nanostructured thin film at different number of coats of seed layers in air and in LPG flow condition.

Fig. 12: Sensitivity versus different number of coating of ZnO thin film.

Fig. 11 shows the sensitivity versus number of coating of seed layer of ZnO thin film at temperature 300°C obtained by hydrothermal growth for 8hrs. 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°C 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. 12 reveals that the response range of sensor is from 22.63% to 28.24% for the different coat of ZnO thin 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 (up to three coats), 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.

4. Conclusion

In this present work, ZnO nanostructures were synthesized by a hydrothermal route for different growth time from ZnO seed layers. The effect of the growth time of ZnO nanostructured thin film and effect of seed layers of ZnO nanostructured thin film were studied. XRD showed that all the ZnO nanostructures were hexagonal wurtzite structure. SEM revealed that the length and width of ZnO nanostructure increased with increase in growth time. The length and width of the nanostructure was found to be 550 nm and 220 nm for nanostructures grown for 2 hrs and 1050 nm and 525 nm for nanostructure grown for 10 hrs. Band gap for ZnO nanostructured thin film decreased from 3.175 eV to 3.092 eV for the increasing seed layers and 3.164 eV to 3.107 eV with increased growth time from 2 hours to 8 hours, while the sensitivity for the same samples increased. The sensing performance of the ZnO nanostructures was observed with LPG
The sensitivity of ZnO nanostructures was observed to be 24% to 35% with increased in growth time and 22% to 28% with different seed layers. From our observation maximum sensitivity was observed at 10 hours growth time.

References
