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. 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. Thereafter, the kenosistec station equipment was used to scrutinise and monitor the mechano-chemically prepared samples for gas sensing application. Ammonia (NH_3) gas is being probed at various temperatures and concentrations in the present work. In all the current against time plots observed, the undoped and double doped ZnO nanoparticles are being favoured at a temperature range 200 – 350 ^oC. Further on, the sensitivity of the undoped and double doped ZnO increase with increasing NH_3 gas concentration. Co doped ZnO nanoparticles were noted to possess a fast recovery while the Co-In doped ZnO nanoparticles possessed fast response time at 10 ppm.

1. Introduction

Over centuries various types of gas sensors such as the optical, electrochemical, catalytic acoustic and semiconductor have being developed [1]. Semiconducting metal oxide gas detectors such as SnO_2-ZnO [2], ZnO-CuO [3], Fe_2O_3-ZnO [4] have been investigated over a range of temperatures to detect most common gases [5], such as H_2S, CO, NH_3, CH_4 and 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 odour and is mostly present in industral areas, dumps and sewers. However, the monitoring of the H_2S gas is very important because it is dangerous to humans lives 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 ^oC. 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

exposure. Further on the H_2 gas sensitivity with detection limit of 20 ppm from room temperature (25 ^oC) to 250 ^oC 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; the method which has been found to be adaptable and followed easily. Undoped and doped ZnO nanoparticles are subjected to ammonia (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 x-ray diffraction (XRD) and the scanning electron microscopy (SEM) characterisations as discussed in Manamela et al. [17] were utilised to investigate the structural properties of all the ZnO nanoparticles considered in this paper. The average crystallite size of the doped and undoped ZnO nanoparticles ranged from 13 to 18 nm as calculated using Williamson-Hall equation [17]. The KENOSISTEC station equipment was used to characterise the prepared samples for NH_3 gas sensing at various temperatures (200-350 ^oC) and concentrations (5 -100 ppm). For gas sensing, the ZnO nanoparticles were mixed with ethanol before being coated on the surface of the aluminium substrate. The latter was placed between two Pt electrodes and a heater. The substrates coated with undoped, Co an In doped and Co-In double doped ZnO nanoparticles were then inserted in a chamber within the KENOSISTEC station machine. All the samples were subjected to concentrations of 5, 10, 20, 40, 60, 80, 100 ppm of NH_3 gas. The station was maintained at constant voltage of 5 V. The gas flow in and out was maintained at 5 minutes. Detailed procedures on how a KENOSISTEC sensing station operates can be found on the station website: www.kenosistec.com [18].

3. Gas sensing applications

The gas sensing applications were performed for the undoped, Co and In single doped and Co and In (Co-In) double doped ZnO nanoparticles in NH_3 gas environment. This NH_3 gas detection was performed at four distinct temperatures: 200, 250, 300 and 350 ^oC. It must be mentioned that there is no need to test sensing properties below 200 ^oC as the metal oxides like ZnO do not react with NH_3 gas at low temperatures [19]. The response curves in NH_3 gas environment are plotted for the said temperatures as shown in figure 3.1. The undoped and the double doped (Co-In)-ZnO nanoparticles respond much greater to the NH_3 gas with higher current as compared to the In-ZnO and Co-ZnO nanoparticles. This may be ascribed to the grain sizes of the undoped and (Co-In)-ZnO nanoparticles being smaller compared to those of In-ZnO and Co-ZnO nanoparticles [17]. This suggest that the Co and In combined doping induce more inward strains in the ZnO nanoparticle matrix resulting in decreased volume. All the samples seem to show uneven pattern from 300 ^oC [20]. 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 ^oC the current increases continuously without returning to the reference baseline as the exposure time is increased. The significance of this is that at 200 ^oC the undoped and double doped ZnO nanopowder samples response instantaneously with recovery time.

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 ^{o}C [21] and 350 ^{o}C. This is in good agreement with what Maswanganye et al. [21] obtained when testing NH_3 gas at 300 ^{o}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 show a decrease in sensitivity as the gas concentration is increased in the temperature range 200-300 ^{o}C, thereafter experiences an increasing trend at 350 ^{o}C. The results suggest that the sensitivity of Co-ZnO nanoparticles is very poor at temperatures below 350 ^{o}C. Furthermore, response and recovery are highly compromised as depicted in figure 3.1 (c) and (d). The behavior is evident on the double doped and undoped ZnO nanopowder samples. In general, all this suggest only Co-In doped and the undoped ZnO nanopowder samples have reliable sensitivity at 200 – 250 ^{o}C temperature range. Non-sensitivity of In-ZnO and (Co-In)-ZnO nanoparticles could still be attributed to less reactivity of metal oxide complexes with NH_3 gas at low temperatures. Possibly, In^{3+} ions in theses complexes contribute more in retarding the reaction of ZnO and the NH_3 gas [19]. In the case of Co-In double doped ZnO sample, the grain size effect could come into play, as when the size of the nanoparticles are decreased greatly, the melting point also get reduced [22].
The response and recovery time for NH_3 gas was also investigated at 250 ^{o}C for concentrations of 5, 10, 20, 40, 60, 80, 100 ppm. In table 1, a 10 ppm concentration has been singled out to depict as reasonably low amount of NH_3 gas in the atmosphere at elevated temperatures. The single doped Co-ZnO sample demonstrates a substantially fast recovery time in all the ZnO nanoparticles tested. On the other hand, the double doped (Co-In)-ZnO sample demonstrates the fast response time of the four ZnO nanoparticle samples tested. Of course it can also be seen that both the undoped and the double doped ZnO nanoparticle samples have the same longest recovery time of all the samples investigated.

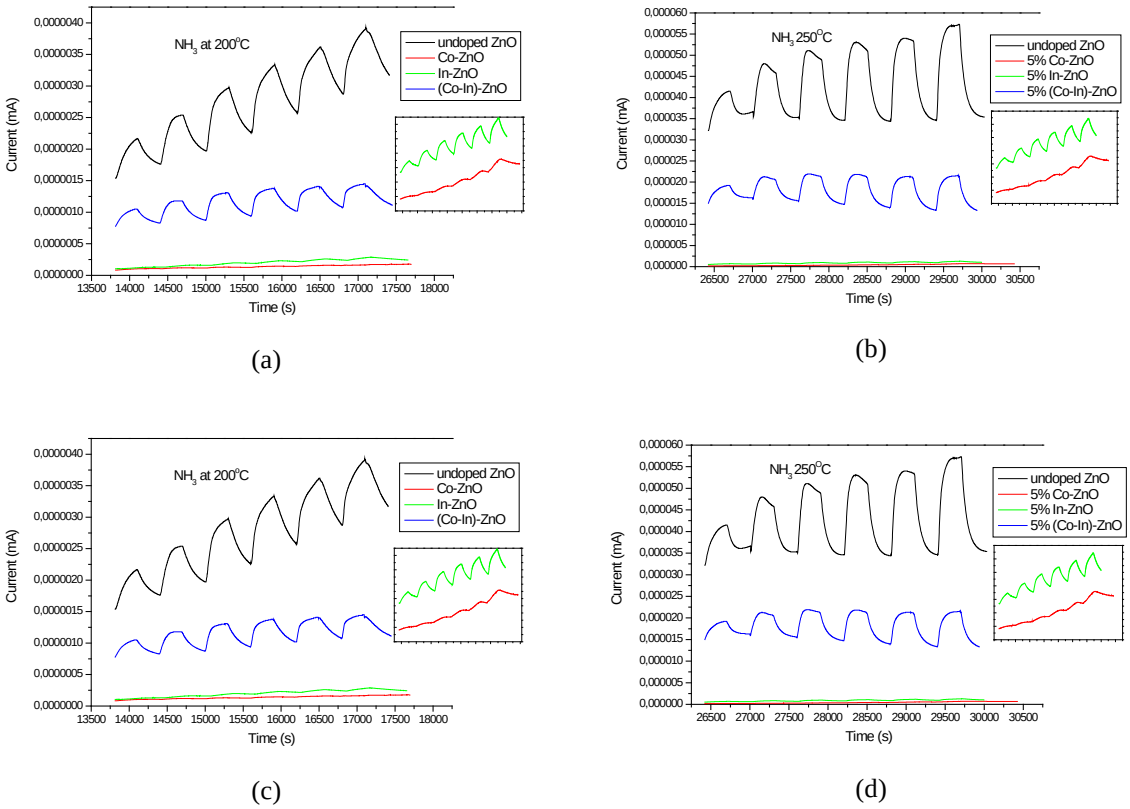

Figure 3.1: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for the concentrations of 10 and 40 ppm respectively.

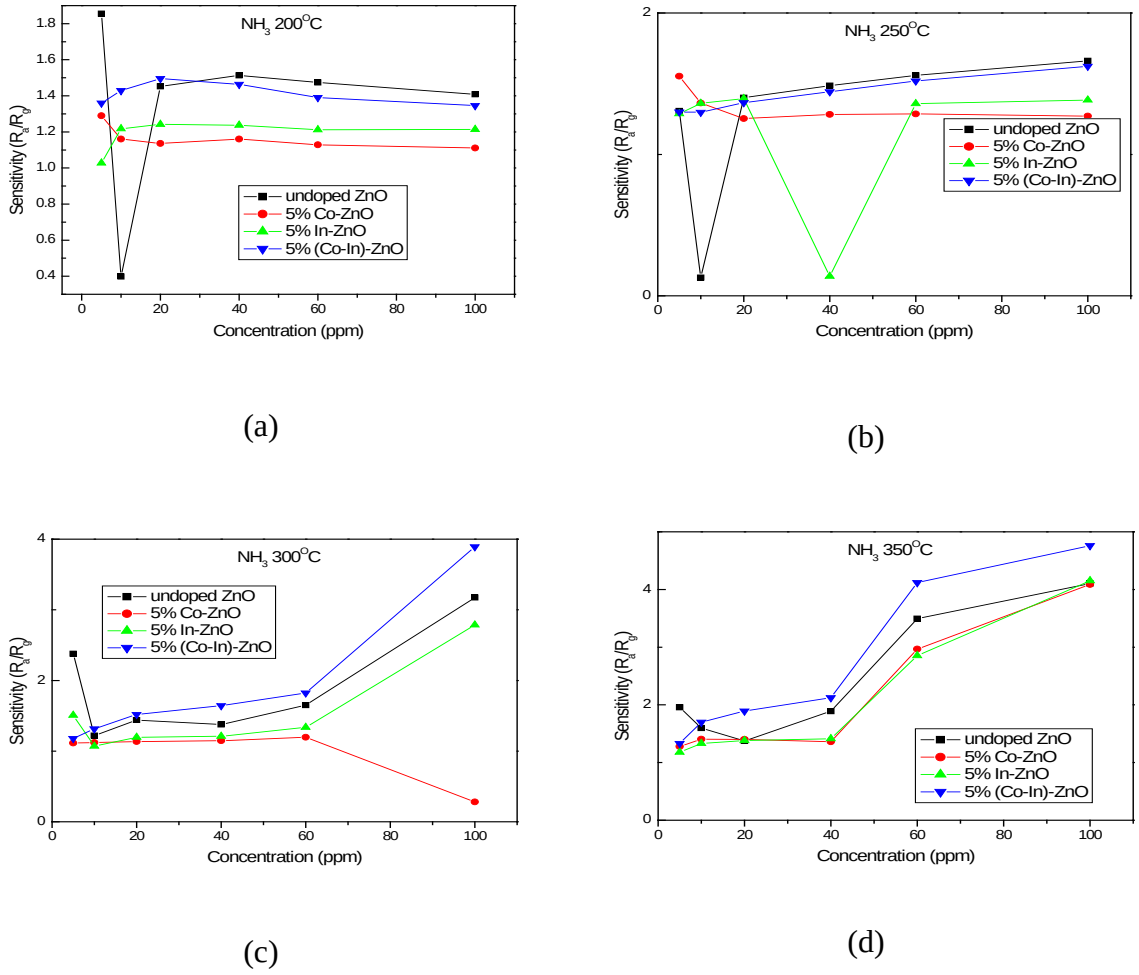

Figure 3.2: The sensitivity versus NH_3 concentration plot for the doped and undoped ZnO nanoparticles at various temperatures.

Table 1. NH_3 gas response and recovery time for the doped and undoped ZnO nanoparticles at 10 ppm.

Sample	Response time (s)	Recovery time (s)
Undoped ZnO	294	304
Co-ZnO	572	23.0
In-ZnO	302	302
(Co-In)-ZnO	289	304

4. Conclusion

ZnO nanoparticles were successfully synthesised by the high energy ball milling technique. The current versus time curves show good response and recovery to the NH_3 gas at lower temperatures, than at higher temperatures. In addition, the undoped and (Co-In)-ZnO nanoparticles are more favoured compared to the Co and In single doped ZnO nanoparticles samples. It has also been observed that the sensitivity of

all the ZnO nanoparticles are much higher at 350 ^{o}C. The Co-ZnO nanoparticles reflect a descending response magnitude with increasing concentration of NH_3 gas at lower temperatures. The Co doped ZnO nanoparticles possess the fast recovery, whereas the (Co-In) double doped ZnO nanoparticles possess the fast response time at 250 ^{o}C.

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