Chapter 3

Preparation, characterization and gas sensing performance of nanostructured ZnO thick film resistors

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3.0 Introduction

Over the past few years, the synthesis and functionalism of nanostructures have attracted great interest due to their significant potential application. ZnO, as an important semiconducting material, has a wide range of applications in optics, optoelectronics, sensors, actuators, energy and biomedical sciences [1–3]. Because of its direct wide band gap of 3.37 eV and large excitation energy of 60 meV exhibit the most splendid and abundant configuration of nanostructure that one material can form. 1D ZnO nanocrystals are considered to be the most promising highly sensing materials of sensors due to the slower electron/hole recombine rate, as well as their higher surface-to-volume ratio than the conventional sensing materials. Consequently, 1D ZnO nanostructures, such as nanowires, nanobelts, nanoflowers and other special nanostructures have been successfully synthesized using various approaches [4-8]. Nowadays, semiconductor-oxide gas sensors have been widely used for environmental monitoring and industrial applications [9, 10]. The sensibility of semiconductor gas sensors is thought to be dominated by surface science. When semiconductor sensing materials are exposed in the air, atmosphere oxygen is adsorbed on the surface. The adsorbed oxygen extracts electrons from the conduction band of semiconductors leading to change in carrier density and conductivity. For example, n-type ZnO shows a high resistance state in the air [11]. Subsequently, the analytes are introduced, such as oxidizing and reducing gas, the adsorbed oxygen concentration on gas sensors will be changed owing to interactions with the analytes, and thereby the conductivity of semiconductor oxides changes. The conductivity change caused by analytes is a measure of analyte concentration and recorded as response signals [12].

More practical and wider applications of gas sensors require their good performance at lower temperatures, especially at room temperature [13, 14]. A simple, yet promising route to enhance the gas-sensing performance is to control the structural features of the materials during the chemical synthesis. In particular, the generation of high specific surface areas and porous systems will result in a higher probability for the gases to interact with the semiconductor, which is likely to increase the sensitivity of the material [15, 16]. Therefore, developing convenient strategies to synthesize nanostructured ZnO
materials is desirable and of significance for improving the gas sensing performance of ZnO.

So far nanocrystalline ZnO with different particle morphologies and sizes have been obtained by several preparation approaches including thermal decomposition, vapor chemical deposition, sol–gel method, wet chemical synthesis, mechanochemical, electrodeposition, gas-phase reaction, hydrothermal synthesis and so on. An excellent review of recent progress on processing, properties and applications of ZnO was recently published elsewhere [17]. However the synthesis of ZnO with particular morphology by a simple method under mild conditions still represents a challenge. The gas phase synthesis processes usually involve high temperatures up to 1000 °C in order to crystallize the ZnO phase. In most cases the high synthesis temperatures lead to the formation of strong aggregates in the ZnO powder, which subsequently have to be excessively milled resulting in poor control of particle morphology and size distribution.

In the present chapter, simple chemical route was employed to obtain nanostructured ZnO. We report here on the optimum processing condition for ZnO powder preparation, phase and morphological characterization of the material and electrical properties as a H₂S gas sensor.

3.1 Experimental procedure

3.1.1 Synthesis of nanostructured ZnO powder by chemical route

Nanostructured ZnO powder preparation by chemical route is summarized in a flow chart shown in Fig. 3.1. All the chemicals used for synthesis are procured from Merck Chemicals Limited and are used without further purification. In a typical synthesis, 3.29 g zinc acetate (0.5 M) was dissolved in 30 ml distilled water, respectively and added into a 10 g stearic acid (0.5 M) in 70 ml as a surfactant. The reaction mixture was then stirred for 1 h at 60 °C temperature, then pH of the solution was brought to 8.5 by drop wise addition of ammonium hydroxide solution (25%). The reaction mixture was heated at 100 °C for 24 h, and then allowed to cool to room temperature. The precipitate was poured out into a tube for centrifugal separating, washing, drying at 100 °C for 3 h. ZnO powder can be gained by firing the dried precursor at 200 °C for 30 min.
3.1.2 Preparation of ZnO thick film resistors

The thixotropic paste was formed by mixing the synthesized material with solution of ethyl cellulose acetate as a temporary binder with mixer of organic solvent such as: butyl cellulose, butyl carbitol acetate and terpenol etc. The binder helps to bind the material
with glass substrate. The ratio of organic part to inorganic part is kept in range of 25:75 during formulating the paste. The thick film prepared by screen printing technique in which paste is robbed on screen printing machine. The uniform film is formed by applying uniform pressure. The film then fired at 550 °C to remove organic material. The gas sensitivity is measured for various gases like ethanol, H_2S, NH_3, LPG, Cl_2, CO, CO_2, H_2 and O_2.

3.2 Characterization results
3.2.1 Structural properties
3.2.1.1 X-ray diffraction analysis (XRD)

XRD spectra of the synthesized ZnO powder are shown in Fig. 3.2 using a BRUKER D8 model. XRD results indicate that the ZnO material has a nanocrystalline structure and it grows with hexagonal wurtzite- type. The main significant peaks for ZnO were found to be (100), (002), (101), (102) and (110).

The d-value of each peak in the diffraction pattern is compared with JCPDS standard d-values for ZnO [18]. Table 3.1 shows the comparison of observed for ZnO d-values with the standard d-values. The indices of all the peaks on XRD pattern are identified as shown in Table 3.1. From the X-ray diffraction data the mean crystallite size (D) was calculated using Debye–Scherrer's formula [19],

\[ D = \frac{0.9\lambda}{\beta \cos\theta} \]

where D is the crystallite size, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg diffraction angle of the (101) peak. The average crystallite size was found to be 34.7 nm and shows the nano-crystalline nature.
Tabel 3.1: Comparison of d-values from XRD data with standard d-value from JCPDS.

<table>
<thead>
<tr>
<th>2θ (degree)</th>
<th>d-values Å</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
<th>d –values Å</th>
<th>h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.80</td>
<td>2.8117</td>
<td>0.254</td>
<td>36</td>
<td>2.8143</td>
<td>(110)</td>
</tr>
<tr>
<td>34.40</td>
<td>2.6048</td>
<td>0.252</td>
<td>37</td>
<td>2.6033</td>
<td>(002)</td>
</tr>
<tr>
<td>36.20</td>
<td>2.4728</td>
<td>0.262</td>
<td>35</td>
<td>2.4759</td>
<td>(101)</td>
</tr>
<tr>
<td>47.70</td>
<td>1.9088</td>
<td>0.290</td>
<td>33</td>
<td>1.9111</td>
<td>(102)</td>
</tr>
<tr>
<td>56.60</td>
<td>1.6248</td>
<td>0.296</td>
<td>34</td>
<td>1.6247</td>
<td>(110)</td>
</tr>
<tr>
<td>62.90</td>
<td>1.4764</td>
<td>0.320</td>
<td>32</td>
<td>1.4771</td>
<td>(103)</td>
</tr>
<tr>
<td>66.40</td>
<td>1.4068</td>
<td>0.372</td>
<td>28</td>
<td>1.4071</td>
<td>(200)</td>
</tr>
<tr>
<td>68.00</td>
<td>1.3775</td>
<td>0.351</td>
<td>30</td>
<td>1.3781</td>
<td>(112)</td>
</tr>
<tr>
<td>69.10</td>
<td>1.3583</td>
<td>0.363</td>
<td>29</td>
<td>1.3582</td>
<td>(201)</td>
</tr>
<tr>
<td>72.60</td>
<td>1.3012</td>
<td>0.440</td>
<td>25</td>
<td>1.3017</td>
<td>(004)</td>
</tr>
<tr>
<td>77.00</td>
<td>1.2374</td>
<td>0.408</td>
<td>28</td>
<td>1.2380</td>
<td>(202)</td>
</tr>
</tbody>
</table>

3.2.1.2 Transmission electron microscopy (TEM) analysis

TEM image and the corresponding selected area electron diffraction (SAED) pattern for nanocrystalline ZnO nanopowder are shown in Fig. 3.3(a) and (b), respectively. The morphology and microstructure of nanopowders were investigated from TEM images. All the samples were scanned in all zones before the picture was taken. The micrographs
showed that the grains were nearly spherical in shape and the grain size distribution was in the range from 30 to 40 nm.

![TEM image of nanocrystalline ZnO powder and SAED pattern.](image)

**Fig. 3.3:** TEM image of nanocrystalline ZnO powder and SAED pattern.

### 3.2.1.3 Scanning electron microscopy (SEM) analysis of ZnO thick films

Fig. 3.4 (a, b), shows the SEM images of ZnO thick films at different magnification. It consists of large number of grain sizes ranging from 40 nm to 80 nm leading to high porosity and large effective surface area available for the adsorption of oxygen species.

![SEM image of nanocrystalline ZnO thick film.](image)

**Fig. 3.4(a, b):** SEM image of nanocrystalline ZnO thick film.
3.2.1.4 Thickness measurements of ZnO thick film

The film thickness was measured by a weight difference method [20, 21] in which weight of the sample, area and densities were considered. The thickness, sample weight and sample area are related as

\[ t = \frac{M_{\text{ZnO}}}{A \rho} \]  

where \( M_{\text{ZnO}} \) is the weight of the sample in g, \( A \) the area of the sample in cm\(^2\) and \( \rho \) the materials density in gm cm\(^{-3}\). The thickness of the film was 27 \( \mu \text{m} \).

3.2.2 Optical properties of the films by UV-visible spectroscopy

Fig. 3.5 shows the variation of absorbance with wavelength of nanocrystalline ZnO powder. The band gap energy of the sample calculated from the absorption edges of the spectra, was 3.36 eV. This value is well matches with the reported value of 3.37 eV [22].

![Absorption spectra of nanocrystalline ZnO.](image)

**Fig. 3.5:** Absorption spectra of nanocrystalline ZnO.

3.2.3 Electrical properties of the sensors

3.2.3.1 I-V characteristics

The basic I-V characteristic of the ZnO thick film was performed on gas sensing set-up, using silver paste as contacts. I-V characteristics of the ZnO thick film show an Ohmic behavior for both -ve and +ve applied potential as can be observed from Fig. 3.6.
The Ohmic behavior is very important the point of gas sensing applications, especially with different concentration of gases or other species [23, 24].

![I-V characteristic of the ZnO thick film.](image)

**Fig. 3.6:** I-V characteristic of the ZnO thick film.

### 3.2.3.2 Electrical conductivity

Fig. 3.7 represent the variation of conductivity with temperature ZnO thick film. It is clear from the graphs that the conductivity is varying with temperature. This is due to semiconducting nature of sample. In the 450–350 °C region, the resistance decreases dramatically. In the 325- 200 °C region, the change in resistance is very small. As the conductance of the ZnO nano-rods hardly changes from 325 to 200 °C has good thermal stability when its operating temperature is in this range.
3.3 Gas sensing performance of ZnO thick films

3.3.1 Gas response with operating temperature

Gas response/Sensitivity (S) of gas sensor is defined as the ratio of change in conductance of the sensor on exposure to the target gas to the original conductance in the air [23, 24].

\[
S = \frac{(G_g - G_a)}{G_a} \quad (2)
\]

(Ga = conductance of sensor in the air and Gg = conductance of sensor in gas.)

The gas sensing performance of the sensor element in the form of thick film was tested to various gases at various operating temperature by using static gas sensing unit [24]. The sensor showed maximum response to H\(_2\)S gas at 300 °C for 100 ppm gas concentrations. Fig. 3.8 shows the variation in gas response of H\(_2\)S gas (100 ppm) with operating temperatures ranging from 50 °C to 450 °C. It is noted from the graph that response increases with increasing temperature, and attains a maximum at 300 °C, and decreases with further increase in operating temperature. The optimal operating temperature for H\(_2\)S gas detection is found to be 300 °C.
3.3.2 Selectivity of ZnO thick film for various gases

Selectivity is defined as the ability of sensor to respond to a certain gas in the presence of other gases. Selectivity is another important parameter of a gas sensor [24]. The sensor must have rather high selectivity for its application. ZnO film is examined for different gases at different operating temperatures and the results are shown in Fig. 3.9.

The bar diagram indicating selectivity of ZnO thick film at 300 °C to H$_2$S gas against the
other gases and the attached table indicates the response values of gases. The sensor is the most selective to H$_2$S gas against the other gases.

3.3.3 Variation of gas response with gas concentration

![Graph showing variation in gas response with H$_2$S gas concentration.](image)

**Fig. 3.10:** Variation in gas response with H$_2$S gas concentration.

To test the H$_2$S gas concentration characteristics, the sensor was exposed to H$_2$S gas of different concentrations at a constant optimal operating temperature. The sensor responses to H$_2$S in concentration range (100-1000 ppm) are shown in Fig. 3.10 at 300 °C operating temperature. The gas response values were observed to increase continuously with increasing the gas concentration up to 100 ppm. The rate increase of response was relatively larger up to 100 ppm and then saturates after 100 ppm. Thus the active region of the sensor would be between 10-100 ppm.

3.3.4 Response and recovery time of ZnO thick film

The response and recovery time profile of nanostructured ZnO thick film sensor is shown in Fig. 3.11. Response and recovery time are the basic parameters of the gas sensors, which are defined as the time taken for the sensor to attain 90% of maximum change in resistance on exposure to gas is the response time. The time taken by the sensor to get back 90% of the original resistance is the recovery time [23]. The response and
recovery time of nanostructured ZnO thick film were 6 s and 15 s respectively as shown in Fig. 3.11. The large recovery time would be due to lower operating temperature. At lower temperature $\text{O}_2^-$ species is more prominently adsorbed on the surface and thus it is less reactive compared to other species of oxygen, $\text{O}^-$ and $\text{O}^{2-}$.

![Fig. 3.11: Response and recovery time of ZnO thick film.](image)

### 3.3.5 Gas sensing mechanism

It is well known that the gas sensing mechanism in the oxide-based materials is surface controlled, wherein, the grain size, surface states and oxygen adsorption play a significant role. The larger surface area usually offers more adsorption-desorption sites and thus the enhanced sensitivity [25, 26]. The atmospheric oxygen gets adsorbed on the surface, and depending upon the temperature of operation; different oxygen species are formed on the surface. The gas response by metal oxide semiconductor, in general, can be described as:

\[
\text{O (gas) + 2e}^- \rightarrow \text{O}_2^-_{\text{(ads)}} \quad (3)
\]

\[
\text{R + 2 O}_2^-_{\text{(ads)}} \rightarrow \text{RO} + \text{e}^- \quad (4)
\]

Initially, [Eq. (3)] the atmospheric oxygen acquires electron from the conduction band of ZnO and forms $\text{O}_2^-_{\text{(ads)}}$ species on the surface thus decreasing the conductance of the ZnO. Further, the high surfaces to volume ratio of nanosized particles offer larger number
of sites for the adsorption of the oxygen species. It is known that the gas response depends directly on the number of $O_2^{-(ads)}$ species. The reducing gas (R), reacts with $O_{ads}^-$ and forms RO [Eq. (4)] with releases of electron back to the conduction band. In the process the conductance again increases. Therefore, sensitivity in general, depends on the reaction [Eq. (4)] that is, availability of R and $O_2^{-(ads)}$ species. The rejuvenation of the conductance takes place on removal of R and the presence of ambient oxygen [Eq. (3)].

More specifically, in the presence of $H_2S$ gas, the reaction [Eq. (5)] takes place thereby forms $H_2O$ and $SO_2$ gas by releasing electrons back to the conduction band, thus increasing the conductance of the sensor. Again on removal of $H_2S$ the reaction [Eq. (3)] takes place leading to a decrease in the conductance. This can be simply described as in Eq. (5),

$$2H_2S_{ads} + 3O_2^{-(ads)} \rightarrow 2H_2O + 2SO_2 + 6e^- \quad (5)$$

3.5 Conclusions

i) Nanostructured ZnO powder was synthesized by chemical route.

ii) XRD analysis confirmed the powder to be ZnO with wurtzite structure, with crystallite size 34.7 nm.

iii) Observation from TEM images confirmed that the grains were nearly spherical type in nature with sizes from 30 to 40 nm.

iv) The ZnO thick film shows the highest response to the $H_2S$ gas at the operating temperature 300 °C and observed to be highly selective to $H_2S$ gas.

v) A quick response (6 s) and fast recovery (15 s) were the special characteristics of the nanostructured ZnO thick film sensor.
References

[18]. JCPDS data card no. 36-1451.