Chapter 5

Precursor Controlled Morphology of Zinc Oxide Nanostructures and its Gas Sensing Behaviour

5.1 Introduction

Research work on synthesis and functionality of nanostructures recently gained much impetus due to their important applications [Huang & Choi (2007), Korotcenkov (2008), Zhang et al. (2008), Charinpanitkul et al. (2011)]. Controlled synthesis of semiconductor nanostructures has been strongly motivated and used for various applications depending upon their structural properties [Chen et al. (2001), Wu & Xue (2010), Zhang et al. (2012)]. The crystal structure and morphology of the ZnO crystals predict their properties and consequently, the applications for which they can be used [Huang & Choi (2007), Ghimbeu et al. (2007), Arca et al. (2009), Durgajanani et al. (2011)]. By using the different techniques during synthesis, the various types of nanostructures of zinc oxide like nanorods, nanowires, nanorings and nanobelts can be formed (Huang & Choi (2007)).

The surface morphology is of specific attention for enhancing gas sensing performance [Korotcenkov (2008), Navale et al. (2008)]. Bacaksiz et al. (2008) have studied the effect of precursor on the investigation of structural and optical prop-

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precursor controlled synthesis of hierarchical ZnO nanostructures, using oligoaniline coated Au nanoparticles seeds. Shouli et al. (2010) have investigated effect of surfactant on morphologies of ZnO nanorods and concluded that their sensing response depends upon their morphologies. In case of thin films the effect of precursors on morphology and other properties have been studied by a number of researchers but in case of bulk or nanocrystalline powder the reports are scarce [Bahadur et al. (2007), Bacaksiz et al. (2008), Arca et al. (2009), Krajewski et al. (2009), Krishnan & Pradeep (2009), Vimalkumar et al. (2010), Durgajanani et al. (2011), Gusatti et al. (2011)].

In this study, distinct morphologies of zinc oxide were obtained chemically by co-precipitation method from different precursor solutions. The samples were characterized by X-ray diffraction and field emission scanning electron microscopy. Furthermore the effect of morphology on gas sensing behaviour of ZnO towards different alcohols has also been investigated.

5.2 Experimental Details

5.2.1 Material

Chemical reagents such as ZnCl₂, Zn(NO₃)₂·6H₂O, Zn(CH₃COO)₂·2H₂O and ammonia solution were all of analytical grade and were used as received without further purification. Distilled water was used throughout the experiment.

5.2.1.1 Preparation of Zinc Oxide Powder

Zinc oxide powder was prepared by following a simple chemical route. Three different solutions of zinc chloride, zinc nitrate hexahydrate and zinc acetate dihydrate, each having 0.2 M concentration, were prepared in distilled water. Precipitates of zinc hydroxide were obtained on adding ammonium hydroxide drop wise to each solution at room temperature with continuous stirring for half an hour. The precipitates thus obtained were washed and separated from rest of the liquids by filtering and were dried into powder at 120°C temperature. The powder thus obtained from three different recipes were crushed and calcined at 500°C for three hours separately. In order to understand the structural properties of synthesized samples, I subjected them to XRD and FESEM techniques for
5.3 Results and Discussion

5.3.1 Material Characterization

5.3.1.1 X-Ray Diffraction

Figure 5.1 represents the X-ray diffraction pattern of materials synthesized with different precursors. The peaks visible in the graphs are in well agreement with standard available data and these depict the wurtzite hexagonal structure of nanosized zinc oxide.
5. Precursor Controlled Morphology of Zinc Oxide Nanostructures and its Gas Sensing Behaviour

5.3.1.2 Field Emission Scanning Electron Microscopy

Figure 5.2-5.4 represents the FESEM images of the nanostructured ZnO powder synthesized using precursors namely zinc chloride, zinc nitrate and zinc acetate respectively. From these images it is clear that samples prepared from different precursors have yielded different morphologies. In Fig. 5.2 nanorods with tapered ends, in Fig. 5.3 short length rods having hexagonal prism geometry and in Fig. 5.4 long length rods having hexagonal prisms geometry can be seen. In Fig. 5.4 there is a growth of particle like structures on the surface of nanorods as well. One dimensional nanostructure is formed due to anisotropic crystal growth.

**Figure 5.1:** X-ray diffraction pattern of zinc oxide powder synthesized from precursors a) zinc chloride, b) zinc nitrate and c) Zinc acetate.
5.3 Results and Discussion

i.e. the crystal grows along a certain direction faster than that along other directions. The driving force for the formation of one dimensional nanostructure by spontaneous growth is the decrease in Gibbs free energy, which arises from either recrystallization or a decrease in supersaturation (Cao (2004)).

The different morphologies of zinc oxide obtained by using different precursors are due to the change of growth rate between different crystallographic planes (Chen et al. (2000)).

The difference in crystal growth rate depends on the nature of the precursor (Bacaksiz et al. (2008)). In the present study growth speed of the different crystal faces depends upon the acidity of the precursor solution, where the acidity of the zinc oxide precursors is in the order: chloride > nitrate > acetate (Halawy & Mohamed (1995)).

Figure 5.2: FESEM image of the nanostructured ZnO powder synthesized using precursor zinc chloride.
5.3 Results and Discussion

**Figure 5.3:** FESEM image of the nanostructured ZnO powder synthesized using precursor zinc nitrate.

**Figure 5.4:** FESEM image of the nanostructured ZnO powder synthesized using precursor zinc acetate.
5.3 Results and Discussion

5.3.2 Sensing Performance

In order to investigate the effect of precursor assisted morphology on the sensing property, sensor fabricated from powder having different morphologies were exposed to 250 ppm of methanol, ethanol and propanol at different operating temperatures. As the electrons are drawn from the conduction band by adsorbed oxygen species, creating a potential barrier, the gas molecules require certain amount of thermal energy to react with adsorbed oxygen species, therefore, at lower operating temperature, the sensing response is low because of the low thermal energy. At higher temperature the thermal energy produced is higher enough to cross the potential barrier which increases the concentration of electron in conduction band and hence increases the gas sensing response (Shinde et al. (2007)). Above certain temperature the sensor response decreases because amount of adsorbed oxygen available at the sensing site on the sensor surface reduces to react with gas molecules leading to small change in conductance. Figure 5.5-5.7 revealed that, the optimum temperature of all the sensors remains invariant at 400°C. The comparative response of volatile organic compounds (VOCs) for all the sensors based on samples is shown in Fig. 5.8. It is evident from figure that sensing response for the ZnO morphology prepared from zinc acetate precursor is exceptionally higher for all VOCs. Also from this figure it is clear that the response and recovery of the fabricated sensors are very fast. Under similar conditions, the sensing response magnitude of samples synthesized from different precursors varies in the following order: zinc acetate > zinc nitrate > zinc chloride. The reason for increase in the sensing response values may be ascribed to the surface area of the material which depends upon the surface morphology. Greater the surface area of the materials, stronger is the interaction between the adsorbed gases and surface of the material and hence higher is the gas sensing response (Chang et al. (2002)). As discussed above in FESEM images, the samples prepared from different precursors have different morphologies. Among these images hexagonal prism geometry has more effective surface area than nanorods with tapered ends. In Fig. 5.4, the nanorods bearing hexagonal prisms geometry are longer than those seen in Fig. 5.3 and in addition there is a growth of some nanostructures on their surfaces which enhances the surface area and hence the sensing response. It may be concluded that the sensing properties depend upon the surface morphology which in the present study was a consequence of precursor solution. The high response of one dimensional nanostructure is due to their high surface to volume ratio which results in enhanced adsorption of oxygen species on
the surface of material. When zinc oxide nanostructured sensors are exposed to air, molecular oxygen gets adsorbed on the surface of the materials to form $O_2^-$, $O^-$, $O^{2-}$ ions by capturing electrons from the conduction band, thereby increasing the resistance of the sensor. When a reducing gas is injected, it reacts with adsorbed oxygen and releases the electrons back to conduction band resulting in the decrease in resistance. After the removal of reducing species, the sensor is allowed to recover completely till the original resistance is obtained. The reaction can be described as follows:

$$R + O_{(ads)}^- \leftrightarrow RO + e^- \quad (5.1)$$

Figure 5.8 shows the variation of sensing response for alcohols in the following order: propanol $>$ ethanol $>$ methanol. The number of methyl groups attached to these alcohols is in the same order as well. Greater the number of methyl group attached, larger is the sensing response. Another reason for enhanced sensing response for ethanol and isopropanol is the presence of $\beta$-H in them. The $\beta$-H of isopropanol is the most reactive, and there is no $\beta$-H in methanol (Jie et al. (2006)). Moreover, it can be explained on the basis of complete oxidation of these alcohols and in the process propanol, ethanol and methanol consumes 9, 6 and 3 $O_{ads}^-$ respectively (Gong et al. (1999)). The trend obtained here is similar to the study discussed in previous chapter.
5.3 Results and Discussion

Figure 5.5: Sensing response towards 250 ppm of methanol for ZnO samples prepared from (a) zinc chloride, (b) zinc nitrate and (c) zinc acetate at different operating temperatures.

Figure 5.6: Sensing response towards 250 ppm of ethanol for ZnO samples prepared from (a) zinc chloride, (b) zinc nitrate and (c) zinc acetate at different operating temperatures.
5.3 Results and Discussion

Figure 5.7: Sensing response towards 250 ppm of propanol for ZnO samples prepared from (a) zinc chloride, (b) zinc nitrate and (c) zinc acetate at different operating temperatures.

Figure 5.8: Sensing Response of ZnO samples synthesized from (a) zinc chloride, (b) zinc nitrate and (c) zinc acetate to 250 ppm of different VOCs at optimum operating temperature of 400°C.
5.4 Conclusion

In this work I used chemical technique to synthesize nanostructured ZnO with different morphologies by using different precursor solutions. The precursors have played a significant role in altering the morphology of the zinc oxide. Powder prepared from zinc chloride, zinc nitrate and zinc acetate has nanorods with tapered ends, short length rods having hexagonal prism geometry and long length rods having hexagonal prisms geometry with growth of particle like structures on the surface respectively. Sensing performance of these powder was investigated for three different alcohols and I perceived that sensing response depends upon surface morphology. Among all precursor solutions, zinc acetate assisted gas sensor gave the best results towards all the alcohols. Therefore, the morphology of zinc oxide derived from zinc acetate has been found to be most favourable for gas sensing application.
5. Precursor Controlled Morphology of Zinc Oxide Nanostructures and its Gas Sensing Behaviour