Chapter 7

Sensing Behaviour of Surface Activated ZnO Nanorods

7.1 Introduction

Gas sensing is a surface phenomenon, resistance or conductance of poly-granular metal oxides change upon exposure to reducing and oxidizing gases (Eranna et al. (2004)). It is imperative to operate metal-oxide gas sensors at elevated temperatures to activate chemical reaction, improve their selectivity and reduce response time (Gardner et al. (2001)).

In the 3rd chapter I have discussed the synthesis of nanorods of zinc oxide and observed its sensing behaviour towards ethanol. Since gas sensing response depends upon the availability of active sites on the surface therefore sensing response can be improved by increasing the active sites on the surface of sensing material. In recent years research has been concentrated on improving the gas sensing by activating zinc oxide with noble metal catalyst, by incorporating additives into it or by surface activation of thick films [Wada & Egashira (1998), Yu et al. (2004), Sahay & Nath (2008), Suryawanshi et al. (2008), Patil & Patil (2009)]. In this chapter the attempt was made to generate more active sites on the surface of zinc oxide nanorods with the help of tin oxide to improve its sensing response.

0Some part of this chapter has been published in the journal Materials Research Bulletin (47 (2012) 557-561) as a paper with title “Enhancement in ethanol sensing response by surface activation of ZnO with SnO₂”
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In this work, surface of synthesized zinc oxide nanorods has been activated with SnO$_2$ and its ethanol sensing behaviour has been investigated.

7.2 Experimental Details

7.2.1 Preparation of Zinc Oxide Nanorods

Zinc oxide nanorods were prepared by following a chemical route, as explained in Chapter 3. The powder thus obtained was crushed and calcined at 500°C for three hours.

7.2.2 Sensor Preparation and Testing Method

For the fabrication of thick film sensors, powder were deposited on the alumina substrate by using masking and painting method. The detailed method has been explained in the Section 2.5.

To activate the sensors, 4 µl of SnCl$_4$ solution of different concentrations (1.0 wt.%, 3.0 wt.%, 5.0 wt.%) was added to the surfaces of a batch of sensors followed by heating at 450°C for one hour. Crystal structure of prepared samples was characterized by powder X-ray diffraction (XRD) technique, using Cu-K$_\alpha$ radiation with Shimadzu 7000 systems. Morphologies and grain sizes of the samples were analyzed by the field emission scanning electron microscope (FESEM) with JEOL, model-JSM 6700F.

The sensing characteristics of ZnO nanostructures were obtained with the method explained in the Section 2.6.

7.3 Results and Discussion

7.3.1 Material Characterization

7.3.1.1 X-Ray Diffraction

The presence of well resolved and sharp lines were compared with standard data, which confirmed that the synthesized samples of ZnO were of hexagonal wurtzite...
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The additional peaks (marked with + and *) appearing in the image are of alumina substrate and gold electrodes. Due to smaller wt.% of SnO\textsubscript{2} in the sample there are no prominent peaks of SnO\textsubscript{2} associated in the XRD pattern.

Figure 7.1 shows the X-ray diffraction pattern of pure and SnO\textsubscript{2} activated ZnO.
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7.3.1.2 Field Emission Scanning Electron Microscopy

Figure 7.2-7.5 represent the FESEM images of pure and SnO$_2$ activated ZnO. Nanorods of pure ZnO of various sizes are visible in Fig. 7.2. The sample activated with 1 wt.% are shown in Fig. 7.3 where one finds very small grains, most likely of SnO$_2$, sticking on the surface of ZnO nanorods. The population of SnO$_2$ grains on the ZnO surface gradually increased as I increased the concentration of tin chloride solution, which is clearly visible in Fig. 7.4 & 7.5. Another observation from Fig. 7.5 is that with an increase in concentration of activating solution, ZnO surface has been completely covered by SnO$_2$ grains and SnO$_2$ grains have grown in size as well.
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Figure 7.2: FESEM of pure ZnO.

Figure 7.3: FESEM of 1wt.% SnO$_2$ activated ZnO.
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**Figure 7.4:** FESEM of 3wt.% SnO$_2$ activated ZnO.

**Figure 7.5:** FESEM of 5wt.% SnO$_2$ activated ZnO.
7.3 Results and Discussion

7.3.2 Sensing Performance

The sensing response of fabricated sensors was investigated at various temperatures. The results are shown in Fig. 7.6 and revealed that the optimum operating temperature is 400°C. Gas species to be detected requires a certain amount of thermal energy to cross the potential barrier to combine with the adsorbed oxygen. At an optimum operable temperature, a large number of gas molecules possess required energy, which reacts with adsorbed oxygen resulting in enormous change in conductance of sensing element. Above 400°C, the amount of adsorbed oxygen on the sensor surface decreases and as a consequence a lesser amount of gas species is being consumed. That is why the sensing response decreases at a temperature more than 400°C. For further investigations, all the sensors were investigated at various temperatures.

Figure 7.6: Ethanol sensing response for pure and SnO₂ activated ZnO thick film at different operating temperatures.
operated at the optimum operating temperature of 400°C. To find out the ideal concentration of tin chloride solution required for the best sensor response, the sensors activated with different wt.% of tin chloride solution were exposed to ethanol. Figure 7.7 shows sensor response to 250 ppm ethanol at 400°C versus time for pure and SnO$_2$ activated ZnO gas sensors. It is clear from Fig. 7.7 that the response of the sensor to ethanol vapour increased gradually with increase in concentration of tin chloride solution and optimized at 3 wt.%.

Figure 7.7: Sensing response versus time for pure and SnO$_2$ activated ZnO gas sensor to 250 ppm ethanol at 400°C.

With further increase of concentration of tin chloride the sensor response decreases. There is a significant improvement in the response of sensor with surface activation. The sensor response increased eight times when activated with 3 wt.% tin chloride solution. The response time (5-10 s) and recovery time (15-20 s) of all the sensors is very quick. Figure 7.8 shows the variation of sensing response of activated...
sensor versus concentration of ethanol, which is linear up to 1000 ppm concentration. The adsorption-desorption of molecules at the sensor surface is the principal

![Figure 7.8: Sensing response of optimum activated ZnO gas sensor to different concentrations of ethanol at 400°C.](image)

mechanism for gas detection. It is well known that when an n-type semiconductor oxide is exposed to air, oxygen molecules can adsorb on the surface of the particle and form $O_2^-$, $O_2^{2-}$, $O^{2-}$ ions by capturing electrons from the conductance band, which in turn produces an electron-depleted space-charge layer in the surface region of the particle. Molecular-type adsorbates ($O_2$, $O_5$), dissociative type one ($O_2^{2-}$) and surface (lattice) oxygen ($O_2^-$) are confirmed to exist on the surface of an n-type semiconductor particle. In addition, all of these adsorbed oxygen species are discerned to desorb depending on the adsorption conditions. The tar-
get gas (ethanol) may undergo different reactions, and then can take two routes of decomposition reaction, i.e., dehydration and dehydrogenation:

\[ C_2H_5OH \rightarrow C_2H_4 + H_2O \quad \text{(acidic oxide)} \quad (7.1) \]
\[ 2C_2H_5OH \rightarrow 2CH_3CHO + H_2 \quad \text{(basic oxide)} \quad (7.2) \]

These primary products thus formed are consecutively oxidized to CO, CO\(_2\) and H\(_2\)O.

\[ C_2H_4 + 3O_2^{-}(ad) \rightarrow 2CO_2 + 2H_2O + 6e^- \quad (7.3) \]
\[ 2CH_3CHO(ad) + 5O_2^{-}(ad) \rightarrow 4CO_2 + 4H_2O + 10e^- \quad (7.4) \]

Since ZnO is a basic oxide, dehydrogenation is favored. The catalytic oxidation of alcohol over ZnO agrees with the above results because only one intermediate product (CH\(_3\)CHO) can be detected. As both the alcohol response and the conversion ratio of C\(_2\)H\(_5\)OH increased with an increase in working temperature, the response of the ZnO sensor toward C\(_2\)H\(_5\)OH is dependent on the conversion ratio of C\(_2\)H\(_5\)OH or formation of CH\(_3\)CHO. The formation of intermediate product (CH\(_3\)CHO) increases the response to alcohol. Namely, formation of acetaldehyde plays a key role in the gas sensing process of alcohol.

\[ 2C_2H_5OH(ad) + O_2^{-}(ad) \rightarrow 2C_2H_5O^{-}(ad) + 2H_2O \quad (7.5) \]
\[ C_2H_4O^{-}(ad) \rightarrow CH_3CHO(ad) + e^- \quad (7.6) \]

Thus, the gas sensing mechanism of ZnO toward C\(_2\)H\(_5\)OH is the mode controlled by chemisorption of negatively charged oxygen (Xu et al. (2008a)). ZnO sensor exhibited an optimum response when it was activated with 3 wt.% tin chloride solution. In this sample, small grains of SnO\(_2\) on the ZnO surface are arranged in such a way that its effective surface area have become largest among all the samples. It appears that morphology created by the combination of nanorods, and nanoparticles is the most favorable condition for gas sensing behavior of a material. As samples are only surface activated therefore, it is very unlikely that tin has been substituted in the ZnO lattice. The tin dioxide sits on the zinc oxide which leads to the generation of a large number of surface states. Thus, the number of active sites has increased enormously. As a result, the number of oxygen species adsorbed on the activated surface would be more. Larger the
number of oxygen species adsorbed, larger would be the amount of ethanol oxidised on the sensor surface. This would decrease the resistance of the film crucially, enhancing gas response.

7.4 Conclusion

Zinc oxide powder can be easily synthesized by a chemical route. Activation of ZnO surface with SnO$_2$ enhances its effective surface area. The modified surface of ZnO nanorods has shown exceptionally enhanced sensing response to ethanol vapour. The surface activation with an addition of 3 wt.% tin chloride solution on the sensor surface shows eight-time improvements in sensor response. The optimum operating temperature for all the samples for ethanol gas was 400°C. Surface properties of the ZnO can be modified by surface activation without affecting the bulk properties. The sensor showed a very quick response (5-10 s) and recovery (15-20 s) to ethanol. The results reveal that tin dioxide is an appropriate additive to improve sensing response of ZnO nanorods to ethanol.
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