The structural and sensing properties of cobalt and indium doped zinc oxide nanopowders synthesised through high energy ball milling technique

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Abstract. The high energy ball milling technique was employed to synthesise the undoped ZnO, 5% Co and In single doped and Co-In double doped ZnO nanoparticles. The x-ray diffraction (XRD) was used to probe the structural properties. It was found that the diffraction pattern for In-ZnO nanoparticles display an additional peak which was associated with In^{+3} dopant. Now, incorporating Co and In into ZnO nanoparticles resulted in the reduction of the average grain sizes. The scanning electron microscopy (SEM) images shows that the nanoparticles have a spherical shape. The kenosistec station equipment was used to characterise the prepared samples for gas sensing application. Ammonia (NH_3) gas is being probed in the present work. In all the diffraction patterns observed, the undoped and double doped ZnO nanoparticles are being favoured at a temperature range 200 – 350°C.

1. Introduction

Over centuries various types of gas sensors such as the optical, electrochemical, catalytic acoustic and semiconductor have being developed [1]. The semiconducting metal oxide gas detectors such as SnO_2-ZnO [2], ZnO-CuO [3], Fe_2O_3-ZnO [4] have being investigated over a range of temperatures to detect most common gases [5], like H_2S, CO, NH_3, CH_4 and more to monitor the environment. Report by Feng et al. [6] indicated that enthanol (C_2H_5OH) gas is highly sensible and reflects fast response for ZnO-based sensors. The gas sensing properties of SnO_2 based sensors are found to be greately influenced by the size and the Debye length of the polycrystalline SnO_2 particles [7]. Mean while, Wang et al. [8] investigations revealed that the gas sensing process depends mainly on the surface reaction where the chemical components, temperature, micro/nano-structure of the sensing layer and humidity play an important role. H_2S is an acidic gas with the density slightly higher than that of air. It is known to have bad odor and is mostly present in industrial areas, dumps and sewers. However, the monitoring of the H_2S gas is very important because it is dangerous to humans even at low concentrations [9]. It has been mentioned in several papers that the selectivity and sensitivity of gas sensors to H_2S can be improved through additives of hydrophobic silica [10], ceria or basic oxides to the sensing element and even doping with nobel metals like Ag to SnO_2 [11]. Tamaki et al. [7] reported on the extreme sensitivity of 5wt.% SnO_2-CuO to H_2S gas at 200°C. The one dimensional metal oxide (nanobelt or nanowire base sensors) have proved to possess numerous advantages, like higher sensitivity at parts-per-billion (ppb) and above, lower operating temperature and better compatibility compared to the traditional metal oxide sensors [12]. Wang et al. [13] reported on the ZnO nanorods arrays prepared using a hydrothermal route for gas sensing application. In the report ZnO nanorods showed excellent response to NH_3 and CO

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exposure. Further on the H_2 gas sensitivity with detection limit of 20 ppm from room temperature to 250°C was also observed. ZnO is known to be transparent to visible light and more electrically conductive through doping [14]. The n-type ZnO semiconductor occurs naturally, while the p-type ZnO semiconductor can be produced through co-doping techniques (N and Ga dopants) as indicated by Joseph et al. [15]. Amongst the high-performance gas sensing devices, ZnO nanorods have being found to be sensitive to gases such as H_2, NH_3 and C_2H_5OH at room temperature [16]. In the present work ZnO nanoparticles are prepared using high energy ball milling method, as it has been found to be adaptable and followed easily. Undoped and doped ZnO nanoparticles are subjected to NH_3 gas to check their sensitivity and selectivity.

2. Procedure

The high energy ball milling technique was utilised in preparing the undoped ZnO nanoparticles, 5wt. % of Co-ZnO, In-ZnO and (Co-In)-ZnO nanoparticles samples. These samples were in a powder form, hence they were sonicated in ethanol for 5 minutes before being placed on the micro-hotplate sensor. The average crystallite size of the doped and undoped ZnO nanoparticles ranged from 13 to 18 nm as calculated using Williamson-Hall equation. The kenosistec station equipment was used to characterise the prepared samples for NH_3 gas at various temperatures (200-350°C) and concentrations (5 -100 ppm). The station was maintained at constant voltage of 5V.

3. Gas sensing applications

The gas sensing applications were performed for the undoped, Co and In single doped and Co and In double doped ZnO nanoparticles for NH_3 gas. This characterisation was performed at four temperatures: 200, 250, 300 and 350°C. The response curves for NH_3 gas are plotted for different temperatures as shown in figure 3.1 below. It is observed that the undoped and double doped ZnO nanoparticles are favoured such that the In-ZnO and Co-ZnO nanoparticles are hardly visible. This may be due to the grain sizes of the undoped and (Co-In)-ZnO nanoparticles being smaller compared to those of In-ZnO and Co-ZnO nanoparticles. All the samples seem to show uneven pattern from 300°C [17]. This indicates that the NH_3 gas sensors performs badly at higher temperatures. In figure 3.1 (a) it has been noted that at 200°C the current increases continuously without returning to the reference baseline as the gas concentration is increased.

In order to investigate the behaviour of sensitivity against concentration the equation: $S = \frac{R_{air}}{R_{NH_3}}$, was used. $R_{gas(NH3)}$ is the resistance in the presence of NH_3 gas and R_{air} is the resistance in the air environment. Now $R_{gas(NH3)}$ contributes 90 % of the response time, while R_{air} holds 10 % of the recovery time. Figure 3.2 shows the graphs of sensitivity against concentration. The sensitivity of the undoped ZnO and (Co-In)-ZnO nanoparticles are constantly increasing with the increasing gas concentration. In addition, it is observed that the double doped ZnO exceeds the sensitivity of the undoped ZnO at 300°C [18] and 350°C. This is in good agreement with what Maswanganye et al. [18] obtained when testing NH_3 gas at 300°C for (Co-In)-ZnO nanoparticles prepared by sol-gel method. Sensitivity of the undoped ZnO nanoparticles drops at 10 ppm but increases rapidly at 20 ppm to 100 ppm in figure 3.2 (a) and (b). The Co-ZnO nanoparticles shows a decrease in sensitivity as the gas concentration is increased in the temperature range 200-300°C, thereafter experiences an increasing trend at 350°C. The results suggest that the sensitivity of Co-ZnO nanoparticles is very poor at temperatures below 350°C. In figure 3.2 (d) all the doped-ZnO nanoparticles samples display similar pattern of increase when the gas concentrations are increased. But it can be noted that the double doped ZnO nanoparticles is more sensitive compared to the single doped ZnO nanoparticles. In general all this suggest an enhanced sensitivity at 350°C as shown by figure 3.2 (d).

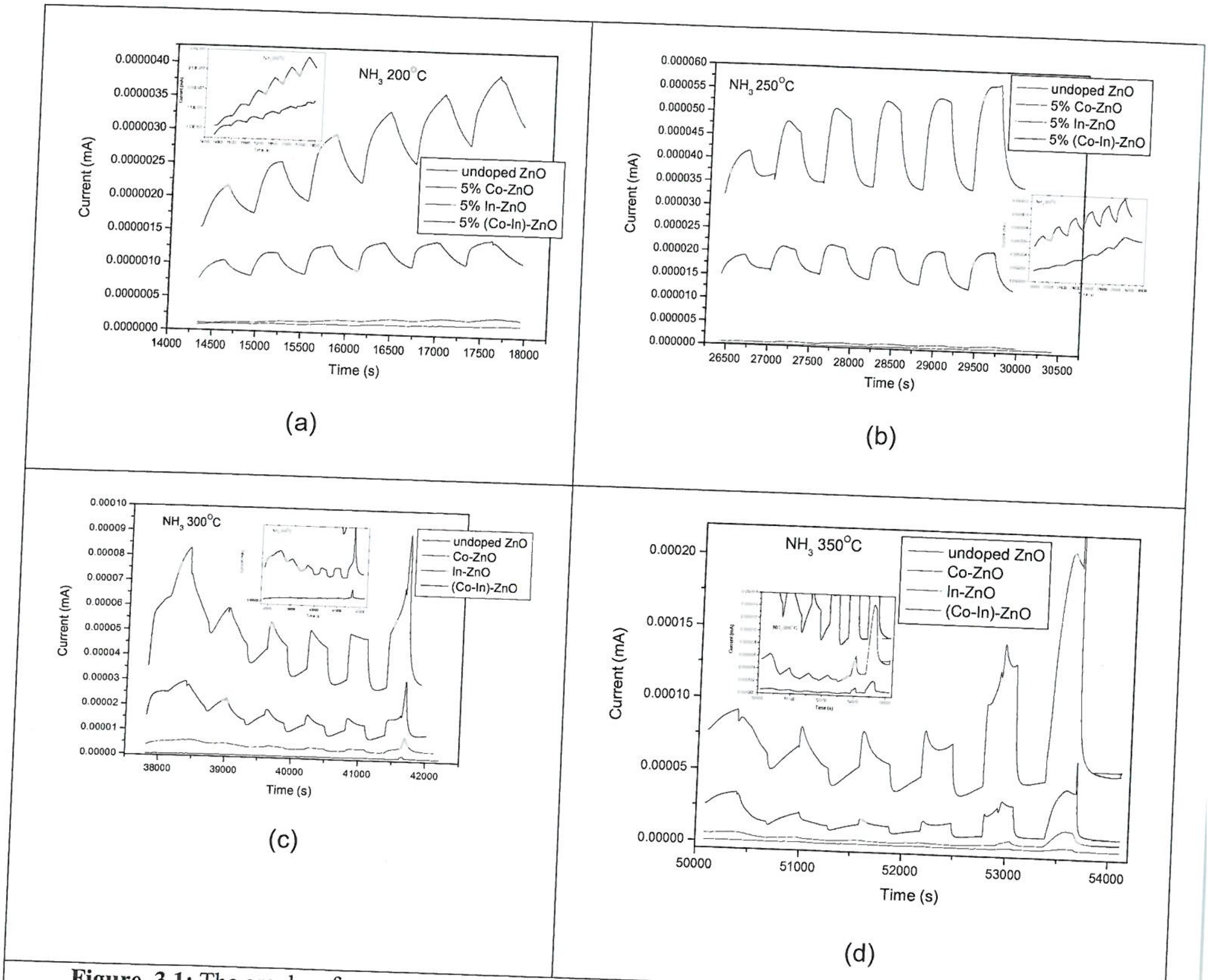
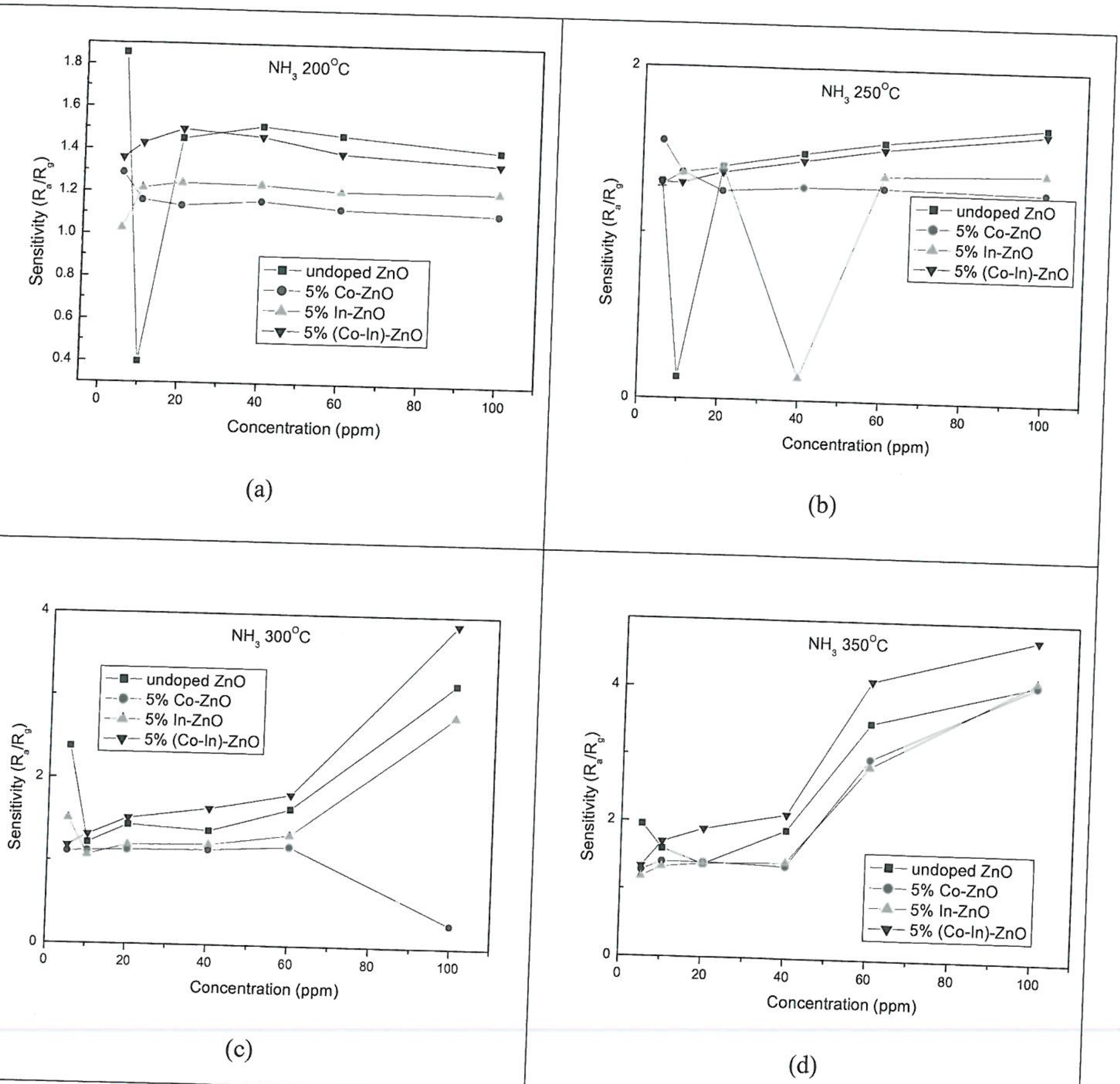


Figure 3.1: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for concentrations ranging between 5-100 ppm.



(a)

(b)

(c)

(d)

Figure 3.2: The sensitivity versus NH3 concentration plot for the doped and undoped ZnO nanoparticles at various temperatures.

4. Conclusion

ZnO nanoparticles were successfully synthesized by the high energy ball milling technique. The current versus time curves show good response and recovery at lower temperatures (< 250°C), than at higher temperatures (> 250°C). The undoped and (Co-In)-ZnO nanoparticles are more favored compared to the Co and In single doped ZnO nanoparticles samples, see figure 3.1 (a)-(d). In figure 3.2 (d) it can be observed that the sensitivity of the doped and undoped ZnO nanoparticles are much higher compared to all other graphs. The Co-ZnO nanoparticles reflect a descending response magnitude with increasing concentration of NH_3 gas at lower temperatures (<300°C). At 350°C the response magnitude of Co-ZnO is ascending when the concentration is increasing, suggesting that the Co-ZnO performs better at higher temperature.

Acknowledgements

The authors are grateful with the financial support from UL, NRF and IBSA. National Centre for Nano-Structures Materials at CSIR is thanked for characterization facilities.

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