Structural, optical and sensing properties of cobalt and indium doped zinc oxide prepared mechano-chemically

by

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A dissertation submitted in partial fulfilment of the requirements for the degree of Master of Science in Physics in the Department of Physics, School of Physical and Mineral Sciences, Faculty of Science and Agriculture, University of Limpopo, RSA

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Declaration

I declare that the work reported under the title “Structural, optical and sensing properties of cobalt and indium doped zinc oxide prepared mechano-chemically” submitted to the University of Limpopo for the fulfilment of a Master of Science degree in Physics is my own work that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references and that this work has not been submitted before for any other degree at any other institution.

_________________________  ______________________.

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Acknowledgements

I would like to thank:

- My supervisors, Dr T. E Mosuang and Dr B. W Mwakikunga for their exclusive guidance and support for the success of this research. I would like to thank all my colleges and friends at the University of Limpopo for the sufficient input.
- I acknowledge the National Research Foundation (NRF) for their financial assistance throughout during my research.
- The Council for Scientific and Industrial Research (CSIR) branch of National Centre for Nano-structured Materials for giving access to use their equipment’s.
- I am grateful to my family for being there for me, their constant support and encouragements.
Dedications

This work is dedicated to:

My mother
Phuthego Floriah Manamela

My daughter
Potego Precious Manamela

My partner
Franciscas Maropeng Komape
Abstract

The mechano-chemical technique was employed to synthesise the undoped, cobalt and indium single and double doped ZnO nanoparticles powder samples. The x-ray diffraction (XRD), scanning electron microscopy (SEM), raman spectroscopy (RS), ultraviolet-visible spectroscopy (UV-vis), and photoluminescence (PL) spectroscopy were employed to characterise the prepared samples. The XRD and energy dispersive spectroscopy (EDS) results confirmed that the prepared samples were of hexagonal wurzite form. In addition, it was found that the diffraction pattern for In-ZnO nanoparticles display an additional peak which was associated with In$^{3+}$ dopant. The peak suggest that In$^{3+}$ ions prefer the interstitial site in the hexagonal ZnO structure. Doping the ZnO nanoparticles with Co and In did not significantly affect the lattice parameters but the average grain sizes of the nanoparticles were found to be reduced. The morphology of the samples revealed by the SEM images appear to be more spherical. The Raman modes obtained from the excitations wavelength of 514.532 nm further indicated that the prepared samples were of hexagonal ZnO structures. The energy band gap of the prepared samples were calculated from the UV-vis data which showed that the doped ZnO nanoparticles had smaller energy band gap compared to the undoped ZnO nanoparticles. The excitation wavelength of 350 nm were used in the PL study where various defects related emissions were observed for the doped and undoped ZnO nanoparticles. The kenosistec station equipment was used to investigate the prepared samples for gas sensing application. Ammonia (NH$_3$), methane (CH$_4$) and hydrogen sulphide (H$_2$S) gases were probed. In all the response curves observed, the undoped and double doped ZnO nanoparticles are being favoured at a temperature range 200 – 350$^\circ$C. In addition, the double doped ZnO nanoparticles was found to be more sensitive to CH$_4$ at low temperatures and low
concentrations.
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Chapter 1

General Introduction

1.1 Introduction

Zinc oxide (ZnO) which is the 25th most abundant element in nature has drawn the attention of many researchers through its fascinating properties. It is a non-toxic material, highly transparent, chemically stable and is less expensive compared to other materials [1]. ZnO is formed when metallic zinc is exposed to air and forms a protective coating that protect the rest of the metal. ZnO has the three well known structural polymorphs: wurtzite (hexagonal, WZ), zincblende (cubic, ZB), and rocksalt (cubic, RS) of which among all, the wurtzite phase has received outstanding attention because it has the highest thermodynamic stability and can be synthesised easily compared to the pristine RS and ZB metastable phases [2]. Figure 1.1 shows the typical structural polymorphs of ZnO [3]. This ZnO phases have the band gap ranging between 3.27 eV (WZ) and 3.19 eV (ZB) [4], which is suitable for ultra-violet (UV) light activity only [5]. The unit cell for WZ structure has the lattice parameters being $a = b = 3.250 \, \text{Å}$ and $c = 5.206 \, \text{Å}$ [6].

It is an inorganic n-type semiconducting material which exhibit 60 meV for exciting binding energy at room temperature and that gives ZnO remarkable advantage in photoelectronic applications [7]. At present, ZnO is used at electronic industries as a varistor ceramic, used as an additive in rubber, and cream lotions to protect against sunburn in cosmetic industries [8]. This material is proposed for many applications in different fields of science and technology such as catalysis, sensory, photocatalytic field emission devices and solar cells [9].
Bulk and ZnO nanoparticles are very sensitive to toxic gases which are dependent on the size and morphology of sensing materials. Like, the morphology in the short nanorod indicates higher antibacterial activities compared to long nanorod and nanoplate morphologies [10]. Similarly, the nanorod-shaped particles, flat-like hexagonal shape of ZnO structures display more than fivefold increase in the photocatalytic activity for the degradation of methylene blue [11]. It is also regarded as the most efficient material in demonstrating the high efficient gas sensors for its sensitivity to gases like NH$_3$, O$_3$, NO$_2$, ethanol and other species [12]. Nanomaterials can appear in any nanostructure form such as nanotubes, nanowires, nanorings, nano-tetrapod and nanoparticles that allow gas molecules to diffuse into and out of the film easy [13]. These ZnO nanoparticles can be synthesised either under physical or chemical methods [14]. The physical methods include vapor condensation method [15], spray pyrolysis [16], and ball milling technique [17] while the chemical methods are thermal evaporation [18], hydrothermal processes [19], or sol-gel [20]. The method of preparation together with composition, annealing temperature and the rate of decomposition display a principal factors affecting the structural, optical and electrical properties of films and nanoparticles [21]. The advantages of using the ball milling technique is that large quantities can be produced and a wide range of different classes of materials can be obtained within speculated time [17, 22].

Transition metal (TM) oxides; SnO$_2$, ZnO, TiO$_2$, WO$_2$ and Ga$_2$O$_3$ are some of the oxide materials which have been examined for monitoring industrial processes and for gas sensing applications [23]. Literature has reported that tin oxide (SnO$_2$) and zinc oxide (ZnO) reveals higher sensitivity over a range of organic vapors and their surface area also increase when combinational sensors are incorporated by different dopants such as Co, Cu, Fe, Cr, Al, Mg, P, S, Mn at various concentrations [24]. Single and double
doping of the preferred material is possible depending on the desirable application. Extensive studies confirmed that dopants can be able to improve the reduction of grain size while the surface area of ZnO is stabilized [25]. Doping transition metals into ZnO structures are good candidate for enhancing the optical and electrical properties and were also found fascinating when observed from ferromagnetism point of view [26], [27]. In the present work ZnO nanoparticles is prepared through high energy ball milling mechano-chemical method, since it’s easy to follow and operate the machine.
Figure 1.1: (a) Rocksalt (b) Zinc blende (c) Wurtzite [3].
1.2 Aim and objectives

1.2.1 Aims

The aim of the study is to determine the effect of Co and In as combinational dopants on the structural, optical and sensing properties of ZnO nanoparticle powder samples synthesised mechano-chemically.

1.2.2 Objectives

The objectives of the study is to:

i. synthesise ZnO nanoparticles simultaneously doped with two metals (Co and In) mechano-chemically using ball milling,

ii. determine the structural properties of the undoped and doped ZnO nanoparticles using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM),

iii. determine optical properties of the undoped and doped ZnO nanoparticles using Raman Spectroscopy (RS), Photoluminescence (PL) and Ultraviolet-visible (UV-vis) spectroscopy,

iv. determine the effect of nano-sized pure, single doped and double doped ZnO as gas sensors.
Chapter 2

Literature review

2.1 Structural properties of ZnO

Over the past decade a great interest in semiconducting metal oxides (SMOs) has developed drastically because of their diverse properties. Especially, when SMOs particles are in their nanometer range, they display an enormous change in their optical and magnetic properties [28]. SMOs can be obtained in different forms such as the bulk and single crystals, nanoparticles, thick and thin films materials [29]. The interesting thing about the SMOs is that they can appear in different phases depending on the kind of experimental technique followed when preparing a particular material. Various techniques are employed to control the shape, size, distribution and morphology of these oxides. ZnO nanoparticles is one of the SMOs species identified to be photosensitive, highly reactive and strong oxidizing agents, hence is a good material for photocatalytic processess [30, 31]. TiO$_2$ has a durable stability against photocorrosion and chemical corrosion. Now, because of this unusual optical and electronic properties of TiO$_2$ it makes it possible to be used in the photoelectric conversion and photocatalytic reaction [32].

Chemical methods have great achievement in controlling morphology and crystallite size than physical methods. Now, bulk and nanoparticles are obtained through techniques such as sol-gel [33], hydrothermal [34], ball milling [35] and physical vapour deposition methods [36], while the thin and thick films are synthesised using spray pyrolysis technique (SPT) [37], and chemical vapour deposition methods [38], just to name a few. Sol-gel method is easy to control, inexpensive and require low fabricating temperature which makes it an attractive method of preparing nanoparticles. Pechini’s
method [33] is one of the sol-gel methods which in comparison with others yields better compositional homogeneity, lower cost and toxicity. The hydrothermal method is one of the popular method used because it is simple, inexpensive, involves low temperature, produces high yield, is scalable and the process is more controllable. This method was used by Kiomarsipourn et al. [34] by preparing various pigments of ZnO on a large scale at low temperature without using supplements such as surfactants and templates. SPT is used to prepare transparent conducting oxides. This technique is very easy, has low cost, safe and good for the production of large area uniform film coatings [39]. The chemical bath deposition (CBD) technique is simple to perform at low temperatures, environmentally friendly, catalyst free and inexpensive [40].

Properties such as: the phase structure, the structural orientation and amorphous state of the material are obtained from analysing the XRD pattern. Gandhi et al. [41] and Norton et al. [42] show in their studies that ZnO shift from diamagnetic behaviour to ferromagnetic behaviour when ZnO nanoparticles is doped with cobalt (Co) and this has also being predicted theoretically [43]. Karak et al. [44] reported that the XRD pattern of the undoped and cobalt doped ZnO appear as single phase of hexagonal wurtzite structure, which indicate the Co ions was successfully doped throughout the ZnO lattice [45]. Even though from the same pattern of XRD there is a shifting of diffraction peaks to the higher angle for those doped ZnO pattern and this might be the fact that the ionic radius of cobalt (0.58 Å) is smaller compared to the ionic radius of zinc (0.60 Å) [46]. Also Cong et al. [47] and El-Hilo et al. [48] reported on Mn doped ZnO, where no disturbance occurred when Mn were introduced in the structure. On the studies of Lamba et al. [49], a clear EDS spectra of ZnO doped SnO$_2$ nanoparticles
prepared by facile hydrothermal process shows only several peaks of Zn, Sn and O are well defined, which reveals that the prepared material does not contain impurities.
Figure 2.1 (a) Hexagonal (Wurtzite) [50], (b) Zincblende (ZB) and (c) Rocksalt (RS) model of ZnO nanostructures.
The ZnO nanostructures can be obtained either in gaseous phase or in a solution form. The gaseous phase is the least explored method as compared to the solution phase because it’s complicated and expensive [51]. The hexagonal WZ ZnO is observed under normal pressures [52]. It is transparent in the visible light range and it has been reported that dopants such as (B, Al, In, Ga) of group III and (Pb, Sn) in group IV can enhance its conductivity [53]. At Zn-rich conditions ZnO is considered as n-type semiconductor [54]. Studies show that n-type doping of ZnO is more adaptable as compared to the p-type doping [55]. The polar surface is an important characteristic of ZnO, in which basal plane (0001) is the common polar surface [56]. Zn$^{2+}$ and O$^{2-}$ are the two interconnecting sub-lattices found in the ZnO crystal structure [57], along the c-axis each Zn$^{2+}$ ions is surrounded by a tetrahedral of O$^{2-}$ ions and vice-versa [58], meaning the one end is partially positive zinc lattice site; Zn-(0001) and the other partially negative oxygen lattice site; O-(000̅1), see figure 2.1 (a). ZnO has two most observed facets namely {211̅0} and {011̅0} which are non-polar and have lower energy than the {0001} facets [56].

Semiconductors such as ZnO, CdS and ZnS can be cubic zincblende (ZB) and hexagonal wurtzite (WZ) [59]. The ZnO RS and ZB crystal structure have their conventional unit cell as cubic while the WZ crystal structure has a hexagonal lattice [60]. This cubic phase has been reported as metastable at atmospheric pressures [61]. The lattice parameter for rocksalt is a= 4.283 Å [62] and for zinc blende is a= 4.62 Å [63]. The ZnO nanoparticles transform to Rocksalt (RS) nanoparticles structure at high pressures. These transformations were studied both theoretically [64], [65] and experimentally [66, 67]. The stability of the RS phase can be increased by doping ZnO with Mg, Mn, and Co metals [68]. While the First-principle calculations done by Zhang et al. [68] and Wang et al. [69] shows that the transition pressure from WZ-RS
decreases when Mn and Co dopants are introduced. The index direction of ZB-ZnO is [011], [70].

2.2 Optical properties of ZnO
Defects are unavoidable and they are contained in every material, hence there is no such thing as perfect materials. Crystal defects can be of single atom, row of atoms and ensemble atoms which explains the existence of point defects, line defects and complexes. There are two distinct deep level defect(s) of emission; namely intrinsic and extrinsic level defects. Vacancies such as zinc vacancy (V_{Zn}) and oxygen vacancy (V_{O}) are classified as the intrinsic level defects, while the interstitials and substitutional such as zinc interstitial (Zn_i), oxygen interstitial (O_i), zinc anti-site (Zn_O) and oxygen anti-site (O_{Zn}) are classified as the extrinsic level defects [71]. These type of defects are found in ZnO nanostructures and prediction shows that ZnO is a semiconductor that contained a large number of point defects that influences its thermal conductivity [72]. The intrinsic defects control the electrical conductivity of ZnO since they act as n-type donors. The electrical resistivity property decreases when ZnO is doped with group III elements [73, 74].

ZnO is classified as a compound semiconductor. Its band gap can be controlled by adjusting the carrier concentration with donor such as the oxygen vacancies (V_{O}) and interstitial zinc (Zn_i) atoms [74]. The performance of these semiconductors can be improved by introducing dopants into the lattice of the SMOs [75]. Wang et al. [76] reported about ZnO nanocrystal doped with Mg were the absorption spectrum shows a blue shift indicative of an increase in the band gap, but Cd-ZnO nanocrystal indicate a decrease in band gap as the doping concentration of Cd increases from 0-10 \%.
Wang et al. [77] reported about ZnO nanoparticles synthesised by colloidal chemistry method in which state that as the crystallite size increases the oxygen vacancy decreases, leading to the increase in UV emission. When ZnO nanoparticles are doped with Cu$^{2+}$ ions they do not change the crystal structure, instead they increase the energy band gap up to 3.93 eV [78]. Even Tong et al. [79] report shows the band gap of ZnO nanoparticles increases as the doping concentration of Mn$^{2+}$ increases. This is due to the substitution of Zn$^{2+}$ ions in the ZnO lattice by Mn$^{2+}$ ions. The thickness of the film has a great influence on the structural, optical and electrical properties of ZnO thin films. When the grain size increases, the thickness of the film also increase, thus the crystalline quality of the films gets better. Prasada et al. [80] also reports that the heat treatment improves the electrical conductivity of ZnO thin films. But while doing that we should also keep in mind that the charge carrier concentration increase at higher temperatures while the Debye length decrease. This indicates that a temperature has an effect on the semiconducting sensor material and this changes the physical property of a material as reported by Mizsei [81].

The optical properties are influenced by the energy band structure and lattice dynamics [82]. ZnO nanostructure has a band gap of 3.4 eV which is suitable for short wavelength optoelectronic applications [83]. SnO$_2$ and In$_2$O$_3$ are weak n-type semiconductors with band gap of 3.62 eV [84] and 2.9 eV [85], respectively. They both exhibits great electrical and optical properties [86, 87]. Like SnO$_2$ which possess low electrical resistance and high transparency in the UV-visible region [88]. SnO$_2$ has a rutile crystal structure while In$_2$O$_3$ has a cubic crystal structure [89]. Even CdO is a face centred cubic (FCC) crystal structure with very low band gap of 2.28 eV. CdO is less desirable because of the cadmium (Cd) for its toxicity [90].
2.3 Sensing properties of ZnO

The most important parameters in developing gas sensors are sensitivity and selectivity which draw attention of many researchers. Sensitivity can be defined as \( \frac{R_g}{R_a} \) for oxidizing gases and \( \frac{R_a}{R_g} \) for reducing gases, where \( R_g \) is for the resistance in the reference gas containing target gases and \( R_a \) is for the resistance of gas sensors in the reference gas (usually the air). There is a significant relationship between \( R_g \) and \( R_a \) with the surface reaction(s) taking place [91].

\[
\text{sensitivity}(S) = \frac{R_a - R_g}{R_a} = \frac{\Delta R}{R_a}.
\]  

(2.3.1)

The transition metal oxides (TMO) are solid materials normally tested for gas sensing applications; for example we have WO\(_3\), SnO\(_2\), ZnO, and In\(_2\)O\(_3\) which are the most investigated group of sensors among other types reported recently by Gurlo [92]. Figure 2.2 shows the schematic diagram of static gas system that is similar to the one which Gurlo [92] used to test all those gases. These TMO have large band gap ranging between (3 eV - 4 eV) [93] and are expected to be quite inert under normal temperatures. They have an excellent electrical and optical characteristics and are known to be transparent within the visible electromagnetic region of about 400 nm to 700 nm [94]. They are amorphous materials and also known to be very conductive in their amorphous state [95]. Among the semiconducting material, In\(_2\)O\(_3\) has been studied for possible chemical sensing due to its advantageous features such as a wide band gap of about 3 eV, good catalysis and low resistivity [96]. But in the ZnO structure, the crystal defects such as the oxygen vacancies or shallow donor are the key factors in determining the gas sensing properties, since they play a role in the absorption sites for the gas molecules and along the ZnO nanostructure surface [97]. Sensors are extremely important in detecting toxic and flammable gases such as CH\(_4\),
H₂, NH₃, H₂S and CO in mines, gas storage plants, petroleum industries and households [98]. This helps in maintaining healthy working and living environment, to avoid risk of accidental explosion and public safety in general. H₂ is the most useful gas in many chemical processes and numerous industries including aerospace, petrochemical, medical and energy [99]. This gas has a perfectly clean combustion action which does not release any pollutants or greenhouse gases, thus making it a promising clean energy source for future generation of automobiles and household appliances. However, when H₂ is concentrated in air by about 4% to 75% by volume, it may cause explosions. Bearing in mind that H₂ is a colourless, odorless and tasteless gas that human sensors can not detect [99, 100]. On the other hand there is CO which is colourless and odourless. This gas has the highest contribution to air pollution. CO is usually produced by incomplete combustion of industrial and domestic fuels jointly with veld fires [101]. There is also H₂S gas which is also colourless, flammable with a very bad smell produced from city sewage, hot springs, natural gases, gasoline and volcanic gases. H₂S smells rotten eggs and is a highly toxic chemical gas which can lead to unconsciousness or death even at low concentrations [102, 103, 104, 105].

Semiconductor sensors such as WO₃, ZnO, In₂O₃ and some perovskite type materials have been found to be sensitive to H₂S gas. ZnO were reported to show high sensitivity with fast response and recovery time for low concentration of H₂S gas [106]. Wang [107] reported that the morphology of the nanoparticles have high sensitivity and quick response to the gases because they are 1-dimensional. It has being verified both experimentally and theoretically for various sensing materials like In₂O₃ and SnO₂ that the decrease in crystallite size exhibit an increase in the sensor response. Parthbavarman [108] reported that doping with Co can enhance the sensing behaviour of TMO, and also the detection of ethanol gas were performed using Co-doped SnO₂.
nanoparticles. There are many materials which are being used for sensing applications but they are not effective and often suffer from low sensitivity, slow response, poor selectivity and slow recovery time.
Figure 2.2: Schematic diagram of static gas system according to Gurlo [92].
Chapter 3

Experimental techniques and characterisation

3.1 Methodology

Zinc oxide (99.9 %), cobalt (99.8 %) and indium (99.9 %) where purchased from Sigma-Aldrich and used without further purification. The undoped ZnO, Co-ZnO and In-ZnO nanoparticles were synthesised mechano-chemically using an 8000 MIXER ball milling machine [109] for 12 hours doped by 2 %wt, 5 %wt and 10 %wt. This was attained by directly putting proportionate amounts of ZnO and Co or In into the steel vial. The double doping ZnO nanoparticles with two metals cobalt and indium were also performed as follows: 2 %wt (1% In/ 1% Co), 5 %wt (2.5% Co/ 2.5% In) and 10 %wt (5% Co/ 5% In) doped and ball milled for 12 hours as well. 3 g of ZnO powder was measured and placed into the hardened steel vial (that can grind up to 10 g of the sample) with two stainless steel balls of diameter 6.825 mm.

3.2 Ball milling

Ball milling machine also called a shaker mill, the SpexMill or high-energy ball mill has been utilised for mechano-chemical synthesis. It comes with 8001 hardened steel vial set and a set of different sizes of stainless steel balls having different diameters. It has safety interlock system, a variable-range electronic timer, and shock-mounted electric motor for table top operation. It runs for 0-100 minutes and it can be extended to 1000 minutes or more by the user. It can grind up to 10 g of a sample and up to 60 mL for blending powders. An extensive part of the machine’s limitations lays in the fact that the particles are characterized only by size [110].
Figure 3.1: (a) 8000M Mixer/Mill, (b) 8001 hardened steel vial set, (c) Changes in the material trapped between colliding balls in a ball mill and (d) micrometer screw gauge.
This ball milling machine has served analytical chemists and spectroscopists for over forty years. It has being used for grinding or mixing raw materials for further processing. Each ball develops fairly high G-forces, enough to grind the samples into powder-like substances (analytical fineness) as the machine shake the vial in complex motion of back-and-forth swing. It can also be utilized for mechanical alloying and nano-milling [111]. A 8000M Mixer together with its contents are shown in figure 3.1.

3.3 Characterisation techniques

Characterisation of the samples was carried out using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Raman Spectroscopy (RS), Photoluminescence (PL), Ultraviolet-visible (UV-vis) spectroscopy and the kenosistec station equipment.

3.3.1 X-ray diffraction (XRD)

The XRD experiment were performed using the Phillips analytical X-Ray B.V diffractometer machine with Cu Kα1 (λ= 1.54 Å) monochromatic radiation source. The measurements were collected at 45.0 keV and 40.0 mA. The XRD were collected by scanning between 2θ = 20° and 60° in 0.02° steps. Figure 3.2 shows the schematic diagram of a usual X-Ray powder diffractometer. The average crystal size was determined using the Debye-Scherrer’s formula [112]:

$$D = \frac{k\lambda}{\beta h k c o s\theta},$$ (3.3.1.1)

where $k$ is a constant of 0.9 (the shape factor for spherical surface), the wavelength ($\lambda$) of X-rays ($\lambda$= 1.54 Å for Cu Kα1 radiation), $\beta$ is the full width at half maximum (FWHM) and theta ($\theta$) of the Bragg’s angle.

The strain induced in powders due to crystal imperfection and distortion were related by:
\[ \varepsilon = \frac{\beta_{hkl}}{4\tan \theta}. \] (3.3.1.2)

Now, a different approach is employed where the total integral breadth of Bragg peak is obtained by adding the crystallite size and the strain broadening components [113].

From equation (3.3.1.1) and (3.3.1.2) it is clear that the peak width from crystallite size varies as \( \frac{1}{\cos \theta} \), whereas the strain varies as \( \tan^{-1} \theta \). Combining the Scherrer’s equation and \( \varepsilon = \frac{\beta_{hkl}}{4\tan \theta} \) results in the Williamson-Hall equation [114]:

\[ \beta_{hkl} = \beta_D + \beta_s, \] (3.3.1.3)

\[ \beta_{hkl} = \frac{k\lambda}{D\cos \theta} + 4\varepsilon \tan \theta. \] (3.3.1.4)

Rearranging equation (3.3.1.4) gives:

\[ \beta_{hkl}\cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta. \] (3.3.1.5)

The d-spacing was calculated using the Bragg’s law:

\[ 2d_{hkl}\sin \theta = n \lambda, \] (3.3.1.6)

where \( d_{hkl} \) is the interplanar spacing, \( n \) is an integer specifying the order of diffraction and \( \theta \) is the diffraction angle.

The following equation relate the interplanar spacing to the \((h k l)\) planes and lattice constants \( a = b \) and \( c \) in the hexagonal structure of ZnO.

\[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}. \] (3.3.1.7)

Where \( a = b \neq c \) are lattice parameters. Now for plane orientation \((100)\), the lattice constant is calculated using the following relation:
\[ a = \frac{4}{3} (d_{hkl})^2. \]  

(3.3.1.8)

Now for the plane orientation (002)

\[ c = \sqrt{4(d_{hkl})^2}. \]  

(3.3.1.9)
Figure 3.2: The schematic diagram of X-ray powder diffractometer (XRD) [115].
3.3.2 Scanning Electron Microscope (SEM)

When preparing the samples for SEM characterization, acetone is used to clean the aluminium-stub. Thereafter a carbon tape is placed on the stub so that the ZnO nanoparticles can be deposited on it. When taking the SEM images, an electron beam is emitted from the electron gun, see figure 3.3. The anode determines the accelerating voltage of the gun and also polarises the electron beam. The magnetic lens magnify the image of the beam source exciting the electron gun and to focus the beam on the specimen [116]. There are also scanning coils which operate to control the raster of the beam and to construct the image from point to point [117]. Those electron beams will interact with the sample and create the secondary electrons which are collected in the secondary electron detector (SED) to create an image [118]. A mechanism of how a SEM creates images is shown in figure 3.3.
Figure 3.3: Scanning electron microscope (SEM) [119].
3.3.3 Photoluminescence (PL) spectroscopy

PL spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials. It also provides more information on bandgaps, defect identification and material quality. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation [120]. PL originates from absorption or emission process experienced in different energy states in a sample [121]. A PL spectroscopy instrument is pictured in the figure 3.4 below.
Figure 3.4: Nano$_{c9}$Photoluminescence.
3.3.4 Ultraviolet-visible (UV-vis) spectroscopy

The UV-vis spectrometry is used to measure the transmittance, reflectance and absorption of the sample. A UV-vis spectrum can be obtained when the electromagnetic radiation of diverse wavelength (near UV and near IR) is ideally irradiated on to the sample. Hence, a monochromatic radiation is employed at a time. The spectrum is a measure of the radiation absorbed at each wavelength against the wavelength [122]. The position of the maximum of the absorption band called \( \lambda \)-max, and the intensity of the bands are the two major parameters used to characterise the UV spectra of substances [123]. Even the energy band gap of the materials is calculated from the UV-vis data [124]. A schematic diagram demonstrating how a UV-vis spectrophotometer generates data is shown in figure 3.5.
Figure 3.5: The schematic diagram of UV-visible spectrophotometer (UV-vis) [125].
3.3.5 Raman spectroscopy (RS)

RS is used to determine modes of molecular motions, especially vibrations [126], [127]. The RS is obtained by illuminating a monochromatic laser beam on to a sample to generate a scattering light. Now only the wavelength different to that of the incident light is analysed. It is applicable to the qualitative and quantitative analysis of covalently bonded molecules [128]. The instrument is used for identification of phases, molecular and crystalline symmetries, crystalline polymorphs and measurement of stress. RS databases are used to plot a spectrum (a graph of light intensity as a function of light frequency) of the measured results [126]. The peaks in the spectrum provide information about molecular structure and from the molecular structure, the compound constituents can be identified [129]. A raman spectroscopy equipment picture is shown below in figure 3.6.
Figure 3. 6: Raman spectroscopy (RS).
3.3.6 The kenosistec station equipment

The kenosistec station equipment is used to test the prepared compound materials such as SnO₂, ZnO etc. for gas sensing response, operating temperature, recovery time and more. A sample is placed on the micro-hotplate sensor [130] and thereafter all the grouping is placed in the machine where there are two channels; one responsible for the flow of current and the other for the flow of heat. When the sample is in the machine, one type of gas pipe is open for some time for a particular concentration to infiltrate the sample area. The gas pipe is then closed in order to observe the recovery and response time of the material. This is done for constant time while varying gas concentration and temperature for different gases such as the carbon monoxide (CO), methane (CH₄), hydrogen (H₂), ammonia (NH₃) and sulphurous gases (H₂S, SO₂) [131]. In order to analyse what material detects which gases best, graphs of response (Rₓ/R₀) against time (s), temperature (°C) and concentration (ppm) are plotted from the measured data. Now the type of material produced limits the sensing ability in a sense that if Cu-ZnO nanoparticles detect only NH₃, even if CH₄ is present in the area it would not be able to detect it [132, 133, 134]. The kenosistec station equipment is shown in the figure 3.7 below.
Figure 3.7: The kenosisteck station equipment.
Chapter 4

Structural and optical properties

4.1 Introduction

Zinc oxide (ZnO) is a promising inorganic n-type semiconducting metal oxide. Its physical and optical properties are important for short-wavelength optoelectronic applications with a wide band gap of about ~3.3 eV [135]. This material enjoys superfluous advantage such as low cost, rich material source, non-toxicity and low temperature synthesis, as compared with other semiconductors like GaN and CuO [136, 137]. The investigations reveal that the crystal structure of a material hold routes to various applications [138]. ZnO has being found to have a large family of nanostructures including nanowires, nanorods, nanoballs, nanosheets and so on. The nano- scaled properties enhances the applications of manufactured macro- devices such as smart windows, gas sensors, solar cells, and ultraviolet light-emitters [139]. Djerdj et al. [140] investigated the ferromagnetic behaviour of ZnO nanoparticles, and obtained that they possess more strength when doped with Co metal. Literature reports by Donesha and Jayanna et al. [141] indicate that the crystal structure of ZnO does not change when co-doped by Fe and Co. Many methods are being developed in order to produce nanoparticles of controlled size, such as ZnO nanoparticles [142]. As such, sol-gel method, one of the well-known technique was used by Spanhel et al. [143], Bahnemann et al. [144] and Maswanganye et al. [145] to prepare zinc oxide nanoparticles. The aim of this work is to study the structural and optical properties of ZnO nanoparticles prepared using high energy ball milling method, as it has been found to be adaptable and can be followed easily.
4.2 Structural characterisation

4.2.1 X-ray diffractometer (XRD)

The crystal structure of ZnO nanoparticles was investigated using XRD having incident Cu Kα1 radiation (\( \lambda = 1.541 \text{ Å} \)). The XRD results were collected by scanning the samples with diffraction angle between 2θ=20 and 60° in 0.02° steps. In figure 4.2.1 there is an XRD pattern which exhibit several diffraction peaks that can be indexed as hexagonal wurtzite structure, since peaks at 2θ = 31.77, 34.43, 36.27, 47.56 and 56.63° belonging to the (100), (002), (101), (102) and (110) planes respectively (JCPDS No.36-1451) were observed. This implies that the Co\(^{2+}\) ions were successfully incorporated into the lattice position of Zn\(^{2+}\) ions. Looking at the XRD pattern of In-ZnO nanoparticles, a new peak along the (400) plane (*) was observed between 31.78° and 34.44°. This peak is associated with an indium dopant [146]. Speculation were that Co\(^{2+}\) prefers the interstitial site which leads to great stress in the structures when compared to filling in a Zn\(^{2+}\) vacancy of which In\(^{3+}\) seems to be preferring. The crystallite size, strain and lattice parameters of undoped ZnO, Co doped ZnO, In doped ZnO and Co-In doped ZnO nanoparticles are listed in table 4.1. The results show the crystallite size of Co-ZnO nanoparticles being the largest of all the calculated nanoparticles, except for the purchased ZnO sample. When looking at the strains, the reverse was observed. The explanation could be extracted from the ionic radii of both In\(^{3+}\) and Co\(^{2+}\). Since the ionic radius of Zn\(^{2+}\) is 0.60 Å while that of In\(^{3+}\) is 0.62 Å which is greater than that of Co\(^{2+}\) 0.58 Å [147]. The fact that strain values are consistently higher for Co-ZnO nanoparticles than for In-doped ZnO nanoparticles may point to the varying preferred sites of Co\(^{2+}\) and In\(^{3+}\) in the ZnO structure. It can also be observed that the crystallite size of all the single doped ZnO nanoparticles are larger than those of the double doped ZnO nanoparticles. Another fact is the crystallite sizes calculated
using Debye-Scherrer’s equation [148] are large compared to the ones calculated by Williamson-Hall equation [149]. This is caused by the contribution of the strain parameter calculation that is included in the Williamson-Hall equation and not in the Debye-Scherrer’s equation. While the strain of single doped ZnO nanoparticles are smaller than those of double doped ZnO nanoparticles. The percentage difference between the reported lattice parameters [150, 22] and the calculated ones are comparable.
Figure 4.2.1: XRD pattern of the undoped and 5 %wt doped Co-ZnO, In-ZnO and (Co-In)-ZnO nanoparticles milled for 12 hours.
Table 4. 1: The calculated crystallite size (by Williamson-Hall and Debye-Sherrer), strain and lattice parameters of 5% doped and undoped ZnO.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Debye-Sherrer (nm)</th>
<th>Williamson-Hall (D) (nm)</th>
<th>Strain (ε)</th>
<th>Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-purchased ZnO</td>
<td>49.414</td>
<td>43.036</td>
<td>0.0015</td>
<td>3.252</td>
</tr>
<tr>
<td>Undoped ZnO</td>
<td>18.258</td>
<td>16.080</td>
<td>0.0057</td>
<td>3.251</td>
</tr>
<tr>
<td>Co-ZnO</td>
<td>21.791</td>
<td>18.804</td>
<td>0.0047</td>
<td>3.250</td>
</tr>
<tr>
<td>In-ZnO</td>
<td>20.570</td>
<td>17.765</td>
<td>0.0048</td>
<td>3.249</td>
</tr>
<tr>
<td>(Co-In) ZnO</td>
<td>15.354</td>
<td>13.263</td>
<td>0.0064</td>
<td>3.254</td>
</tr>
</tbody>
</table>

4.2.2 Scanning electron microscope (SEM)

The Joel [JSM-750OF] model of SEM was used to examine the morphology of the ZnO nanoparticles. The images were taken at 100 nm scale and a magnification of x50. The SEM images appear to be spherical in shape as shown in figure 4.2.2 (a) and (b) for undoped ZnO nanoparticles and co-doped ZnO nanoparticles. The morphology of the ZnO nanoparticles were not significantly affected by the dopants added.

The energy dispersive spectroscopy (EDS) shows all the elements present in the sample (Zn and O); see figure 4.2.3 (a) for undoped ZnO nanoparticles. The elemental composition of the undoped ZnO nanoparticles was analysed and found to have Zn = 46.57, O = 26.90, C = 25.02 and Al = 1.51. The samples were mounted on carbon (C) tape, hence the presence of the weak C peak on the EDS spectra. The EDS of the undoped ZnO nanoparticles show the presence of a peak that belongs to aluminium element. This was caused by the aluminium step used when collecting data from the sample.
SEM. There are several peaks for Zn in the EDS spectra as compared to other as ZnO was the host material.
Figure 4.2.2: (a) The SEM of undoped ZnO nanoparticles (b) The SEM of 5 %wt co-doped (Co-In)-ZnO nanoparticles.
Figure 4.2.3: The EDS of undoped ZnO nanoparticles.
4.3 Optical characterisation

4.3.1 Raman spectroscopy (RS)

The Raman scattering method was employed to probe the phase purity and the vibrational modes of the ZnO nanoparticles [151]. Figure 4.3.1 shows the room temperature Raman scattering spectra of the doped and undoped ZnO nanoparticles prepared mechano-chemically. It is well known that the hexagonal wurtzite ZnO display three vibration modes in the Raman spectra: $A_1$, $E_1$ and $E_2$. $A_1$ and $E_1$ modes split into two modes, namely longitudinal optical (LO) and transverse optical (TO) components respectively, while $E_2$ (high) mode also consists of two modes of low and high frequency phonons [152]. The intense peak observed at 436.4 cm$^{-1}$ for the undoped ZnO nanoparticles is known as the Raman-active dominant $E_2$ (high) mode, indicating that all prepared samples are of the hexagonal wurtzite phase of ZnO [153]. The increase in the compressive stress on the sample cause the frequency shift to the blue region of $E_2$ (high) mode from 436.4 to 429.0 cm$^{-1}$. This is consistent with the XRD patterns as shown in figure 4.2.1. At a frequency of 329.6 cm$^{-1}$ a peak associated with the $E_{2H}$-$E_{2L}$ mode can be observed. The third peak centered at 573.5 cm$^{-1}$ represent two modes: $A_1$ (LO) and $E_1$ (LO) modes that are superimposed. This peak is believed to result from intrinsic defects in ZnO nanoparticles such as oxygen vacancy, zinc interstitial, or their complexes [151, 154, 155]. The defects can also be observed in the PL spectra of the material which clearly confirms that the prepared samples are actually hexagonal wurtzite ZnO nanoparticles. It is observed in figure 4.3.1 that all the graphs of the doped ZnO nanoparticles experiences a blue-shift and they display the same pattern of mode. The intensity of the peaks decreases as dopants are introduced into the ZnO nanoparticles. The defects induce the internal
strain in the original nanoparticle structure [156]. In addition, the blue-shift is associated with the modification of the material property. The In-ZnO nanoparticles were observed to be favoured, hence the obtained frequencies are close to that of the undoped ZnO nanoparticles as compared to others. The position of the peaks obtained in figure 4.3.1, are in good agreement with what Schumm et al. [157] had obtained, where peaks at 329.5 cm⁻¹, 436.4 cm⁻¹ and 573.5 cm⁻¹ are for E₂H⁻E₂L, E₂H and A₁ & E₁ respectively for the excitation wavelength of 514.532 nm [158].
Figure 4.3.1: Raman spectra of the undoped and 5% doped Co-ZnO, In-ZnO and (Co-In)-ZnO nanoparticles.
4.3.2 Ultraviolet-visible (UV-vis) spectroscopy

UV-vis absorption spectra were recorded using Perkin-Elmer Lambda 750S UV-vis spectrometer. This UV-vis spectrometer was used to probe the optical band gap of the doped and undoped ZnO nanoparticles along the wavelength range of 350-800 nm. The calculations were done using the following equation [22]:

\[ E_g = \frac{hc}{\lambda} \]  

(4.4.2.1)

here \( E_g \) is the energy band gap, \( h \) is the plank’s constant \( (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \), \( c \) is the speed of light \( (2.998 \times 10^8 \text{ m/s}) \) and \( \lambda \) cut off wavelength in nm. The cut off wavelength was determined by extrapolating a straight line along the absorption edges through the wavelength axis. A point where the straight line intercepts the wavelength axis is our cut off wavelength, see figure 4.3.2. The \( E_g \) for undoped and doped ZnO nanoparticles was also calculated and presented in table 4.2. The values obtained are ranging from 2.08 to 2.58 eV. The \( E_g \) of the co-doped (Co-In)-ZnO nanoparticles are much smaller than the Co-ZnO and In-ZnO nanoparticles. Previous literature by Wang et al. [159] shows that the bulk ZnO has the absorption edge at 387 nm in the UV-vis spectra which is obviously larger than that of the undoped ZnO nanoparticles (480 nm). Thus, the \( E_g \) of bulk ZnO is found to be greater than the \( E_g \) of undoped ZnO nanoparticles.
Figure 4.3.2: UV-vis absorption spectra for undoped and 5% doped ZnO nanoparticles.
Table 4.2: The calculated energy band gap of the doped and undoped ZnO nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping (wt %)</th>
<th>Wavelength (nm)</th>
<th>Energy band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk ZnO [159]</td>
<td>-</td>
<td>387.000</td>
<td>3.20</td>
</tr>
<tr>
<td>Undoped ZnO</td>
<td>0</td>
<td>479.917</td>
<td>2.58</td>
</tr>
<tr>
<td>Co-ZnO</td>
<td>5</td>
<td>509.830</td>
<td>2.43</td>
</tr>
<tr>
<td>In-ZnO</td>
<td>5</td>
<td>588.976</td>
<td>2.11</td>
</tr>
<tr>
<td>(Co-In)-ZnO</td>
<td>5</td>
<td>596.074</td>
<td>2.08</td>
</tr>
</tbody>
</table>

4.3.3 Photoluminescence (PL)

The NanoLog [iHR320 Horibo JOBINYVON] model of PL was used to collect data at room temperature. PL emission spectra of the undoped and doped In-ZnO, Co-ZnO and (In-Co)-ZnO nanoparticles are shown in figure 4.3.3. These spectra were obtained with an excitation wavelength of 350 nm. The first near band edge ultraviolet (UV) emission peaks that appear in the PL spectra are for In-ZnO and (Co-In)-ZnO centered on 380 nm, which is attributed to the excitonic recombination. This is the recombination of an electron in the conduction band and a hole in the valence band [160]. A higher blue PL intensity is due to the presence of high number of ionised oxygen vacancy defects [161]. In-ZnO and (Co-In)-ZnO samples display similar trend in the behaviour of intensity as a function of wavelength even though the intensities are differing. This outcome may indicate that the ZnO nanoparticles synthesised by the high energy ball milling technique may possess high crystalline perfection. The undoped ZnO nanoparticles shows three defects, namely zinc interstitial (Zn\textsubscript{i}), zinc vacancy (V\textsubscript{Zn}) and oxygen vacancy (V\textsubscript{o}) at 415 nm, 437 nm and 555 nm, respectively. Co-ZnO has two visible peaks along the 400 nm and 555 nm for valence band (VB) and V\textsubscript{o} defects respectively. All the samples display the V\textsubscript{o} and they range within 500-570 nm, which is the emission wavelength of green light [162].
Figure 4.3.3: The Photoluminescence spectra for 5% doped and undoped ZnO nanoparticles at the excitation wavelength of 350 nm.
4.4 Conclusion

ZnO nanoparticles were successfully synthesised using high energy ball milling technique. The XRD characterisation confirms that the prepared samples were of hexagonal wurtzite ZnO nanoparticles. SEM images further validate the formation of spherical granular ZnO nanoparticles. The Raman spectra of the undoped ZnO nanoparticles displays a very strong peak of $E_2$ (high) that clearly indicate that the prepared material was of a hexagonal wurtzite ZnO phase. As the dopants were introduced in the ZnO nanostructure samples, a blue shift was experienced. The PL spectra indicated that doped ZnO nanoparticles have a strong UV emission peak at 380 nm and green emission band at 555 nm. Doped samples show very obvious peaks in the visible region of the spectrum. These peaks are an indication of defects in the original ZnO nanoparticles. From the UV-Vis results it can be concluded that as dopants are introduced into the ZnO structure the band gap decreases, which further decrease with co-doping the ZnO nanoparticles with Co-In.
Chapter 5

Gas sensing applications

5.1 Introduction

Over centuries various types of gas sensors such as the optical, electrochemical, catalytic acoustic and semiconductor have being developed [163]. The semiconducting metal oxide gas detectors such as SnO$_2$-ZnO [164], ZnO-CuO [165], Fe$_2$O$_3$-ZnO [166] have being investigated over a range of temperatures to detect most common gases [167], like H$_2$S, CO, NH$_3$, CH$_4$ and more to monitor the environment. Report by Feng et al. [168] indicated that enthanol (C$_2$H$_5$OH) 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 commonly influenced by the size and the Debye length of the polycrystalline SnO$_2$ particles [169]. Mean while, Wang et al. [170] 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$_2$S 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$_2$S gas is very important because it is dangerous to human health even at low concentrations [171]. It has being mentioned in several papers that the selectivity and sensitivity of gas sensors to H$_2$S can be improved through additives of hydrophobic silica [172], ceria or basic oxides to the sensing element and even doping with nobel metals like Ag to SnO$_2$ [173].

Tamaki et al. [169] reported on the extreme sensitivity of 5wt.% SnO$_2$-CuO to H$_2$S gas at 200$^\circ$C. The one dimensional metal oxide (nanobelt or nanowire based 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 [174]. Wang et al. [175] further reported on the ZnO nanorods arrays prepared using a hydrothermal route for gas sensing application. In the report ZnO nanorods showed excellent response to NH₃ and CO exposure. Further on the H₂ 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 [176]. 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. [177]. Amongst the high-performance gas sensing devices, ZnO nanorods have being found to be sensitive to gases such as H₂, NH₃ and C₂H₅OH at room temperature [178]. In this chapter, the undoped ZnO and (In or Co) single and (In and Co) double doped ZnO nanoparticles are subjected to NH₃, CH₄ and H₂S gases to check their sensitivity and selectivity.

5.2 Results and discussion

5.2.1 Ammonia (NH₃) gas

The ammonia (NH₃) gas sensing applications were performed for the undoped, Co and In single doped and Co and In double doped ZnO nanoparticles. These applications were performed at four temperatures: 200, 250, 300 and 350°C. The response curves for NH₃ gas are plotted for different temperatures as shown in figure 5.2.1.1 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. Similar results were also obtained by Acuautla et al. [179] where a laser
Ablation technique was used to manufacture ammonia gas sensing device which is ZnO nanoparticles based. This indicates that the NH$_3$ gas sensors performs badly at higher temperatures. In figure 5.2.1.1 (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:

$$ S = \frac{R_{\text{air}}}{R_{\text{gas(NH3)}}} $$

was used. $R_{\text{gas(NH3)}}$ is the resistance in the presence of NH$_3$ gas at a given concentration and $R_{\text{air}}$ is the resistance in the air environment. Now $R_{\text{gas(NH3)}}$ contributes 90% of the response time, while $R_{\text{air}}$ holds 10% of the recovery time. The sensitivity of the undoped ZnO and (Co-In)-ZnO nanoparticles are constantly increasing with the increasing gas concentration, (see figure 5.2.1.2). In addition it is observed that the double doped ZnO exceeds the sensitivity of the undoped ZnO at 300°C [91] and 350°C. This is in good agreement with what Maswanganye et al. [91] 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 5.2.1.2 (a) and (b). In table 5.2.1, Co-ZnO nanoparticles show slow response time to NH$_3$ gas at 10 ppm but fast recovery time of 23 seconds. The Co-ZnO nanoparticles show 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 5.2.1.2 (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 the samples show an enhanced sensitivity at 350°C as shown in figure 5.2.1.2 (d).
Figure 5.2.1: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for concentrations ranging between 5-100 ppm.
Figure 5.2.1: The sensitivity versus NH$_3$ gas concentration plot for the doped and undoped ZnO nanoparticles.
5.2.2 Methane (CH\textsubscript{4}) gas

The response curves for methane (CH\textsubscript{4}) gas plotted in figure 5.2.2.1 below show that the prepared samples of undoped, single and double doped ZnO nanoparticles display good response at 200°C. When the temperature is elevated to temperatures above 250°C, a poor response even with low CH\textsubscript{4} concentrations is observed. This means that the various ZnO nanoparticles samples operate very well at lower temperatures for CH\textsubscript{4} gas. Stolper et al. [180] reported that the thermogenic gases get produced in the temperature range of 157° to 221°C. This in turn also suggest that the sensors studied in this sub-section are good in this temperature range.

In figure 5.2.2.2 the undoped ZnO nanoparticles shows poor sensitivity of CH\textsubscript{4} gas through out all the tested temperatures. The double doped ZnO nanoparticles also reflect descending results in sensitivity when operating tempature is increasing (200-350°C). At 350°C, all the samples reflect poor response at low concentrations (<40 ppm). The double doped ZnO nanoparticles sample seems to operate very well at 200°C for the concentration of 40 ppm. The In-ZnO nanoparticles show high sensitivity at 20 ppm for 300°C. In figure 5.2.2.2 (b)-(d) it is observed that Co-ZnO nanoparticles is the most sensitive to CH\textsubscript{4} gas, especially at 300°C [181]. Motaung et al. [181] also observed similar results for ZnO nanostructures which were exposed to CH\textsubscript{4} concentrations at 300°C for 24 hours.
Figure 5.2.1: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for concentrations ranging between 5-100 ppm.
Figure 5.2.2: The relationship between the sensitivity of the sensors and CH$_4$ gas concentrations at various temperatures.
5.2.3 Hydrogen sulphide (H$_2$S) gas

In the case of hydrogen sulphide (H$_2$S), the plot of response curves show an increase in sensitivity when the temperature and concentrations are increased for all the doped and undoped ZnO nanoparticles, (see figure 5.2.3.1). The undoped and double doped ZnO nanoparticles demonstrate the most dominant peaks. Moreover, when the temperature is $>200^\circ$C the current remain constant for some time before it recovers. Making the peak flat at the top for higher concentrations of $>40$ ppm.

Like in the previous two sub-sections, figure 5.2.3.2 show the sensitivity plots against the H$_2$S gas concentrations for the undoped, (Co and In) single and double doped ZnO nanoparticles. The Co-ZnO nanoparticles are less sensitive amongst all the samples tested. Even at 350$^\circ$C it can be observed that the Co-ZnO nanoparticles sensitivity are decreasing as the gas concentrations are increased, while the sensitivity for undoped ZnO nanoparticles constantly increases with the increasing H$_2$S gas concentration. The double doped ZnO nanoparticles samples are the most sensitive to H$_2$S gas at 20 and 40 ppm for 300$^\circ$C and 350$^\circ$C, respectively [182]. In addition to what appears in figures 5.2.3.1 and 5.2.3.2, table 5.2.1 displays the response time for Co-ZnO nanoparticles as much slower compared to the recovery time. Meanwhile, the In-ZnO nanoparticles and double doped ZnO nanoparticles show equivalent time for both the response and recovery time. The sensitivity of In-ZnO nanoparticles is directly proportional to the gas concentrations at 200$^\circ$C and 250$^\circ$C [183]. Zeng et al. [184] reported on In$_2$O$_3$ nanowire gas sensors. In the study, he observed that In$_2$O$_3$ nanosensors are sensitive to H$_2$S gas both at room temperature and at 120$^\circ$C. The most outstanding results were obtained by Cuong et al. [185], where the ZnO nanorods on a chemically converted graphene film were found to detect 2 ppm of H$_2$S gas at room temperature.
Figure 5.2.3: The graphs of current against time for the doped and undoped ZnO nanoparticles at various temperatures for concentrations ranging between 5-100 ppm.
Figure 5.2.3. 2: The relationship between the sensitivity of the sensors and H$_2$S gas concentrations at various temperatures.
Table 5.2: The calculated results of response and recovery for the undoped ZnO, Co-ZnO, In-ZnO and (Co-In)-ZnO nanoparticles on NH₃, CH₄ and H₂S gases at 10 ppm exposed to 250°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped ZnO</td>
<td>NH₃</td>
<td>2.94 x 10²</td>
<td>3.04 x 10²</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>3.00 x 10²</td>
<td>2.89 x 10²</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>3.15 x 10²</td>
<td>2.94 x 10²</td>
</tr>
<tr>
<td>Co-ZnO</td>
<td>NH₃</td>
<td>5.72 x 10²</td>
<td>2.30 x 10¹</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>2.99 x 10²</td>
<td>3.00 x 10²</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>3.01 x 10²</td>
<td>2.89 x 10²</td>
</tr>
<tr>
<td>In-ZnO</td>
<td>NH₃</td>
<td>3.02 x 10²</td>
<td>3.02 x 10²</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>2.98 x 10²</td>
<td>2.97 x 10²</td>
</tr>
<tr>
<td></td>
<td>H₂S</td>
<td>2.82 x 10²</td>
<td>3.24 x 10²</td>
</tr>
<tr>
<td>(Co-In)-ZnO</td>
<td>NH₃</td>
<td>2.89 x 10²</td>
<td>3.04 x 10²</td>
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<tr>
<td></td>
<td>CH₄</td>
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<tr>
<td></td>
<td>H₂S</td>
<td>2.98 x 10²</td>
<td>3.02 x 10²</td>
</tr>
</tbody>
</table>

5.3 Conclusion

ZnO nanoparticles were successfully synthesized by the high energy ball milling technique. The undoped and (Co-In)-ZnO nanoparticles are more favored compared to the Co and In single doped ZnO nanoparticles. The current versus time curves are plotted for all the three gases: NH₃, CH₄ and H₂S, in which it can be observed that the double doped and undoped ZnO nanoparticles are dominating throughout the study. The NH₃ gas show good response and recovery at lower temperatures (< 250°C), than at higher temperatures (> 250°C). The Co-ZnO nanoparticles reflect an ascending response magnitude with increasing concentration of NH₃ gas, suggesting that the Co-ZnO nanoparticles performs better at higher temperature(< 350°C). The CH₄ gas sensor seems to work better at lower temperatures and higher gas concentrations.
The double doped ZnO nanoparticles shows high CH$_4$ sensitivity at 200°C which is good for monitoring the environment. The response curve for H$_2$S gas become smooth at the top as the temperature and concentration is increased. The double doped ZnO nanoparticles is most sensitive to 5 ppm at temperature range of 200-300°C. In summary, the sensitivity is in the order of CH$_4$ > H$_2$S > NH$_3$ gas for all the tested temparetures. The current agianst time trend is in the order of H$_2$S > NH$_3$ > CH$_4$ gas for all the tested temperatures. The sesntivity of the double doped ZnO nanoparticles reveals a good selectivity to CH$_4$ gas at low temperature and concentrations. Co-ZnO nanoparticles demonstrate favourable recovery time to NH$_3$ gas, but the double doped ZnO nanoparticles show minimal response and recovery time ($2.99 \times 10^2$ s) for CH$_4$ gas.
Chapter 6

Summary

In summary, the undoped, 5 % (In or Co) single and (In and Co) double doped ZnO nanoparticles have been successfully synthesised using the ball milling technique. The XRD characterisations were subsequently performed for all the prepared samples. The results showed that when the dopants are added on the undoped ZnO nanostructures, there is no significant effect (JCPDS No.36-1451). Only the In-ZnO nanoparticles display a new peak that is associated with the indium dopant. The new peak is attributed to the ionic radius of In$^{3+}$ being larger compared to that of Zn$^{2+}$ and also the preferred occupation site in the crystallite structure. In overall, this give the calculated crystallite size of the (Co-In)-ZnO nanoparticle as the smallest of all the prepared ZnO nanoparticles. The size effects can also be observed in the SEM images which demonstrate similarities in the morphology of the doped and undoped ZnO nanoparticles (more spherical).

Further investigations using the Raman spectroscopy were carried out and the well-known Raman modes for ZnO nanostructures were obtained. It can be observed from the Raman spectra that the undoped and In doped ZnO nanoparticles are favoured because of their high peak intensities. In addition, the A$_1$ and E$_1$ (LO) modes are being superimposed, making a broad peak. All the doped ZnO nanoparticles experience a blue-shift, which is in good agreement with the XRD patterns. The decrease in the energy band gaps of doped ZnO nanoparticles indicate that the introduction of (Co and In) dopants in the ZnO nanostructure can improve its performance such that the double doped ZnO nanoparticles have the lowest energy band gap. This results from the substitution of In$^{3+}$ on the Zn$^{2+}$ lattice site and some vacancies created during
doping process. In the PL study, the undoped ZnO nanoparticles revealed three types of vacancy defects [154]. Introduction of In and Co impurities influence the creation of intrinsic vacancies and interstitial type defects [154]. This is observed through an emerging peak from the double doped and In-ZnO nanoparticles spectra. Impurities further contribute to the decreased energy band gap in these doped nanoparticles.

The kenosistec station equipment was also used to probe the sensing properties of the doped and undoped ZnO nanoparticles to NH₃, CH₄ and H₂S gases. The double doped ZnO nanoparticles were found to be sensitive to CH₄ gas at low concentrations and low temperatures of 40 ppm and 200°C, respectively. As the temperature is increased to 250°C and above, the Co-ZnO nanoparticles acquire enhanced sensitivity to CH₄ gas. The NH₃ gas is best detected at 300 and 350°C by the double doped ZnO nanoparticles, such that the sensitivity increases with the increasing concentrations. Good sensitivity to NH₃ gas were also observed at 350°C for all the doped and undoped ZnO nanoparticles. The In doped ZnO nanoparticles were found to be sensitive to H₂S gas at 200°C for 40 ppm. At higher temperatures the double doped ZnO nanoparticles show an enhanced sensitivity to the H₂S gas even at low concentrations (<40 ppm). The results also show that the double doped ZnO nanoparticles has low resistance to current as such is sensitive at much lower temperatures compared to the single doped ZnO nanoparticles. It can also be seen that the sensitivity is more related to conductivity of these nanoparticles.
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8. Publications and conference presentations

8.1 Publications

8.1.1 Manamela M.F, Mosuang T.E and Mwakikunga B.W “The structural and sensing properties of cobalt and indium doped zinc oxide nanopowders synthesised through high energy ball milling technique.” The 62\textsuperscript{nd} annual conference of the South African Institute of Physics (SAIP2017), held at Stellenbosch University, Cape Town, South Africa, 03 - 07 July 2017 (paper submitted).

8.1.2 Manamela M.F, Mosuang T.E and Mwakikunga B.W “Structural and optical property changes of zinc oxide nanopowders doped with cobalt and indium metals mechano-chemically.” Advanced materials proceedings (paper accepted).

8.2 Conference presentations

8.2.1 Manamela M.F, Mosuang T.E and Mwakikunga B.W “The structural and sensing properties of cobalt and indium doped zinc oxide nanopowders synthesised through high energy ball milling technique.” The 62\textsuperscript{nd} annual conference of the South African Institute of Physics (SAIP2017), held at Stellenbosch University, Cape Town, South Africa, 03 - 07 July 2017.

8.2.2 Manamela M.F, Mosuang T.E and Mwakikunga B.W “Structural and optical studies of mechano-chemically prepared zinc oxide nanopowders co-doped with indium and cobalt.” Faculty of Science and Agriculture Research Day, held at Bolivia Lodge, Polokwane, 24 - 25 October 2016.

8.2.3 Manamela M.F, Mosuang T.E and Mwakikunga B.W “Structural and optical studies of cobalt and indium simultaneously doped zinc oxide nanopowders prepared using high energy ball milling technique.” The 61\textsuperscript{st} annual conference
of the South African Institute of Physics (SAIP2016), held at University of Cape Town, Cape Town, South Africa, 04-08 July 2016.


8.2.5 Manamela M.F, Rammutla K.E and Mosuang T.E, “Structural and optical studies of cobalt (Co) and indium (In) co-doped zinc oxide nanoparticles prepared using ball milling method.” Faculty of Science and Agriculture Research Day, held at Bolivia Lodge, Polokwane, 01 - 02 October 2015.