SYNTHESIS AND CHARACTERISATION OF HYBRID ZnO-CARBON NANOSTRUCTURES FOR POTENTIAL APPLICATIONS IN HYDROGEN STORAGE

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Supervisor: Prof. O.M. Ndwandwe

Department of Physics and Engineering
University of Zululand

Submitted by:
Charles Thulani Thethwayo

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DECLARATION

I, the undersigned, hereby declare that the work contained in this dissertation is my own original and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature: …………………………………………………………………………………

Date: ………………………………………………………………………………………
ABSTRACT

This work presents the synthesis of hybrid zinc oxide carbon nanofibers (ZnO-CNFS) using ZnO nanorods as template and to investigate if they can be used as the hydrogen storage materials. The synthesis of ZnO nanoparticles (ZnO NPs) was carried out using direct current (DC) reactive magnetron sputtering at different deposition times, pressure and temperature, and were used as a seeding in the synthesis of ZnO nanorods (NRs). Using the hydrothermal process, vertically aligned ZnO NRs were grown on different seed particles which resulted in the different sizes and distribution of nanorods. ZnO NRs were used as templates in the deposition of ZnO-CNFS at various temperatures (500, 600, 700 and 800 °C), using chemical vapour deposition (CVD). Acetylene (C₃H₆) was used as the source of carbon during the depositions of ZnO-CNFS. Scanning electron microscopy (SEM) was used to study the surface morphology of all samples (ZnO NPs, ZnO NRs and ZnO-CNFS). The results from SEM images showed that the size of ZnO NPs increased with deposition time and ZnO NRs morphology depended on the seeding particle sizes. The size of ZnO NPs which ranges from 6.73 to 19.60 nm was measured from SEM images and was confirmed by Scherrer equation. The vertically aligned ZnO NRs average diameter and the average length ranges from 55.64 to 78.93 nm and 106.92 to 129.15 nm, respectively. ZnO-CNFS retained the hexagonal structure of ZnO NRs when annealed at 500 to 700 °C. When the temperature was raised to 800 °C the ZnO-CNFS completely lost the hexagonal structure of a template material. Chemical compositions of all samples prepared were determined using energy dispersive x-rays spectroscopy (EDS). From EDS results, it was discovered that the content of carbon on ZnO-CNFS annealed at 500 °C to 700 °C increases but decrease for the sample annealed at 800 °C. Crystal structure was studied using X-rays diffraction (XRD). XRD results of ZnO NPs and ZnO NRs confirmed that ZnO was crystalline with a wurtzite hexagonal structure. The disorder in ZnO-CNFS was studied using Raman spectroscopy. Raman showed that ZnO-CNFS have both sp² and sp³ hybridisation which is a result of disordered carbon materials. ZnO-CNFS samples were tested for hydrogen absorption/adsorption using elastic recoil detection analysis (ERDA). From the ERDA results it was shown that more hydrogen was absorbed/adsorbed when ZnO-CNFS was annealed at 700 °C, and less when annealed at 800 °C. These results on hydrogen profiling show that ZnO-CNFS can be good candidates for hydrogen storage applications.
DEDICATION

Dedicated to my mother, Miss Princess Hloniphile Ntibane
I would like to extend my gratitude to the following people:

God for giving me strength, courage, and guiding me through all difficulties.

Prof O.M Ndwandwe for his supervision, designing the project and guidance of this work and for giving me his time for discussions which contributed to the success of this work.

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CHAPTER ONE – Background

1.1. Introduction

The demand for energy has increased tremendously, due to the increase in energy usage for transportation, industries and in households. The production/generation of energy has become one of today’s major challenges. Sources of energy (oil and coal) that were once in abundance are rapidly dwindling as world population increases [1]. Not only are sources of energy dwindling, but most sources pollute the environment. This high demand, call for alternative energy sources that will produce not simply the desired amounts of energy, but also produce it safely without polluting the environment. Fossil fuels are currently the most used energy source all over the world and produces a high amount of pollution, which may leads to global warming [1, 2]. Nuclear energy on the other hand produces radioactive by-products which are harmful to humans and the environment. Renewable energy is the energy produced/generated from resources that are continually replenished such as sunlight, wind, tides, geothermal heat, waves and rain. Renewable energy is environmentally friendly and possesses good economic benefits such as improved local air quality [1, 2, 3, 4, 5]. The renewable energy sources have no negative environmental impact, social impact, do not deplete natural resources, and have little or no carbon and other greenhouse gas emissions. They meet the need of people today and in the future in an accessible, equitable and efficient manner.

There are numerous forms of renewable energies including; (i) wind power, (ii) run-of-river hydro, (iii) geothermal power, (iv) biomass power, (v) fuel cell, and (vi) bio fuel [6, 7, 8]. The challenges with solar power, it has low efficiency, increasing the efficiency increases the cost of the solar panel. Photovoltaic panels need a large land space and the pollution on the environment can reduce the efficiency. The run-of river has little or no capacity for the energy storage; hence it cannot coordinate the output amount of electricity to match consumer demand. The energy efficiency of wind power entirely depends on wind pressure, places with low wind pressure will have a low energy and those with high wing pressure will have a high energy. Although geothermal power is clean, it has negative impact in the surrounding environment [7]. The biomass power is expensive, inefficient as compared to fossil fuels, harmful to the environment (produce methane gas which is harmful to earth
ozone layer), consume more fuel, and requires more land [8, 9]. A fuel cell is a device that converts chemical energy from fuel into electricity through a chemical reaction with oxygen or other oxidizing agent. Fuel cell technology is the promising technology for generating electricity and heat for households, industries and as the electrical power source for electric motors propelling vehicles [2, 3, 10]. A fuel cell operates best on pure hydrogen [6]. The good thing about hydrogen is the fact that it cannot be destroyed; it is derived from water to hydrogen and back to water. Hydrogen has a very high energy; the engine which operates on pure hydrogen produces almost no pollution. Hydrogen can play an important role in clean energy systems.

Most researchers are looking at hydrogen energy as an alternative candidate to substitute fossil fuels, since it is renewable, environmental friendly and has abundance reserves globally. Hydrogen produces energy by reacting with oxygen and the by-product is clean water and heat [1, 2, 3]. Hydrogen is also used in fuel cells and fuel cell vehicles, therefore hydrogen storage materials that will store high yield of hydrogen plays an important role during the progressing of hydrogen economy [24]. The storage systems which can store desired hydrogen capacity have not been developed yet. An eligible hydrogen storage material should meet certain criteria such as lower cost, light weight, stability of substrate material, high capacity storage and environmental safety [25]. There are currently three on-board automobiles hydrogen storage systems, (i) gas compressed to high pressures; (ii) the use of a cryogenic liquid at temperatures near to its boiling point (20.3 K), and (iii) reversible metal and chemical hydrides [2, 4, 11, 12]. Hydrogen stored as a compressed gas occupies a relatively high volume [4, 11, 12]. Liquid hydrogen evaporates very easily during delivery, transfer and refuelling and pressurizes quickly during on-board storage as it absorbs heat from the environment [2, 4]. Hydrogen stored as metal and chemical hydrides adds significant weight, cost, and thermal complexity to onboard storage systems [4, 11]. The United States Department of Energy (U.S. DOE) has set a target system energy density at a values of 9 wt.% by 2015 [4, 12]. According to U.S. DOE’s report, hydrogen storage capacity of greater than 6.5 wt.% is required for automotive applications [5, 12]. In South Africa the Department of Science and Technology (DST) has invested a lot of money on hydrogen and fuel cell technology [1]. DST has funded three Centres of Competence (CoC) to implement the hydrogen South Africa (HySA) strategy. The three CoCs are: (i) HySA systems hosted by the University of the Western Cape, (ii) HySA catalysis co-hosted by the University of Cape Town and MINTEK, and (iii) HySA infrastructure co-hosted by the North West University
and the Council for Scientific and Industrial Research. The targeted goal by these three CoCs is to supply 25% of global platinum group metals (PGM) based catalyst demand by 2020. The other goal is to work with industries to develop technologies to produce high quantities of hydrogen at low cost, store, transport and use hydrogen as the source of energy [19].

The current study focuses on zinc oxide carbon nanofibers hybrid (ZnO-CNFs) to be used as one of the materials in developing a high yield hydrogen storage system. Carbon materials are lightweight absorbent with high porosity and high surface area and can be used for hydrogen absorption/adsorption application [11, 13]. The properties and morphology of carbon material can be manipulated by the type of catalyst or the dopant used during the synthesis. Hydrogen can be absorbed onto carbon materials in two ways by chemisorption or/and physisorption [2, 4]. Physisorption occurs when hydrogen maintains its molecular structure and is trapped in the carbon material pores by Van der Waal forces. Chemisorption is when atoms of hydrogen create chemical bonds with carbon atoms. The precise mechanism of hydrogen adsorption on carbon material is not well understood, it is difficult to determine whether hydrogen is adsorbed exclusively by physisorption or if chemisorption also take place [4, 13]. Other approach that has been investigated to enhance hydrogen sorption in carbon material is by doping with alkali metals such as Li and K [14]. Introducing zinc oxide (ZnO) into carbon nanostructures (CNs) will change the properties of both materials and we believe it will also enhance hydrogen absorption/adsorption. ZnO NRs was used as the template in the synthesis of CNs to form hybrid zinc oxide carbon nanofibers (ZnO-CNFs). Studies have shown that hydrogen can be absorbed by ZnO single crystal and also hydrogen diffusivity can take place on ZnO single crystal [15, 16, 17].

ZnO is wide band gap (3.37 eV) transparent semiconductor with a large free exciton binding energy of 60 meV [15, 17]. It has wide variety of applications including; optoelectronic devices, gas sensors, UV light emitting diodes, and transparent electrodes for solar cells [15, 16, 17, 18]. Properties of ZnO crystals are influenced by intrinsic point defects and impurities. Van de Walls predicted using theoretical calculations that hydrogen incorporated into ZnO lattice and form shallow donor state [15, 16]. The properties of ZnO crystals and carbon materials are both showing possibilities of hydrogen absorption/adsorption and their properties able to change with the synthesis methods and dopant. With the progress on the crystal growth techniques making it possible to make high quality ZnO single crystals with one-dimension (1D), this increases the surface area. Using hydrothermal process we
successfully synthesized vertically aligned single crystal of ZnO nanorods which are 1D. ZnO NRs morphology was used to control the growth and morphology of carbon nanostructure into forming vertically aligned zinc oxide carbon nanofibers hybrid (ZnO-CNFs). The depositions of ZnO-CNFs were conducted at different temperatures to study the effect of temperature on the morphology and hydrogen absorption/adsorption efficiency. The resulting material has never been tested before for hydrogen absorption/adsorption concentration. The method used to test for hydrogen absorption/adsorption in this research work is ERDA, which only allows studying hydrogen concentration profiling.

1.2. Properties of hydrogen

Hydrogen is the element with a single electron orbiting around the nucleus with a single proton. Hydrogen is the most abundant element in the universe, making 75% of the mass of all visible matter in stars and galaxies [19]. Most of the hydrogen mass is concentrated on the nucleus as the mass of the proton is 1800 times bigger than the mass of electron. It has two know isotopes, the one with a single neutron and a proton (deutrium) and the other with two neutrons and single proton (tritium). These isotopes however are unstable, decay radioactively. At room temperature (25 °C) hydrogen is a gas and liquefies at -252 °C, it is a colourless, tasteless and odourless gas. It is a lightest gas and it is slightly soluble in water. It is a highly inflammable and burn with a blue flame forming water. The electron negativity is 2.1 and the bond energy of H-H is 431 kJ/mole. The ionisation potential energy of hydrogen is 13.54 eV. Hydrogen is used in fuel cell technology, manufacturing of fertilisers, rocket fuel and for preparation of tungsten filament. It is used to prepare ammonia (NH₃), CH₃OH and other organic compounds. It is used in filling weather balloons and also used to prepare a low temperature in liquid state. There are many more uses of hydrogen that we can think of that are not mention above. In this work we will focus more in hydrogen energy and hydrogen fuel cell technology and how it can improve our standard of living.

1.3. Hydrogen production and resources

Hydrogen does not occur naturally as a gas on earth, it is always combined with other elements [19, 20], and for example water is a combination of hydrogen and oxygen (H₂O). About 96% of hydrogen is manufactured from fossil fuel, produced by steam reforming of
natural gas and about 4% from electrolysis of water [20]. Hydrogen is mostly found on organic compounds (hydrocarbons) and other inorganic compounds. Figure 1.1 shows different types of resources of hydrogen and production processes.

![Figure 1.1: Schematic diagram showing different resources of hydrogen gas and production processes [21].](image-url)

The idea for the future use of hydrogen as energy is to use renewable resources such as solar energy, biomass, wind energy, and biological organisms to extract hydrogen from these resources. Hydrogen can be separated from these resources (Figure 1.1), by different methods. These methods includes, production from coal, natural gas, splitting of water, alkaline electrolysis, PEM electrolysis, high-temperature electrolysis, photolysis, biophotolysis, high-temperature decomposition and thermo-chemical water splitting [19, 20]. The yield of hydrogen produced should be evaluated, because at the moment the renewable resource produces low amount compare to fossil fuel. Investigations to develop technologies and processes that can produce hydrogen without requiring energy source which have negative impact on human health and the environment is the researcher’s focus [19, 22, 23].
Table 1.1: hydrogen generations methods, commercially, research and development [26].

<table>
<thead>
<tr>
<th>Technologies</th>
<th>Raw Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercialized</td>
<td>Steam reforming</td>
</tr>
<tr>
<td></td>
<td>Light hydrocarbon gases (mainly CH₄) and water</td>
</tr>
<tr>
<td>Gasification</td>
<td>Coal and water</td>
</tr>
<tr>
<td>Water electrolysis</td>
<td>Water</td>
</tr>
<tr>
<td>Research and Development</td>
<td>Gasification</td>
</tr>
<tr>
<td>(R&amp;D)</td>
<td>Biomass and water</td>
</tr>
<tr>
<td>Thermo–chemical</td>
<td>Sulphur-iodine water-splitting cycle</td>
</tr>
<tr>
<td>Bioprocess</td>
<td>Biomass and water</td>
</tr>
<tr>
<td>Photolysis</td>
<td>Water</td>
</tr>
</tbody>
</table>

Hydrogen can be produced via water splitting thermo-chemical cycles (WSTC), which are the processes used to decompose water into hydrogen and water via chemical reactions that use intermediate substances which are recycled [22], Table 1.1 illustrates the hydrogen generation methods. These methods can provide a solution in producing hydrogen without using fossil fuel. The method operates at extremely high temperatures e.g. the main endothermic reaction requires temperature ranging from 700 - 1200 °C; therefore the source of energy is required [22, 24]. The biomass on the other hand is one of the renewable energy sources, it energy usage include the production of energy. The disadvantage of biomass as the source of hydrogen production is that it produces insufficient hydrogen compared with fossil fuels. The hydrogen production methods available at present which uses renewable resources need to be improved to meet the consumer need and stop fossil fuel dependency. Researchers need to focus more on the R&D to improve the existing hydrogen production technologies and the developing hydrogen technologies.
1.4. **Aim of the research work**

The aim of the research is to synthesis and characterise hybrid zinc oxide carbon nanofibers (ZnO-CNFS) for hydrogen storage applications.

1.5. **Objectives of the research work**

i. To deposit zinc oxide nanoparticles (ZnO NPs) on silicon (100) wafer by direct current reactive magnetron sputtering system.

ii. To synthesis vertically aligned ZnO nanorods (ZnO NRs) on ZnO NPs seeding via hydrothermal process.

iii. To use ZnO NRs as a template in synthesis to control the growth and morphology of zinc oxide carbon nanofibers hybrid (ZnO-CNFs).

iv. To characterise ZnO NPs, ZnO NRs, ZnO-CNFS, using field emission scanning electron microscopy (FE SEM), X-rays diffraction (XRD), Transmission electron microscopy (TEM) and Raman Spectroscopy.

v. To test for hydrogen absorption/adsorption concentration in ZnO-CNFS using Elastic Recoil Detection Analysis (ERDA).

vi. To use hydrogen and nitrogen Isotherm to test for hydrogen adsorption and to measure BET surface area of ZnO-CNFS.
1.6. References


2.1. Hydrogen energy

Hydrogen is considered as the ultimate energy carrier in the conceivable future and can play an extremely significant role in the clean energy system [1]. The ability of hydrogen to produce clean energy by reacting with oxygen is what makes it unique and special from other source of energy [2]. It is the most high efficient energy source, produces no environmental pollutions of any kind. Hydrogen produces water and heat as by-products. The water produced is clean in such a way that it can be used for drinking and can be splitted into hydrogen and oxygen. About 80% of today’s global primary energy supply is generated from fossil fuels (oil and natural gas) [3]. The problem with fossil fuels is that they are not environmental friendly; they produce greenhouse gases and heavy metals which are harmful to the environment [3, 4, 5]. There is a need to change from fossil fuels dependent to environmental friendly hydrogen energy. Since the 1970s, the industrial countries have been developing new energy technology in both national and international programmes to meet these challenges [6]. Most studies are focusing on fuel cells for energy generation and on the application of automobile vehicles [6, 7, 8, 9]. Fuel cells operate best on hydrogen source and only produce water as by-product; **Figure 2.1** illustrates the hydrogen fuel cells operation. If the world has to be forced to use hydrogen as the main source of energy, there are number of things that have to be considers such as new infrastructures, safe and cost. At presence the price of hydrogen fuel cells are expensive for the users [7]; the price must be reduced. Hydrogen must be produced mostly by the renewable resource than fossil fuel, at present we have more hydrogen produced from non-renewable (fossil fuels) sources. Also hydrogen has to be stored and transported; the safety of the people must be taken in to consideration. The most challenge is the hydrogen storage in vehicles powered by fuel cells.
Figure 2.1: The diagram illustrating the sample of hydrogen economy [9].

In the present day’s hydrogen is not only used for fuel cell technology, but for ammonia manufacturing, petroleum refinement and the synthesis of methanol. The National Energy Laboratory (NREL, Denver, Colorado, USA) as part of the US Department Energy’s Hydrogen Program, they are focusing their research on the advanced technologies to produce, store and safely use hydrogen made from renewable resources [4]. As mention in chapter 1 South Africa have also emerge to hydrogen technology, Department of Science and Technology (DST) is currently funding three program (HySA (Hydrogen South Africa) systems, HySA catalysis, and HySA infrastructure) focusing on hydrogen storage and fuel cells technology. More information about the HySA programs is on the HySA website (https://www.hysa.co.za). Table 2.1 illustrates the comparison of the current fuel cell technologies, their advantages and disadvantages.
Despite all the advantages hydrogen has over traditional/available (fossil fuels) sources of energy, it also has its disadvantages as shown on Table 2.1. Hydrogen is very expensive, not easy to store, not easy to replace the existing infrastructures and it is highly flammable. Hydrogen may be abundant in the universe, but is not easy to free it from other elements, it requires lots of work and it consumes lot of time to produce it. Hydrogen storage is also a challenge, since the suitable storage systems are still under research. Researchers have not yet found suitable systems that will store the desired yield of hydrogen to power the desired facilities.

**Table 2.1: Comparison of current fuel cell technologies, advantages and disadvantages [15].**

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Operating Temperature</th>
<th>Typical Stack Size</th>
<th>Efficiency</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Electrolyte Membrane (PEM)</td>
<td>50 – 100 °C</td>
<td>&lt;1 kW – 100 kW</td>
<td>60%</td>
<td>• Solid electrolyte reduces corrosion</td>
<td>• Expensive catalysts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&amp; transportation</td>
<td></td>
<td>• Low temperature</td>
<td>• Sensitive to fuel impurities</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&amp; 35%</td>
<td></td>
<td>• Quick start-up</td>
<td>• Low temperature waste heat</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>90 – 100 °C</td>
<td>10 – 100 kW</td>
<td>60%</td>
<td>• Cathode reaction faster in alkaline electrolyte</td>
<td>• Sensitive to CO₂ in fuel and air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Low cost components</td>
<td>• Electrolyte management</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>150–200 °C</td>
<td>400 kW</td>
<td>40%</td>
<td>• High temperature enables CHP</td>
<td>• Platinum catalyst</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&amp; 100 kW module</td>
<td></td>
<td>• Increased tolerance to fuel impurities</td>
<td>• Long start up time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Low current and power</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>600 – 700 °C</td>
<td>300 kW – 3 MW</td>
<td>45 – 50%</td>
<td>• High efficiency</td>
<td>• High temperature corrosion and breakdown of cell components</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&amp; 300 kW module</td>
<td></td>
<td>• Fuel flexibility</td>
<td>• Long start up time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Can use a variety of catalysts</td>
<td>• Low power density</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Suitable for CHP</td>
<td></td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>700 – 1000 °C</td>
<td>1 kW – 2 MW</td>
<td>60%</td>
<td>• High efficiency</td>
<td>• High temperature corrosion and breakdown of cell components</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Fuel flexibility</td>
<td>• High temperature operation requires long start up time and limits</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Can use a variety of catalysts</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Solid electrolyte</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>• Suitable for CHP</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• CHP &amp; CHHP</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Hybrid/GT cycle</td>
<td></td>
</tr>
</tbody>
</table>
2.2. Hydrogen storage systems

For different applications, hydrogen has to be stored in different types of system that will satisfy the purpose of the application. For example, if hydrogen has to be used to power a motor vehicle, the storage system has to be light in weight and the safety has to be the first priority. For a new technology that has to replace the existing one, it must be safe to use, high efficiency, improve the standard of living and most importantly the cost must be relatively low. Hydrogen is not a natural source but man-made, the manufacturing cost makes hydrogen fuel cost three times higher than the petroleum products [10]. Hence the storage system that will increase the cost of hydrogen and hydrogen systems is not recommended for the world advancement. However, storage of hydrogen is a substantial challenge especially for applications in vehicles with fuel cells that use proton-exchange membranes (PEMs) [11]. There are different methods of storing hydrogen available on-board including; high pressure and cryogenic-liquid storage [4, 10, 11], adsorptive storage on high surface area adsorbents [10, 13], chemical storage in metal hydrides and complex hydrides [10, 11, 13], and storage in boranes [10]. Although each hydrogen storage method has desirable attributes, no approach satisfies all of the efficiency, size, weight, cost and safety requirements for personal transportation vehicles [13]. For example, hydrogen stored as a compressed gas occupies a relatively large volume [14]. Looking at the hydrogen technologies, fuel cells is one showing a good progress, Figure 2.2 shows a weight and volume of various fuels and tanks systems required for a 500 km range vehicle. Liquefied hydrogen is denser than gaseous hydrogen, it contains more energy in a given volume, but more energy is required to liquefy hydrogen. Special tanks to store liquefied hydrogen that will reduce cost, prevent hydrogen loss to the weight and volume are required. Solid-state storage systems that are safer than the physical storage system and can potentially store more hydrogen per unit volume are being developed [4]. Solid-state storage system store hydrogen by two process, (i) chemisorption (chemically bonded) and (ii) physisorption (bind hydrogen into a solid material). NREL’s laboratory has developed a solid-state system which uses microscopic carbon nanotubes (CNTs) to adsorb hydrogen. Their system can store high volume of hydrogen at high temperatures than other systems at near ambient pressure levels [4]. Hydrogen adsorbed by the surface of the CNTs is released by changing temperature and pressure levels.
Light weight absorbers such as carbon materials (carbon nanotubes (CNTs), carbon nanofibers (CNFs), and amorphous carbon) are interesting and have attracted a lot of research activity due to their high porosity and high surface area [14, 18, 19, 20]. The goal is to pack hydrogen as closely as possible in order to achieve the highest volumetric density by using little additional material and weight as possible [14]. In this study we want to achieve this goal by testing for hydrogen absorption/adsorption in ZnO-CNFs, which are light weight absorbers and are easy to synthesis them. Figure 2.3 shows hydrogen storage technologies and their operating conditions. The pressure and temperature are very important when developing the storage system. The pressure and temperature at which hydrogen will be absorbed/adsorbed at and the temperature and pressure at which hydrogen will be retained at for personal, households and industrial usage.
The diagram illustrates available technologies of hydrogen storage and their operating conditions [16, 17].

2.2.1. Physisorption of hydrogen

Physisorption (physical storage) is the process whereby hydrogen is trapped in the pores of an absorber compound by Van der Waals forces. In this process, no strong chemical bonds (covalent or ionic interactions) between hydrogen and an absorber compound is involved [11]. This process occurs in the solid-state storage systems, an example of a solid-state material is carbon nanostructures/materials. Pure carbon materials have binding energies in the range of 4–15 kJ/mol [21]. The lower bound is typically for activated carbon and graphite, and the upper bound is typical of internal and interstitial sites of SWNT and SWNT bundles [21]. The higher energy binding sites are associated with confined geometry effects and as such are associated with smaller specific surfaces [21]. Most prototypes of fuel cell powered cars uses physical storage technologies, 70 MPa CGH2 is considered to be the greatest technology [11]. Figure 2.4 shows a physisorption of hydrogen, the atom is adsorbed near a perfect conductor interacting with its images charges.
Modelling by image charge: consider an adsorbed hydrogen atom in front of a perfect conductor, as shown in Figure 2.4. A nucleus with positive charge is located at \( \mathbf{R} = (0, 0, Z) \), and the position coordinate of its electron, \( \mathbf{r} = (x, y, z) \) is given with respect to the nucleus. The adsorption process can be viewed as charges of both the nucleus and electron in the conductor. As a result, the total electrostatic energy is the sum of attraction and repulsion terms:

\[
V = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{-1}{|2\mathbf{R}|} + \frac{-1}{|2\mathbf{R} + \mathbf{r} - \mathbf{r}'|} + \frac{1}{|2\mathbf{R} - \mathbf{r}'|} + \frac{1}{|2\mathbf{R} + \mathbf{r}|} \right)
\]

The first term is the attractive interaction of nucleus and its image charge, and the second term is due to the interaction of the electron and its image charge. The repulsive interaction is shown in the third and fourth terms arising from the interaction of nucleus-image electron and electron-image nucleus, respectively. By Taylor expansion in powers of \(|\mathbf{r}|/|\mathbf{R}|\), this interaction energy can be further expressed as:

\[
V = \frac{-e^2}{16\pi\varepsilon_0 Z^3} \left( \frac{x^2 + y^2}{2} + z^2 \right) + \frac{3e^2}{32\pi\varepsilon_0 Z^5} \left( \frac{x^2 + y^2}{2} z + z^3 \right) + O \left( \frac{1}{Z^5} \right)
\]

One can find from the first non-vanishing term that the physisorption depends on the distance \( Z \) between adsorbed atom and surface as \( Z^{-3} \), in contrast with the \( r^{-6} \) dependence of the molecular van der Waals potential, where \( r \) is the distance between two dipoles. Even though the van der Waals interaction is attractive, as the adsorbed atom moves closer to the surface the wavefunction of electron starts to overlap with that of the surface atoms. Further the
energy of the system will increase due to the orthogonality of wavefunction of the approaching atom and surface atoms. This Pauli exclusion and repulsion are particularly strong for atoms with closed valence shells that dominate the surface interaction. As a result, the minimum energy of physisorption must be found by the balance between the long-range van der Waals attraction and short-range Pauli repulsion. The information on modelling by image charge was found on reference [22].

2.2.2. Chemisorption of Hydrogen

Chemisorption is the process whereby hydrogen is chemically bonded with an absorber compound. In this process, new chemical bonds (covalent or ionic interaction) are generated between hydrogen and surface of an absorber is available. In general, any metal with a redox potential below that of the H⁺/H₂ system at the corresponding pH could be considered a hydrogen storage system, as upon reaction with water, hydrogen is released and the metal hydroxide or oxide is formed [11]. Self-assembled monolayers (SAMs) are formed by chemisorbing reactive reagents with metal surfaces. A famous example involves thiols (RS-H) adsorbing onto the surface of gold. This process forms strong Au-SR bonds and releases H₂. The densely packed SR groups protect the surface. Gas-surface chemisorption (GSC), the adsorbed particle comes into contact with the surface of the absorber. The particle needs to be trapped onto the surface by not possessing enough energy to leave the gas-surface potential well. If it elastically collides with the surface, then is retained to the bulk gas. If it loses enough momentum through an inelastic collision, then it sticks onto the surface, forming a precursor state bonded to the surface by weak forces, similar to physisorption. The particle diffuses on the surface until it finds a deep chemisorption potential well. The reaction with the surface is dependent on the chemical species involved. Applying Gibbs free energy equation for reactions:

\[ \Delta G = \Delta H - T\Delta S \quad \text{(2.3)} \]

General thermodynamics states that for spontaneous reaction at constant temperature and pressure, the change in free energy should be negative. Since a free particle is restrained to a surface, and unless the surface atom is highly mobile, entropy is lowered. This means that the enthalpy term must be negative, implying an exothermic reaction. The information on chemisorption is obtained from reference [22].
2.3. **Hydrogen absorption/adsorption in zinc oxide (ZnO) nanostructures**

ZnO is an inorganic compound which is insoluble in water. ZnO is widely used as additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants [23], paints ointment, adhesives, sealants, pigments, food (as a source of zinc as a nutrient), batteries, ferrites, fire retardants, and first aid tapes [24]. ZnO is wide band gap (3.37 eV) transparent semiconductor with a large free exciton binding energy of 60 meV [25, 28]. It has wide variety of applications including: optoelectronic devices, gas sensors, UV light emitting diodes, and transparent electrodes for solar cells [25, 26, 27, 28]. Properties of ZnO crystals are influenced by intrinsic point defects and impurities. With the progress on the crystal growth techniques makes it possible to grow high quality ZnO single crystals with one-dimension (1D), which increases the surface area [25]. Using hydrothermal process we successfully synthesis vertically aligned single crystal of ZnO nanorods which are 1D.

![Diagram of hexagonal wurtzite structure of ZnO](image)

*Figure 2.5: The diagram illustrating hexagonal wurtzite structure of ZnO.*

Van de Walls predicted by the theoretical calculation that hydrogen incorporated into ZnO lattice and form shallow donor state [25, 26]. For hydrogen to be absorbed/adsorbed to a certain material, that material should be porous and have high surface area. ZnO nanostructure can be inched by KOH hydroxide making pores on the surface of the single crystals. The process involves the interaction of OH⁻ ions with the oxygen on ZnO, coursing
oxygen vacancies on surface of the crystals. Also on hydrothermal synthesis of ZnO crystals, varying the synthesis pH can result in porous ZnO crystals. The development of the porous structure on ZnO will result in the increase in hydrogen absorption. Using hydrothermal process we successfully synthesis vertically aligned single crystal of ZnO NRs which are 1D. For the purpose of this work, 1D ZnO NRs were synthesis for the purpose of controlling the growth of carbon nanostructures (to use ZnO NRs as template for carbon growth) and use ZnO and Carbon nanostructure for hydrogen absorption/adsorption purposes.

2.4. Carbon Materials

Carbon is a chemical element with an atomic number six (6), found in group fourteen (14) of the periodic table, it has four (4) valence electrons to form covalent chemical bonding, and it is non-metallic. There are three isotopes of carbon, $^{12}\text{C}$ and $^{13}\text{C}$ which are stable, and $^{14}\text{C}$ which is radioactive or unstable. Carbon has unique properties due to its different allotropes, these allotropes include, diamond, graphite, fullerenes and carbon nanotubes/nanofibers. Hybridization and the bonding of the surrounding carbon atoms identify the physical and chemical properties of each allotrope. Carbon has three possible types of bond hybridization ($sp^3$ tetrahedron, $sp^2$ hexagonal, and $sp^1$ linear), which results in different solid state phases [29, 30, 31]. The material could have a band gap as large as 5.5 eV or one that is negative [31]. The diamond structure has $sp^3$ hybridisation, with tetrahedron lattice structure (atoms bridge together), while the graphite structure has $sp^2$ hybridisation with hexagonal sheets arrangement (in plane). Out of plane graphite are bonded by van der Waals force [1]. Graphite is softer than diamond and diamond is one of the strongest know material; diamond is transparent, while graphite is black in colour. Graphene is another allotrope of carbon, it is arranged in a regular hexagonal pattern, and it has $sp^2$ hybridization. It can form other allotropes of carbon such as carbon nanotubes, carbon nanofibers, fullerenes as it is shown on Figure 2.6. Graphene is like a sheet of paper that can be wrapped or rolled or stacked to take any shapes/dimensions, many layers of graphene stacked together effectively form crystalline flake graphite. In fullerene, carbon atoms are bonded in $sp^2$ and $sp^3$ hybridize states [29].
Graphene is the mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotube or stacked into 3D graphite [30].

Amorphous carbon allotropes (a-C) refer to carbon allotropes that do not have any crystalline structure. Some short-range order can be observed, but there is no long-range pattern of atomic positions. Amorphous carbons have all three types of bond hybridization; this enables the unique and large variation in the physical and chemical properties to be extended to amorphous carbon thin films [31]. Most of amorphous carbon actually contains microscopic crystals of graphite-like or diamond-like carbon. Amorphous carbon thin films fall into one of the following categories: polymerlike amorphous carbon (PAC), graphitelike amorphous carbon (GAC), diamondlike amorphous carbon (DAC), tetrahedral amorphous carbon (TAC), hydrogenated amorphous carbon (HAC) and nanocomposite amorphous carbon (NAC). Amorphous carbon materials are light in weight, porous, low cost and are adsorbent materials [32, 33]. These materials can be prepared in different morphologies (as powder, pellets, fibers/tubes) and with different porous texture and surface functionalities [33]. Figure 2.7 shows a representation of sp³, sp², and sp¹ hybridized bonds and the resultant crystalline and model amorphous structures.
Figure 2.7: A schematic representation of $sp^1$, $sp^2$, and $sp^3$ hybridized bonds and the resultant crystalline and model amorphous structures. The structures shown for $sp^1$ hybridized carbon are hypothetical structures showing the formation of triple bonded carbon from a graphite plane, and the packing of the carbon chain around Na atoms. The model amorphous structure for $sp^3$ bonded carbon illustrates a TAC film that is hydrogenated (light circle) and has a density of 3.0 g cm$^{-3}$. The model amorphous $sp^2$ structure is a-C that has 86% $sp^2$ bonding and has a density close to 2.0 g cm$^{-3}$[41].

2.5. Carbon nanofibers

Carbon nanofibers (CNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates [32], hence there exist three kinds of fibers; herringbones CNFs, platelets CNFs and ribbon CNFs [32, 34]. In herringbone CNFs, the graphene layers are stacked obliquely with respect to the fiber axis; in platelet CNFs, the graphene layers are perpendicular to the fiber axis and in ribbon CNFs, the graphene layers are parallel to the growth axis [34], as shown in the schematic diagram in Figure 2.8.
Carbon nanofibers are $sp^2$ hybridised carbon allotrope, like graphite it has hexagonal lattice crystal structure. CNFs are used in different kind of application such as; hydrogen storage [14, 20, 32, 33, 36, 37, 41], gas sensor [33, 39], catalyst support [30], super-capacitors [29, 29], electrical arc lamp electrodes [30, 38], screen displays [30] and they can also be used in thermochemistry due to their stability. The method of synthesis determines the morphology and the structure of CNFs. CNFs can be synthesised in different methods such as catalytic decomposition [36, 37], carbon vapour deposition [36], polymer blend technique [33], electrodeposition technique [38], electrospining methods [32, 33]. The choice of method of synthesis is very important; in this work we are going to grow CNFs using the chemical vapour deposition method, using ZnO NRs as the template to control the morphology of carbon nanofibers.

2.6. Hydrogen absorption/adsorption in carbon nanomaterial’s

Most researchers are focusing on carbon materials as the potential hydrogen storage material due to their porosity characteristic and high BET surface area [29, 30, 31, 35]. The focuses are more on nanostructured carbon materials due to their multiples applications and there are easily fabricated with different methods. Studies have been done on carbon nanotubes (single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes
(MWCNTs)), carbon nanofibers (CNFs), amorphous carbon nanofibers (a-CNFs) and activated carbon nanofibers/nanotubes (ACNFs/ACNTs) [29, 30, 31, 32, 33, 34, 35]. Hydrogen storage materials must have the following characteristics: a high specific surface area, well-developed micropores, and many active sites on the surface, such as oxygen functional groups, fluorine groups, or rare-earth-metal nanoparticles [42]. Carbon materials are promising candidate on these mention characteristics [14, 21, 32, 33, 36, 42]. The most interesting result is that CNFs can store up to 68 wt. %, this results has enhanced researchers to try to discover the mechanism of hydrogen uptake and testify the experiments [37]. However, these researchers have not yet mastered the mechanism and corroboration of those experiments [37]. The use of lightweight materials such as aluminium could push the gravimetric storage density of cryogenic liquid hydrogen storage up to 18 wt. % [21]. However, the volumetric density cannot be pushed beyond 2.3 kWhl⁻¹, which is the energy density of liquid hydrogen at normal boiling point without the volume of the storage system.

The recent studies have reported that carbon nanotubes can absorb hydrogen less than 3 wt. %, some theoretical results have been studied by Monte Carlo simulation and other calculations have supported the theory [20]. Studies show that carbon nanofibers can absorb more hydrogen depending on the catalyst used. A study that was recently done on CNTs and CNFs where Cobalt (Co) was used to modifies these carbon materials, where they reported that CNF/Co and CNT/Co (carbon nanofibers modified with Co and carbon nanotubes modified with Co) can have a storage capacity of hydrogen of 2.62 wt. % and 2.70 wt. % respectively [43]. Since CNFs can be found in different types, amorphous CNFs show the high hydrogen storage capacity compared to platelet CNFs, fishbone and ribbon [32]. Amorphous CNFs have high BET surface area and higher porosity than these other three types of CNFs. The study shows that amorphous CNFs can absorb up to 1.98 wt. % while others types of carbon nanofibers can absorb less than 0.49 wt. % at temperature of 77K and pressure of 10 bar [32]. Activated amorphous CNFs can absorb even more hydrogen up to 3.98 wt. %, while other types when activated can store up to 2.22 wt. % [32]. This results shows that we can enhance hydrogen absorption by activating carbon materials.

In our study, we are using vertically aligned zinc oxide nanorods (ZnO NRs) as our catalyst in fabrication of CNFs, to form Zinc oxide carbon nanofibers hybrids (ZnO-CNFS). The morphology of ZnO-CNFS will be controlled by ZnO NR. The presence of ZnO NR in CNFs will alter the properties of CNFs and enhance the hydrogen absorption; our aim for this study
is to pack more hydrogen at lower temperature and at lower pressures, for mobile and industrial use. ZnO NRs are vertically aligned, which will result in an increase in surface area of the ZnO-CNFs. Properties of ZnO crystals are influenced by intrinsic point defects and impurities. The hydrothermal process will alter the morphology of the crystals into nanorods which are perfectly vertically aligned and we believe these changes can enhance hydrogen absorption and diffusivity in ZnO NRs. Chemical vapour deposition (CVD) of carbon nanofibers on ZnO NRs template will result in the formation of ZnO-CNFs, which we believe will have a very good hydrogen storage capacity, since the two candidate materials can be able to absorb hydrogen. For further studies we can study gas sensing application in our sample, since we know that ZnO can be used as gas sensor, we also believe that the introduction of CNFs can enhance the sensing ability.
2.7. References


CHAPTER THREE – Characterisation techniques

3.1. Sputtering technique

Sputtering is the process whereby atoms/molecules are ejected from a surface of the solid target material due to the bombardment of the target by energetic charged particles. Atomic particles can be easily controlled by electromagnetic fields if they are charged, a weak charged gas of particles that exhibit collective behaviour is called plasma. The primary particles for the sputtering process can be supplied in a number of ways including: plasma, an ion source, an accelerator or by a radioactive material emitting alpha particles [1]. For this work, argon gas is used to form the plasma for sputtering.

*Figure 3.1:* The sputtering process, showing a solid target material, an ionized argon gas (Ar+ plasma), reactive gas and sputtered atoms on the substrate [2].

The solid target material is the source of atoms/molecules that are emitted and sputtered/deposited on the substrate. The voltage is applied between the target material and the substrate, the target material is in the cathode position and the substrate in the anode position. The target material and the substrate are placed in the vacuum chamber. *Figure 3.1* show the process of sputtering, the ionized sputtering gas (Ar+) enters the vacuum chamber and create the plasma. The sputtering gas bombards the target material and sputters off the atoms/molecules the target material and gets deposited to the substrate. Ions and neutralized
gas atoms may also get embed on the substrate as impurities and chemical reactions may occur. The average number of atoms ejected/emitted from the surface of the target material per incident ion is called the sputter yield, and it depends on the ion incident angle, the energy of the ion, the binding energy of the target atom, type of target atom and relative mass of ions and atoms. Figure 3.2 shows that sputter yield do not increase indefinitely with increasing beam energy but approach a maximum and ultimately decrease again [3]. The sputter yield is expressed by the following equation:

\[
\text{sputter yield} = \frac{\text{number of sputtered atoms}}{\text{number of incident ions}}
\]

Sputtered atoms have relatively small energies, typically between 2-7 eV (in thermal evaporation, these values are even smaller, around 0.1 eV) [1, 3].

**Figure 3.2:** Sputter yields of polycrystalline copper bombarded by N, Ne, Ar, Kr, and Xe ions [3].

When the incident ion particles collide with the surface of the target material, the energy transfer can knock off some of these atoms from the surface. The principle of energy and momentum conservation applies. Since the energies required for sputtering are much higher than lattice bonding or vibrational energies (which are the causes of inelastic interactions), therefore sputtering collisions can be considered elastic. The collision of any two particles can be easily explained using classical mechanics. The deposition rate depends on the pressure of the system and is proportional to the sputter yield. High pressure results in high
collision rates thus fewer particles deposited to the substrate. At low pressure there are fewer collisions and it may thus lead to a higher rate of deposition. The distribution in angle, relative to an experimentally specified direction of intensity of photons or ionised particles resulting from a nuclear or extranuclear process is called angular distribution. Angular distribution depend on pressure, higher pressures result in more isotropic flow and better coverage, lower pressures result in a more direct flow which result in less uniform films [3].

They are different types of sputtering; radio frequency (RF) sputtering, direct current (DC) sputtering, balanced and unbalanced sputtering. RF sputtering involves running an energetic radio wave through an inert gas to create positive ion. When sputtering gas enters the chamber, the RF power source is turned on sending radio waves through the plasma to ionize the gas atoms. Once the ions began to contact the target material, it is broken into small pieces that travel to the substrate and begin to form a coating. RF sputtering differs from DC sputtering in the voltage, system pressure, sputter deposition pattern, and ideal type of target material. DC sputtering involves the direct bombardment of the gas plasma atoms by the electrons, while RF sputtering uses energy to remove the electron from the gas atoms outer electron shell. The radio waves require more power input to achieve the same effect as electron current. DC sputtering is limited by resistivity of the of the target material, the lack of current will reduce the plasma and stop the process. DC is limited to metal which are conductive but RF can sputter an insulator like quartz.

3.2. Scanning electron microscopy (SEM)

In a Scanning Electron Microscope (SEM) a beam of highly energetic electrons is used to probe specimen on a very fine scale [4, 5]. An SEM gives more understanding about the surface morphology, microstructure and chemical composition of a sample. The electrons are emitted from the electron gun. There are three known electron guns; tungsten hairpin, lanthanum hexaboride (LaB₆) and field emission [FE] [5, 6]. Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field [4, 6]. The field emission scanning electron microscopy (FE SEM) is a very useful instrument for high resolution surface imaging, since it produce the electron beam which is about 1000 times smaller than that produced by standard microscopy with thermal electron gun [4]. When the electron beam is emitted, it is accelerated down the column by accelerating voltages (positive
Because of the negative voltage of the Wehnelt cap, all electrons are repelled towards the space charge (filament tip and cap). Electrons at the bottom can exit the gun area through the small hole (< 1mm) in the Wehnelt cap and move down the column [6]. Figure 3.3 shows the schematic diagram of an electron gun.

Figure 3.3: The diagram is illustrating the electron gun geometry of FE SEM [6].

The diameter of the electron beam is controlled by the condenser and objective lenses, to focus the beam on the specimen [5]. Figure 3.4 shows the interior components of the FE-SEM.

Figure 3.4: Schematic diagram showing the interior components of the FE SEM [7].
When the electron beam (primary electron) is bombarded on the specimen the electrons interact with electric charge of the specimen nucleus and electrons of the specimen. This interaction result in the number of signals as shown on Figure 3. Secondary electrons are collected by a detector to form the image on the screen. The generated signals undergo two types of scattering: elastic and inelastic scattering. In elastic scattering the electron beam (incident electron) interact with the electric field of the nucleus of a specimen atom. The incident electron is reflected or back-scattered out of the specimen without a significant change in the energy of the electron beam (< 1eV) [5]. The production of backscattered electrons varies directly with the specimen atomic number, thus the element with a higher atomic number will appear brighter than lower atomic number elements.

Inelastic scattering result when an electron beam interacts with the electric field of the electron of the specimen atom. Secondary electrons are produced when an incident electron excites an electron in the specimen and loses most of its energy in the process. Due to their low energy (5 eV) only electron that are very near the specimen surface (<10 nm) can exit the specimen and be analysed [6]. Secondary electron imaging provides high resolution imaging of the surface morphology. If the vacancy due to creation of a secondary electron is filled from a higher level orbital, an X-rays characteristic of that energy transition is produced. Electron solid interaction is shown by the schematic diagram of Figure 3.6 below.

**Figure 3.5:** This diagram illustrate possible signal generated when a primary electron beam interact with a specimen [5].
When signals are produced, they are analysed with different detectors;

**Secondary electrons**: are generated within a few nanometres (nm) of the specimen surface, the beam generates electrons when entering the specimen (SE1) and when leaving the specimen (SE2). These SE2 electrons are those which are analysed and form the image, thus the detector that analyse them is called SE2 detector. SE2 have low energy (3 eV – 5 eV) thus provide surface topographical image, no information on the atomic composition of the specimen. Production of SE2 is primarily independent of atomic number; however, since backscattered electrons do produce SE2, heavier elements produce more SE2 signals.

**Backscattered electrons (BSE)**: The primary electrons are scattered in an interaction volume inside the specimen. If an electron is scattered back to the surface it can leave the specimen. The yield of BSE depends on the atomic number. BSE have high energy (50 eV) thus it provides information on the atomic composition and depth image of the specimen. They have a large width of escape depth, and heavy elements produce more BSE. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle.

**Characteristic X-rays**: The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-
energy shell and the lower energy shell may be released in a form of X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer (SEM). The energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted; this allows the elemental composition of the specimen to be measured.

Other detectors that are used for other signals include: Wavelength Dispersive X-ray Spectroscopy (WDX), Electron Backscatter Diffraction (EBSD), X-ray Fluorescence spectroscopy (XRF), Cathodoluminescence (CL) and Scanning Transmittance Electron Microscopy (STEM).

3.3. Ion Beam Analysis

Ion Beam Analysis is a process whereby an energetic ion beam (incident particles He\(^+\)) is accelerated towards the surface of the target material (specimen). When the beam bombards the surface of the specimen, the beam interacts with the atoms of the specimen resulting in different types of scattering. The possible scattering and the analysis is shown on the schematic diagram of Figure 3.7, it also shows electromagnetic excitation and nuclear radiations and the detectors that are used for analysis are shown.

3.3.1. Elastic Recoil Detection Analysis (ERDA)

Elastic Recoil Detection Analysis (ARDA) is used, in this investigation, to measure hydrogen depth profiles. Rutherford Backscattering Spectroscopy (RBS) has been used to measure the thickness of the specimen. In these methods a MeV ion beam is bombarded into the surface of the material (specimen), resulting in the interaction of the atoms of the targeted material and the incident ion beam. During bombardment of the specimen different scattering (elastic and inelastic), electromagnetic excitation and nuclear radiations are observed.
Figure 3.7: The interaction between the energetic ion beam (MeV) with the surface of a sample [9].

Backscattered particles can be analysed using RBS, recoil atoms can be analysed by ERDA, gamma radiation can be analysed by Proton Induced Gamma-ray Emission (PIGE) and X-rays can be analysed by Particle Induced X-ray Emission (PIXE). Figure 3.7 show all possible interaction and possible analysis. In this work we will focus on ERDA since we want to analyse hydrogen depth profiling on our specimen and RBS for thickness measurement of the specimen. If the atoms of a target are less heavy than those of the incident beam, then target atoms are recoiled and if the atoms of the target are heavier than those of the incident beam, the incident beam atoms are backscattered. The energy of the recoiled atoms can be measured using an ERDA detector and the backscattered can be measured using the RBS detector. The recoiling target atoms can be detected in a grazing angle [10]. Figure 3.8 is the experimental diagram of ERDA-RBS set-up. ERDA and RBS are quite similar to each other but different uses in practise. The main interest in ERDA is the recoiled target atoms, while in RBS the backscattered projectiles are measured.
**Figure 3.8:** The schematic diagram showing two detectors used to study recoiled atoms and back-scattered atoms. RBS detector is used for back-scattered atoms and ERDA for recoiled atoms [10].

When the accelerated particle (incident ion beam) collides with the atoms of the surface of the target material (specimen), the collision is governed by the coulomb repulsive force and can be described as elastic collision [10]. **Figure 3.9** illustrate the projectile (accelerated particle) with mass $M_1$ and velocity $v_0$ colliding with a stationary target (atom of a target material) with mass $M_2$. $M_2$ recoils with velocity $v_2$ at a recoiling angle $\phi$ and $M_1$ is backscattered with a velocity $v_1$ at a scattering angle $\theta$.

**Figure 3.9:** The collision between two atoms ($M_1$ & $M_2$). $M_1$ has energy $E_0$ and is scattered with energy $E_1$, $M_2$ is initially at rest with zero energy and is recoiled with the energy $E_2$ [10].
Since the collision is said to be elastic kinetic energy and momentum are conserved.

Conservation of kinetic energy:

\[ \frac{1}{2} M_1 v_0^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2 \tag{3.2} \]

Conservation of momentum:

\[
M_1 v_0 = M_1 v_1 + M_2 v_2 \rightarrow 0 = M_1 v_1 \sin \theta + M_2 v_2 \sin \phi \tag{3.3}
\]

The incident ion beam has energy \( E_0 \) just before it interacts with the sample surface and the recoiling atom (target atom after interaction) has energy \( E_2 \) as illustrated on Figure 3.9. The ratio \( \left( \frac{E_2}{E_0} \right) \) of these energies is the most important quantities in ERDA and called kinematic factor. Kinematic factor is derived from conservation equations (3.2) and (3.3)

\[
k_1 = \frac{E_2}{E_0} = \frac{4M_2/M_1}{(1+M_2/M_1)^2} \cos^2 \phi \tag{3.4}
\]

The kinematic factor equation shows that the energy after recoiling is determined by the masses of the particles, the target atoms and the recoiling angle. The recoiling angle can never be greater than \( \pi/2 \), this limits is reaches when \( M_1 = M_2 \) since \( \sin \phi_{\text{max}} = M_2/M_1 \).

ERDA technique measures the energy spectra of the recoiled ion at a given detector angle and a peak in this spectra corresponds to the corresponding kinematic factor. To increase the sensitivity of the method it is important to choose experimental parameters in such a way to make as large as possible the difference between kinematic factor describing spectral components of different kinds of recoiled target atoms. The sensitivity of ERDA is increased at smaller recoil angles and it is advantageous to select \( M_1 \gg M_2 \) \([9, 10]\).
3.4. X-ray diffraction (XRD)

X-ray diffraction is the study of materials with any beam, e.g. ions, electrons, neutrons and protons, with a wavelength similar to the distance between the atomic or molecular structure. X-rays are a form of electromagnetic radiation with a wavelength ranging from 0.01 nm to 10 nm, corresponding to the frequencies in the range of $3 \times 10^{16}$ Hz to $3 \times 10^{19}$ Hz and energies in the range of 100 eV to 100 keV. X-rays are produced whenever a high-speed electron collides with a metal target (specimen). When an X-ray beam is used as a probe in a material, they interact with the atoms of the material hence scattering and transmission occurs. Diffraction occurs only when Bragg’s law is satisfied. The condition for constructive interference from plane with spacing $d$, is shown in Figure 3.10.

![Diagram of X-ray diffraction](image)

**Figure 3.10:** Illustration of x-ray diffraction in the specimen/sample, the incident x-rays interact with the lattice planes and are diffracted, the diffracted rays are then analysed by a detector at different detector angles [11].

Hence X-ray diffraction on randomly oriented crystal is described by Bragg’s law:

$$n\lambda = 2d \sin \theta$$  

3.5

It relates the characteristic crystal lattice spacing $d$, with the X-ray wavelength $\lambda$ and the angle between the incident beam and scattered beam $2\theta$, $n$ is an integer ($n=1, 2...$).

A crystal consists of planes of atoms spaced a distance $d$ apart, but can be resolved into many atomic planes, each with a different $d$ – spacing, and that can be determined by XRD.
3.5. **Raman spectroscopy**

Raman spectroscopy is a spectroscopic technique used to observe vibrational, and other low-frequency modes in a system. Raman analysis relies on the inelastic scattering of monochromatic light (from a laser source), in the visible, near infrared, or near ultraviolet range. Photons of the laser source are absorbed by the samples and reemitted, frequency of the re-emitted photons is shifted up or down in comparison with the original frequency. This is called the Raman effect. Raman effect occurs when monochromatic light impiges on the a molecule and interact with the polarizable electron density and the bonds of the molecule in the phase (solid, liquid or gaseous) and environment in which the molecule find itself [12]. The shift provides information about vibrational, rotational and other low frequency transitions of molecules. Raman effect is based on molecular deformations in electric field E determined by molecular polarization $\alpha$, laser beam can be considered as an oscillating electromagnetic wave with electrical vector $E_0$ [12, 14].

![Energy-level signal diagram showing the states involved in Raman signals. The line thickness is roughly proportional to the signal strength from the different transition [13].](image)

Figure 3.11: Energy-level signal diagram showing the states involved in Raman signals. The line thickness is roughly proportional to the signal strength from the different transition [13].

When the electromagnetic radiation interacts with the sample it induces electric dipole moment $P$ which deforms molecules. The possible energy shift is given by Figure 3.11; the thickness of the line is proportional to the signal strength from different transitions. Raman spectroscopy is a standard non-destructive tool for the characterization of crystalline, nanocrystalline, and amorphous materials [15].
3.6. Transmitting electron microscopy (TEM)

TEM is a kind of microscopy technique which uses a beam of electrons to probe through an ultra-thin sample, electrons interacting with the specimen as it passes through it. When an electron beam interacts with the sample, the signals are generated during the process. The signals generated include elastic and inelastic scattering; see Figure 3.5 and Figure 3.6. The schematic diagram in Figure 3.12 is showing the interior component of transmitting electron microscopy. They are different type of electron gun used to probe the sample this includes; hairpin style tungsten filament and single crystal LaB$_6$ filament. The different between SEM and TEM is the signals they used to form the images. SEM uses mostly backscattered electron and secondary electrons. TEM only use transmitted electron to form the image and it has high resolution than SEM.

![Figure 3.12: The schematic diagram illustrating the interior geometry of TEM [16].](image)
3.7. References


CHAPTER FOUR – Sample preparation

4.1. Introduction

Direct current reactive magnetron sputtering (AJA Orion 5 sputtering system) was used for deposition of zinc oxide nanoparticles (ZnO NPs) and for the synthesis of hybrid zinc oxide carbon nanofibers (ZnO-CNFs) using chemical vapour deposition (CVD). ZnO nanorods were grown using hydrothermal process developed by Wang et al. [1].

4.2. Deposition of ZnO NPs

ZnO NPs were deposited on Silicon wafer (100). The substrates were cleaned by ultrasonic bath in alcohols (methanol, acetone, and trichloroethylene), washed with distilled water to remove alcohol (methanol) and dried with nitrogen gas. The process of sputtering, the position of the substrate and the solid target material in a vacuum chamber are shown by Figure 4.1.

Figure 4.1: The full process of sputtering, Ar gas enter the chamber and is ionized by electric field, the ionised Ar gas (Ar+) interact with the surface of the solid target producing atoms in plasma, form which react with oxygen gas (O₂) and accelerated to the substrate where the film grow[2].

The diagram shows the sputtering gas (argon (Ar)) and reactive gas (oxygen (O₂) entering the vacuum chamber and argon gas is ionised (Ar⁺) by the electric field, and strike the surface of the solid target material (Zn), the atoms from the target (in the plasma form) are then
accelerated upward to the substrate. Before the atoms reach the substrate they combine with oxygen gas (O$_2$) to form the oxide (ZnO). High vacuum is required for a deposition of a uniform film. If a vacuum is low, the probability of particles reaching the substrate is reduced because of high collision probability and high vacuum reduce the collision probability. Synthesis of different thicknesses can be achieved by depositing your specimen for different durations of times. The deposition power can also influence the thickness of the specimen, since higher power may increases the number of the atoms that are removed from the surface of the solid target material. **Figure 4.2** shows the schematic diagram of the AJA Orion 5 sputtering system available at university of Zululand.

![Sputtering System](image)

**Figure 4.2:** The AJA orion-5 direct current reactive magnetron sputtering system available at University of Zululand.

The deposition chamber was evacuated to a base pressure of $10^{-7}$ Torr by oil-diffusion-pump and turbo-pump combination. High purity (99.995%) argon gas and high purity oxygen gas 99.995% were used as sputtering and reactive gases, respectively. Zinc metal of 99.999% purity was used as a sputtering target. The flux ratio of argon to oxygen was maintained at 2:1. The sputtering pressure, which is a total pressure of argon and oxygen, was set to
3 × 10⁻³ Torr and the distance of the target to substrate was fixed at 34 mm. The sputtering power was set to 70 W, actual power, current and voltage was maintained at 69 W, 184 mA and 408 V, respectively. The sputtering time was varied from 15, 30 up to 60 minutes. After each deposition the samples were annealed at a substrate temperature of 300 °C in an oxygen environment for further oxidation. Annealing time and pressure was 60 minutes and 3 × 10⁻³ Torr, respectively. The zinc target was pre-sputtered in argon-oxygen atmosphere for 5 minutes to remove the surface oxide layer of the target.

The crystal structure of nanoparticles was investigated using an XRD (Bruker D8 advance). Surface morphology, particle size and chemical composition were examined using an FE-SEM (Carl ZEISS SIGMA VP system and EDS detector from oxford instruments).

4.3. Synthesis of ZnO nanorods (ZnO NRs)

ZnO NRs were grown on ZnO NPs seeds (which provide nucleation site for NRs) using hydrothermal process. The hydrothermal solution was prepared by dissolving 0.05 M Zinc chloride (ZnCl₂) in distilled water. The pH of the solution was measured to be 6.83 before adding ammonia (NH₃) 25%. NH₃ was added on the solution, while continuously stirring until the solution became clear in colour with a pH of 11. ZnCl₂ solution contains Zn²⁺ and Cl⁻ ions; Zn²⁺ ions are responsible for the nucleation of ZnO NRs, by interacting with the O²⁻ ions that are given off by distilled water. When Zn²⁺ and O²⁻ interact under constant heating they form ZnO NRs and these NRs are grown on ZnO NPs seeds. Since NRs are grown on uniform nanoparticle (ZnO NPs) seeding, hence they are influenced by these NPs to align themselves vertically on the surface of the substrate. The experimental setups for the hydrothermal technique are shown on the schematic diagram of Figure 4.3, which displays both the incubator and the autoclave bottle.
A solution of ZnCl$_2$ prepared as described above was transferred to bottles with autoclavable caps. Silicon wafer substrate was inserted vertically in the solution (see Figure 4.3). The substrates were first deposited with ZnO NPs seeding. The autoclave bottles with substrates were then put inside an incubator and the temperature raised to 90 °C. The time for growing ZnO NRs was fixed at 2 hours. The incubator was pre-heated for 30 minutes to stabilise the temperature. The samples were removed immediately after the required time to stop the process, then were washed with distilled water repeatedly to remove impurities on the surface of ZnO NRs and were dried on the incubator for 5 minutes. The crystal structure of the nanorods was investigated using XRD. The morphology, chemical composition diameter and the length was examined using an SEM.

4.4. Synthesis of zinc oxide carbon nanofibers (ZnO-CNFs)

Chemical vapour deposition (CVD) was used for the synthesis of ZnO-CNFs using an evacuated chamber of the DC reactive magnetron sputtering system [3, 4]. High purity (99.995 % pure) acetylene (C$_2$H$_2$) was used as the carbon source. The specific flux of C$_2$H$_2$ was controlled at 10 sccm. The substrate temperature was varied from 500 °C to 800 °C to investigate the effect of temperature on the synthesis of CNFs.
**Figure 4.4:** The schematic diagram showing the chemical vapour deposition process, the gas ($\text{C}_2\text{H}_2$) enter the chamber, at high temperature $\text{C}_2\text{H}_2$ decompose to $\text{H}^*$ and $\text{C}^*$ (* = +1, +2, & +4). $\text{C}^*$ & $\text{H}^*$ interact with the surface of the catalyst, $\text{H}^*$ form $\text{H}_2\text{O}$(g) that pumped out the system and $\text{C}^*$ form $\text{ZnO}$-CNFs.

During the CVD process the chamber pressure was kept constant at $3 \times 10^{-3}$ Torr and the deposition time was also kept constant at 40 minutes for all samples. ZnO NRs were used as a template to control the morphology of CNFs. The catalyst was pre-heated for 1 hour, to remove moisture and to stabilise the temperature. The CVD process is shown on the schematic diagram of **Figure 4.4**, showing the gas ($\text{C}_2\text{H}_2$) interact with the compound of the template. Schematic diagram show the bulk gas ($\text{C}_2\text{H}_2$) entering the vacuum chamber; step 1, the bulk gas move down to the surface of the catalyst; step 2, the bond $\text{C=}$ and $\text{C–H}^{-}$ are decomposed; step 3, the bulk gas becomes $\text{C}^*$ and $\text{H}^*$; step 4, $\text{H}^*$ bond with $\text{O}_2$ that is bonded with ZnO NRs to form $\text{H}_2\text{O}$ gas; step 5, $\text{C}^*$ build as $\text{C–C}$ bonds with ZnO NRs; step 6, $\text{H}_2\text{O}$ gas is vented out of the chamber. The samples were cooled at room temperature before they were removed from chamber.

The surface morphology, diameter, length and chemical composition of ZnO-CNFS were investigated using SEM. We used XRD to investigate the crystal structure. Hydrogen profiling was studied by the method of ERDA. TEM was use to check the type of carbon ZnO-CNFS (nanofibers, nanotube or amorphous carbon). All the results are given in Chapter 5.
4.5. References


Characterisation of ZnO NPs, ZnO NRs and ZnO-CNFs films

ZnO nanoparticles (ZnO NPs) were successfully synthesised at different deposition time. The effect of deposition times on nanoparticle (NPs) sizes were investigated, using different characterisation techniques. ZnO NRs were synthesised using the hydrothermal method and the effect of ZnO NPs seeding on the growth of ZnO NRs was also investigated using different characterisation methods. ZnO-CNFs were successfully synthesis at different annealing temperatures using ZnO NRs as the supporting template. The nanorods themselves were characterised using several techniques.

5.1. Analysis of ZnO NPs

ZnO NPs were characterised using the following methods; scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), Rutherford back-scattering (RBS) and X-ray diffraction (XRD).

5.1.1. SEM and EDS analysis

Surface morphology, chemical composition and average particle sizes were investigated using a Carl ZEIS SIGMA VP 03-67 system. Figure 5.1 shows SEM images of ZnO NPs synthesised at different deposition times, Figure 5.1.(a) 15 minutes, Figure 5.1.(b) 30 minutes and Figure 5.1.(c) 30 minutes. The surface morphology of the particles were spherical and average diameter show that the particle sizes increase with an increase in the deposition times. The average diameter of the particles sizes increases from 6.73 – 19.60 nm, at 15 minutes the average size was 6.73 nm, at 30 minutes it was 12.71 nm, and at 60 minutes the average diameter was measured to be 19.60 nm. ZnO particle sizes were also confirmed by using Scherrer’s equation, which is written as follows:

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]  

5.1
Where:

- \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
- \( K \) is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
- \( \lambda \) is the X-ray wavelength;
- \( \beta \) is the line broadening at half the maximum intensity (FHWM), after subtracting the instrumental line broadening, in radians;
- \( \theta \) is the Bragg angle.

The Scherrer’s equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern [9]. The values used in calculation of particle mean sizes were obtained from Figure 5.2 and the results are presented on Table 5.1, the results are comparable with the values measured from SEM images. The calculated particle sizes varied from 7.99 nm, 13.45, and 18.43 nm (15 minutes, 30 minutes and 60 minutes, respectively). From SEM images we can conclude that the surfaces of the thin films were uniform and we were able to deposit continuous films. The particle sizes increase with the increase in deposition time as shown by calculated values and measured values from SEM images.
Figure 5.1: SEM images of ZnO NPs (a) 15 minutes, (b) 30 minutes, and (c) 60 minutes.

Table 5.1: The table illustrating the relationship between the particle sizes (nm) and sputtering time (minutes), as estimated from SEM and calculated by Scherrer’s equation

<table>
<thead>
<tr>
<th>Deposition time (minutes)</th>
<th>Particles sizes (nm) measured from SEM</th>
<th>Calculated by Scherrer’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>6.73</td>
<td>7.99</td>
</tr>
<tr>
<td>30</td>
<td>12.71</td>
<td>13.45</td>
</tr>
<tr>
<td>60</td>
<td>19.6</td>
<td>18.43</td>
</tr>
</tbody>
</table>

The chemical composition of the films was investigated using the EDS (detector from oxford instruments), which gave the atomic percentage (At. %) of each type of atom involved in the reaction. Table 5.2 shows that the oxygen content varied from 58.76 At. % to 60.12 At. % and zinc content varied from 39.88 At. % to 41.24 At. %. We find a high content for film deposited at 60 minutes and low Zn content for film 15 minutes deposited film. The
difference in chemical composition is very low; it was observed that time only affect mostly the particles size not the chemical composition.

**Table 5.2: ZnO NPs synthesised at different deposition times.**

<table>
<thead>
<tr>
<th>Elements</th>
<th>ZnO NPs (At. %) 15 Minutes</th>
<th>ZnO NPs (At. %) 30 Minutes</th>
<th>ZnO NPs (At. %) 60 Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>60.12</td>
<td>59.71</td>
<td>58.76</td>
</tr>
<tr>
<td>Zn</td>
<td>39.88</td>
<td>40.29</td>
<td>41.24</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

5.1.2. RBS analysis

We used RUMP software to calculate the thickness and chemical composition of the ZnO NPs samples. The data for the calculations was obtained from ion beams analysis called RBS (Rutherford Backscattering Spectrometry). The chemical compositions measured from RBS were comparable to the values obtained from EDS analysis. The results presented on Table 5.3, show the thickness of the films and the chemical composition of the films with the relation to the deposition times, as calculated by RUMP software from RBS data.

**Table 5.3: RBS analysis showing the thickness in angstroms and the chemical composition in atomic percentage with relation to a deposition times.**

<table>
<thead>
<tr>
<th>Deposition time (minutes)</th>
<th>Thickness of the films (angstroms (Å))</th>
<th>Chemical Composition (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>15</td>
<td>330</td>
<td>41.2</td>
</tr>
<tr>
<td>30</td>
<td>769</td>
<td>42.5</td>
</tr>
<tr>
<td>60</td>
<td>1222</td>
<td>42.3</td>
</tr>
</tbody>
</table>

From Table 5.3, we can conclude that the calculated thickness was proportional to deposition times, when the deposition times was increased also the thickness increases. The thickness increased from 330 Å to 1222 Å, at 15 minutes the thickness was 330 Å, 30 minutes was 769 Å and at 60 minutes the thickness was 1222 Å. The deposition times have a very big effect on the thickness and particles sizes. The chemical composition measured for all samples at
different deposition times are relatively comparable to each other and they agree with the EDS results.

5.1.3. XRD analysis

The X-ray diffraction patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer using a Cu Kα (λ = 1.54 Å) radiation source. The measurements were extracted at 40.0 kV and 40.0 mA. The data was obtained in the Bragg-Brentano geometry as from 2θ = 20° to 40° with a step size of 0.0134° for all samples. XRD analysis shows the peaks at the angles 2θ = 33.25° and 2θ = 34.66°, that corresponds to (100) and (002) crystal planes, respectively, as shown in Figure 5.2. These peaks shown by ZnO NPs are both indexed to the wurtzite hexagonal ZnO phase, with the lattice constant a = 0.325Å and c = 5.207Å [3]. As the deposition time is increased the intensity of the peak (002) increases. There were no impurities that were observed on the XRD patterns.
Figure 5.2: XRD results of ZnO NPs prepared at; (a) 15 minutes, (b) 30 minutes and (c) 60 minutes. All peaks indicate the presence of a wurzite ZnO structure.

5.2. ZnO NRs analysis

ZnO NRs were characterized using the following methods; SEM, EDS, XRD, AND Raman spectroscopy.

5.2.1. SEM and EDS analysis of ZnO NRs

The time for growing ZnO NRs was fixed at 2 hours; the temperature was also fixed at 90°. ZnO NRs were successfully grown by hydrothermal process and they were vertically aligned on the c-axis, see Figure 5.3. The effect of seeding on the growth of ZnO NRs was observed, the distribution, diameter and length was affected by seeding particle sizes. Figure 5.3.(a) shows ZnO NRs grown on 15 minutes deposited seeding; with the measured average diameter of 63.40 nm and average length of 106.72 nm. Figure 5.3.(b) ZnO NRs grown on
30 minutes deposited seeding; their measured average diameter was measured 78.93 nm and the average length of 114.05 nm. **Figure 5.3.** (c) ZnO NRs grown for 60 minutes deposited ZnO NPs; the average diameter and length were measured to be between 55.64 nm and 129.15 nm, respectively. The distribution and the orientation of ZnO NRs on different seeding are shown on **Figure 5.3.** The homogeneity of the rods that were grown at 15 minutes and 30 minutes seems to have uniform sizes (length and diameter) and are closely parked to each other, but the rods grown at 60 minutes do not have uniform size and are scattered.

![SEM images of ZnO NRs grown for 2hrs, (a) ZnO NPs for 15 minutes, (b) ZnO NPs for 30 minutes, and (c) ZnO NPs for 60 minutes](image)

**Figure 5.3:** SEM images of ZnO NRs grown for 2hrs, (a) ZnO NPs for 15 minutes, (b) ZnO NPs for 30 minutes, and (c) ZnO NPs for 60 minutes

Using EDS analysis, the chemical composition of ZnO NRs was investigated. **Table 5.4** show the EDS results of ZnO NRs grown on seeding deposited for 15 minutes, 30 minutes, and 60 minutes, respectively. As the deposition time increases (seeding deposition time), the oxygen content decrease and the Zn content increases.
Table 5.4: EDS analysis for ZnO NRs grown for 2 hours

<table>
<thead>
<tr>
<th>Elements</th>
<th>ZnO NRs (At. %) 15 minutes</th>
<th>ZnO NRs (At. %) 30 minutes</th>
<th>ZnO NRs (At. %) 60 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>59.74</td>
<td>55.66</td>
<td>54.91</td>
</tr>
<tr>
<td>Zn</td>
<td>40.26</td>
<td>44.34</td>
<td>45.09</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

5.2.2. XRD analysis for ZnO NRs

![Diagram illustrating the XRD pattern for ZnO NRs grown for 2 hours at ZnO NPs seeding synthesised at different deposition time.](image)

**Figure 5.4:** Diagram illustrates the XRD pattern for ZnO NRs grown for 2 hours at ZnO NPs seeding synthesised at different deposition time; (a) indicate the XRD pattern for ZnO NRs grown on 15 minutes, 30 minutes and 60 minutes seeding, respectively, (b) is the insert of ZnO NRs grown on 60 minutes seeding, (c) is the insert for ZnO NRs grown at 30 minutes seeding, and (d) is the insert of ZnO NRs grown at 15 minutes seeding.

Using the method of XRD the crystal structure of ZnO NRs was investigated. **Figure 5.4** shows the XRD spectrum for ZnO NRs. Three peaks were observed on the XRD spectra at angles 2\(\theta\) = 31.22\(^\circ\), 2\(\theta\) = 34.91\(^\circ\) and 2\(\theta\) = 35.70\(^\circ\) see **Figure 5.4**, these peaks corresponds to
crystal planes of (100), (002), and (101), respectively of ZnO. These peaks are all indexed to the wurtzite hexagonal structure of ZnO, with lattice constant \( a = 0.325 \, \text{Å} \) and \( c = 5.207 \, \text{Å} \) [3]. A very high intensity on (002) crystal plane observed show that ZnO NRs are more crystalline and are single crystalline, the two other peak are very small to compare to this peak (see insets of Figure 5.4). The crystals of ZnO are one dimensional (1D) and perfectly vertically aligned; that is why we have a very sharp and high intensity peak. The ZnO NRs are vertically aligned on the c-axis; they were used as the template on growing ZnO-CNFS.

5.3. ZnO-CNFS analysis

ZnO-CNFS were characterised using; a SEM for surface morphology, EDS for chemical composition, transmitting electron microscope (TEM) to confirm if we were able to synthesis CNFs, XRD for crystal structure, Raman spectroscopy to study disorder, and elastic recoil detection analysis (ERDA) for hydrogen absorption/adsorption profiling.

5.3.1. SEM and EDS analysis of ZnO-CNFS

Carbon was deposited at different annealing temperatures (varied from 500, 600, 700 to 800 °C); all other parameters (chamber pressure and deposition time) were kept constant to investigate the effect of temperature on the growth. SEM images shows that the temperature has an effect on the morphology of ZnO-CNFS and the morphology is controlled by ZnO NRs. When the sample is annealed at lower temperatures (500 °C), ZnO-CNFS retains the morphology of ZnO NRs and start to lose the hexagonal shape on the surface, as its surface is covered by carbon Figure 5.5(a). When the annealing temperature is increased to 600 °C, the diameter of ZnO-CNFS decreases, but the morphology still retains the alignment of the template Figure 5.5(b). At 700 °C the ZnO-CNFS retains the alignment of ZnO NRs and become porous Figure 5.5(c). When the annealing temperature is raise to 800 °C, the template alignment is completely lost, possibly due to a meltdown Figure 5.5(d).
Figure 5.5: Illustrate the SEM images of ZnO-CNFs synthesised at different annealing temperatures varied from 500 °C – 800 °C. (a) show a CVD at 500 °C, (b) CVD at 600 °C, (c) CVD at 700 °C, and (d) CVD at 800 °C; all other conditions (chamber pressure, deposition time, and gas flow rate) were kept constant for all deposition temperatures.

During the CVD process we placed the aligned ZnO NRs facing up inside an evacuated chamber. The temperature of the chamber was then raised to values ranging from 500 °C to 800 °C. For each experiment the annealing temperature was held constant and then C2H2 was let into the chamber. C2H2 is unstable at high temperatures i.e. above 300 °C; it decomposes at these high annealing temperatures. It decomposes into C* and H* (* = +1, + 2, + 4). H* will be attracted to the oxygen of the ZnO NRs, to form H2O (g) causing vacancies on the NRs and H2O (g) is pumped out of the system as gas at these high temperatures. C* will grow on those vacancies left by O, forming a weak bonds with Zn (temporal bonding (weak polar covalent bonding), forming Zn–C), as the concentration of C* increases on the system, C–C or C=C bonds are formed which are very strong covalent bonds [7, 8]. ZnC is characterized by it very high porosity, typically 75-95% of the volume consisting of void spaces [7]. Zinc melts at 419.5 °C; hence when it loses its bonds (with oxygen, and with carbon) it is likely
that it will start to melt, living carbon structures and taking the morphology of the ZnO NRs. As the temperature increases the reaction rate also increases, when the process is faster Zn will melt as it loses oxygen before it can bond with carbon and before C–C or C=C bonds are formed to take the alignment, see Figure 5.5.(d).

Chemical composition changes were investigated using EDS. Table 5.5 shows the EDS result of ZnO-CNFs synthesised by CVD process at different annealing temperatures. EDS show the change in the chemical composition quantities as the temperature changes. As the annealing temperature is increased Zn is consumed.

Table 5.5: EDS table of result for ZnO-CNFs, annealed at different temperatures, all other conditions were kept constant, ZnO NRs that were not annealed in the presence of C₂H₂ is also included.

<table>
<thead>
<tr>
<th>elements</th>
<th>ZnO NRs</th>
<th>CVD at 500 °C, At. %</th>
<th>CVD at 600 °C, At. %</th>
<th>CVD at 700 °C, At. %</th>
<th>CVD at 800 °C, At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>--</td>
<td>75.49</td>
<td>76.32</td>
<td>81.35</td>
<td>45.31</td>
</tr>
<tr>
<td>O</td>
<td>54.91</td>
<td>20.57</td>
<td>22.38</td>
<td>18.60</td>
<td>53.66</td>
</tr>
<tr>
<td>Zn</td>
<td>46.09</td>
<td>3.94</td>
<td>1.3</td>
<td>0.05</td>
<td>1.03</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

There is no carbon on the samples before CVD (not annealed ZnO NRs), this is shown on Table 5.5 (see also Table 5.4 showing the chemical composition of ZnO NRs). The content of carbon shows an increase from 75.49 At.% to 81.35 At.% as annealing temperature rises from 500 °C to 700 °C, and at the annealing temperature of 800 °C a huge decrease in carbon content is observed. This means that we are getting a lower content of CNFs. Zn content decreases from 3.94 At.% to 0.05 At.% at temperatures from 500 °C to 700 °C, and at 800 °C the content is 1.03 At. %. The content of Zn left on ZnO-CNFs samples at temperatures of 500 °C to 700 °C are those that didn’t react during the CVD process. The quantity of Zn present at higher temperature 800 °C is likely due to the unreacted ZnO. What is interesting is that the ZnO-CNFs take the shape of the ZnO NRs from which they were formed (see SEM images in Figure 5.5).
5.3.2. TEM analysis of ZnO-CNFS

TEM analysis was used to investigate two ZnO-CNFS samples deposited at temperatures of 500 °C and 700 °C see Figure 5.6. The purpose of the TEM investigation of these two samples annealed at these temperatures was to try to find out whether we did manage to get CNFs as we expected and to see how porous our samples are at lower and high annealing temperatures. At lower annealing temperatures (Figure 5.6a) we observe more ZnO which has not been consumed; this was also observed from EDS and XRD analysis. We predicted that the high availability of ZnO yield will result in a low porosity development. When the annealing temperature is increased to high values (Figure 5.6b) ZnO is consumed and this results in an increase in porosity. TEM analysis shows that ZnO-CNFS at this temperature is more porous. We can conclude from result shown by Figure 5.6b that we were able to synthesise carbon nanofibers on ZnO NRs template. The morphology of ZnO NRs (1D crystal structure) was able to control the growth morphology of ZnO-CNFS.

![Figure 5.6: TEM images of ZnO-CNFS deposited at, (a) 500 °C, and (b) 700 °C; all other conditions were kept constant.](image)

5.3.3. XRD analysis of ZnO-CNFS

XRD revealed more information about the crystal structure of the samples on which CVD had been done. The interpretation of the diffraction pattern is not straight forward on CNFs/CNTs, due to their size, their strong curvature which induces strain, as well as the disordered stacking of the graphene layers can lead to peak shifts, peak broadening and even
to the suppression of some reflections [1]. Graphite XRD diffraction pattern can be used in explaining the position of the peaks of ZnO-CNFs. Other researchers have already been studying disordered carbon using XRD [2]. They studied turbostratic carbon, which exhibits some stacked graphene layers with a regular spacing in graphite but different degree of stacking order. The results show a different XRD diffraction pattern to that of hexagonal graphite. Using graphite XRD patterns to interpret ZnO-CNFs might be misleading. Carbon nanotubes or carbon nanofibers do not present a 3D crystalline structure [1]. The catalyst/template used in the synthesis of carbon nanostructures plays a very important role, since it is the one controlling the growth of carbon nanostructures. We observed this property on the growth of ZnO-CNFs using ZnO NRs as template; which resulted from vertically aligned ZnO NRs (the growth of ZnO-CNFs is controlled by ZnO NRs). The crystal structure itself is likely to be controlled by the template. ZnO NRs (template) have a single crystal structure and also the ZnO-CNFs should have a single crystal structure. Figure 5.7 shows XRD pattern of ZnO-CNFs, deposited at various annealing temperatures 500 °C, 600 °C, 700 °C and 800 °C.

![XRD pattern of ZnO-CNFs](image)

**Figure 5.7:** The diagram shows an XRD pattern of ZnO-CNFs synthesised using ZnO NRs template at different annealing temperature varied from 500 °C to 800 °C. For sample annealed at 500 °C we observe intense (002) peak as the annealing temperatures are increase the (002) vanished and (100) peak emerge.
The XRD patterns for ZnO NPs and ZnO NRs shows intense peak at angle $2\Theta = 34.81^\circ$ which correspond to (002) plane. When the annealing temperature is increased the intensity of the peak ((002) plane) decreases, this is also reported by reference [15]; they observed that as the annealing temperature increases the peak intensity decreases, this show that the crystallinity of ZnO NRs decreases. In our case we annealed at the presence of $C_2H_2$ which introduces carbon on ZnO NRs, the effect of annealing temperature was investigated. When (002) peak decrease as the annealing temperature increases, another peak at angle $2\Theta = 33.33^\circ$ emerge which corresponds to (100) plane. The peak (100) increases as the peak (002) decreases with the increase in annealing temperature. According to the obtained XRD results we were able to synthesis 1D single crystal of ZnO-CNFs and it morphology is controlled by the template morphology.

5.4. Raman Spectroscopy analysis of ZnO NRs and ZnO-CNFs

Raman is the technique used to study vibration modes of atoms of the materials; it is sensitive to electronic structural changes of the material. We prepared our samples on silicon wafers as substrates. This gave us a problem in studying ZnO NRs vibration modes. It was found that silicon have Raman shift peaks at 300 cm$^{-1}$, 520 cm$^{-1}$, and 964 cm$^{-1}$, as a results these peaks overlap with peaks of ZnO NRs, Figure 5.8 is the illustration of Raman of ZnO NRs. We observed that the silicon peak at 520 cm$^{-1}$ has a very high intensity (Figure 5.8.(a)) which eliminate the entire peaks with very low intensities, Figure 5.8.(b) is the zoomed Raman shift of ZnO NRs to study the peaks at lower intensities.
Figure 5.8: (a) Raman shift spectrum of ZnO NRs on the silicon substrate (b) is the zoomed in Raman shift of ZnO NRs to investigate what we have at lower Raman intensities.

Table 5.6: Raman active phonon modes frequencies (in cm\(^{-1}\)) for bulk ZnO. The presented data are a compilation of the results from different studies [4].

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(_2) (low)</td>
<td>102</td>
</tr>
<tr>
<td>A(_1) (TO)</td>
<td>379</td>
</tr>
<tr>
<td>E(_1) (TO)</td>
<td>410</td>
</tr>
<tr>
<td>E(_2) (high)</td>
<td>439</td>
</tr>
<tr>
<td>A(_1) (LO)</td>
<td>574</td>
</tr>
<tr>
<td>E(_1) (LO)</td>
<td>591</td>
</tr>
</tbody>
</table>

Failing to get the information we wanted on the sample deposited on the silicon substrate, we prepared the same sample on a glass substrate. The Raman shift spectra of the ZnO NRs deposited on the glass sample is illustrated by Figure 5.9, and it doesn’t have the interference of the substrate. ZnO NRs show peaks (Figure 5.9) at 330 cm\(^{-1}\), 415 cm\(^{-1}\), 437 cm\(^{-1}\), and 578 cm\(^{-1}\). Raman shift at 330 cm\(^{-1}\) is due to the vibration modes as a result of multiple photon scattering [3].
Figure 5.9: Raman shift spectrum of ZnO NRs on the glass substrate.

Raman shift at 412 cm$^{-1}$ corresponds to E$_1$(TO) is shifted by 2 cm$^{-1}$ compared to the bulk. The value at 439 cm$^{-1}$ corresponds to E$_2$(high) and the peak at 574 cm$^{-1}$ corresponds to A$_1$(LO), see Table 5.6 for comparison. The peak at 439 cm$^{-1}$ is characteristic of the wurtzite lattice, the high Raman intensity indicate that ZnO NRs is highly crystalline. Raman shift at 574 cm$^{-1}$ is associated with the presence of oxygen vacancies, interstitial zinc and their complexes [3]. LO-phonon peaks are observed on the Raman spectrum because the incident light is perpendicular to c axis of wurtzite ZnO, and TO-phonon are observed in non-resonant Raman spectrum of ZnO nanocrystals [4]. The peak observed at 412 cm$^{-1}$ is a result of ZnO NPs used as the seeding for growing oriented ZnO NRs, which grow on the c axis as shown by SEM results.

The Raman spectra of disordered graphite show two quite sharp modes, the G peak around 1580 cm$^{-1}$ – 1600 cm$^{-1}$ and D peak around 1350 cm$^{-1}$ [5, 6]. Graphitic carbon consists of $sp^2$ hybridisation and diamond like carbon consists of $sp^3$ hybridisation. Disordered graphite consists of both $sp^2$ and $sp^3$ hybridisation, it is also possible to get $sp^1$ hybridisation. Raman shift spectrum for ZnO-CNFS was obtained from the sample deposited on the silicon substrate; we were not able to use glass due to the temperature limits. The peaks observed on Raman shifts spectrum (Figure 5.10 and Figure 5.11) at 300 cm$^{-1}$, 520 cm$^{-1}$, and at 964 cm$^{-1}$ was due to the substrate. The Raman shift at 437 cm$^{-1}$ was due to ZnO NRs used as the catalyst in ZnO-CNFSs, this peak is characteristic of crystalline ZnO. Raman shift at 1340 cm$^{-1}$
\(^1\) correspond to D-band and Raman shift at 1598 cm\(^{-1}\) – 1600 cm\(^{-1}\) are due to G-band. ZnO-CNFs deposited at 800 °C has a lower Raman shift intensity (D-band and G-band intensities) compared to that of ZnO-CNFs deposited at 500 °C to 700 °C, these confirm with the EDS results showing a very low percentage of carbon on ZnO-CNFS at 800 °C. The Raman shift intensity that correspond to silicon on this sample (ZnO-CNFS at 800 °C) was very high, which confirm that the substrate is more exposed to little ZnO-CNFS to cover the substrate.

**Figure 5.10:** (a) Raman Shift spectrum of ZnO-CNFS deposited at different annealing temperatures (500 °C - 700 °C), (b) zoomed raman shift spectrum (600 °C-700 °C) to study the changes in ZnO NRs with the deposition of carbon, and (c) zoomed (inset) Raman shift of 500 °C.
Figure 5.11: (a) Raman shift spectrum for ZnO-CNFs at 800 °C, and (b) inset Raman shift spectrum.

The Raman shift at 1598 cm$^{-1}$ – 1600 cm$^{-1}$ region are due to the dominating C–C and C=C stretching vibration of benzene and quinone type rings respectively [3]. Raman shift for ZnO-CNFs deposited from 500 °C to 700 °C is at 1598 cm$^{-1}$ and that of ZnO-CNFs at 800 °C is at 1600 cm$^{-1}$, shifted by 2 cm$^{-1}$. These peaks tell us that ZnO-CNFs are graphitic, with $sp^2$ hybridisation at this region. We also have Raman shift at 1340 cm$^{-1}$ for ZnO-CNFs deposited from 500 °C to 800 °C, which is a result of a diamond like carbon which has $sp^2$ and $sp^3$ hybridisation. The D-band characterizes the disorder in ZnO-CNFs. We observed that we have both $sp^2$ and $sp^3$ in our ZnO-CNFs, which is a result of disordered graphitic carbon. The strong and sharp Raman shift peaks of D-band and G-band are an indication that ZnO-CNFs are crystalline.

5.5. Hydrogen absorption/adsorption using ERDA method

The ERDA is the method that may be used for profiling hydrogen in samples using high energetic ion beams. ERDA involves the bombardment of the sample surface with energetic ion beams (e.g. He$^+$). There are many possible outcomes that might result from this process. These outcomes include emission of $\gamma$ – radiations or x – rays, ejection of recoil atoms as well as the presence of back – scattered atoms. This research work will focus only on recoil atoms. Recoil atoms are normally those with lower atomic mass compared to the projectile.
The recoiled atoms on the surface and near the surface will have high energy but less energy than the incident ion beam (He\(^+\)); therefore they are detected on the channels corresponding to high energy. The incident ion beam interacts with the atoms at the surface of the sample and loses its energy as it interacts with the bulk atoms. The recoiled atoms in the bulk (inside the sample) have lower energies, because the incident beam interacts with the surface atoms before them, so they are detected on the channels corresponding to lower energies. The beam energy for this study was set to 3 MeV, the tilt angle at \(-75\) °C, and 20 µC of total accumulated charge. A polyimide foil (C\(_{22}\)O\(_5\)H\(_{10}\)N\(_2\))\(_n\) (Figure 5.12.F standard material) was used as a thick hydrogen reference, due to its high concentration of hydrogen. Kepton is a stable compound; it can remain stable at a very wide range of temperatures from \(-273\) °C up to +400 °C.

Four different samples (ZnO-CNFS) were exposed to hydrogen at atmospheric pressure (101.325 kPa) and at the temperature of 300 °C (see Figure 5.5 for samples); the substrate was also studies for hydrogen absorption/adsorption. The samples were profiled for hydrogen using ERDA. Using other characterisation technique (EDS) we noted that, these samples deposited at different annealing temperatures have different yield of carbon. On the silicon wafer (substrate Figure 5.12.A) we observed a very small peak (normalised yield less than 1) at high energies; no peaks were observed at lower energies. We can conclude from this data that there was no hydrogen at the bulk, the very small peak observed was just hydrogen on the surface of silicon; there was no hydrogen sorption observed. The normalised yield represents an equalized yield for each process step, in that each step is assigned the same yield value. ZnO-CNFS annealed at 500 °C (Figure 5.12.C), the peak (normalised yield of about 30) at high energies was observed and lower energies there was no peak (normalised approaching zero) observed. The conclusion that can be drawn from this observation is that hydrogen is only detected mostly on the surface of the sample and nothing on the bulk. The EDS and XRD result show a high concentration of ZnO on ZnO-CNFS at this temperature, we suspect that ZnO is on the bulk of the sample and that is why hydrogen is not adsorbed in the bulk. ZnO NRs used in this work are not porous, which mean there will not absorb any hydrogen and the carbon at this temperature is mostly deposited on the surface of the ZnO NRs.
Figure 5.12: Hydrogen concentration profiling in ZnO-CNfs using the ERDA method, a polyimide foil (kepton) was used as a thick hydrogen reference, and silicon was the substrate for ZnO-CNfs.

When the temperature was increased to 600 °C (Figure 5.12.D), we observed that the peak is now spread from lower energies up to high energies, which tells us that hydrogen is now detected both at the surface and bulk, but the concentration is lower than that of the polyimide foil. The results obtain at the temperature 600 °C; shows us that ZnO-CNfs can be used for hydrogen sorption application. ZnO-CNfs at 700 °C (Figure 5.12.E), we observed a high hydrogen concentration profiling exceeding that of a standard at high energies (about 1 MeV up to 1.8 MeV); at lower energies (less than 1 MeV) it was less than the standard but very high compare to any other samples prepared at other temperatures. ZnO-CNfs at 800 °C (Figure 5.12.B) showed a huge drop on the hydrogen concentration profiling as it was only detected at the surface at a lower yield (normalised yield up to about 15) at lower energies the bulk the yield was almost zero. EDS and Raman results showed a very low carbon on this
sample. Raman showed a very high intensity of silicon which was the substrate, which shows that the substrate at this temperature was more exposed than other temperature and the D–band and G–bands were very small, which also tell us that there was little carbon. On the SEM images we observed that the catalyst ZnO NRs was melting which will be the other course for the decrease in the concentration of carbon which resulted in the decrease in the hydrogen concentration profiling.

5.6. Hydrogen storage and surface area measurements

Hydrogen storage measurements and surface area measurements were investigated based on the ERDA results. We wanted to know the surface area and how much hydrogen is absorbed/adsorbed in weight percentage (wt.%). ERDA results show high hydrogen sorption at the sample annealed at 700 °C; therefore we studied only these sample which shows promising results. The hydrogen adsorption/absorption isotherm at 77 K and at the pressure up to 1 bar was measured using the ASAP2020 HD analyser (micromeritics) instrument. Surface area was also investigated on an ASAP 2020 instrument using nitrogen gas and BET surface area was obtained from the linear region of nitrogen isotherm [10]. The ultra-high purity hydrogen and nitrogen gases (99.999%) were used to obtain the sorption isotherms. Adsorption isotherm is the relationship between the pressure and adsorption amount at a constant temperature. The horizontal axis is the relative pressure ($P/P_0$) which is the equilibrium pressure divided by the saturation pressure. The relative pressure can be 0 to 1 and $P/P_0 = 1.0$ means that the condensation of adsorptive occurs in the sample cell. So an adsorption isotherm is the measurement of adsorptive density which becomes higher than the bulk (gas) phase density due to the interaction between the adsorptive and solid surface atoms below its condensation pressure. Information on adsorption isotherm was obtained from reference [11]. The nitrogen adsorption isotherm at 77 K and a pressure up to 1 bar is shown by Figure 5.13 for a ZnO-CNFs sample annealed at 700 °C. The BET surface area determined from the sorption isotherm for ZnO sample was found to be 7.9 m².g⁻¹. The BET surface area obtain in this work is low compare to the BET surface area values obtain from the literature.
Figure 5.13: Nitrogen sorption isotherm at 77 K and at a pressure up to 1 bar for ZnO-CNFs sample annealed at 700 °C.

Figure 5.14: Hydrogen isotherm at 77 K and at the pressure up to 1 bar for ZnO-CNFs sample annealed at 700 °C.

The monolayer surface area for hydrogen is 85917 m².mol⁻¹ [12]. The maximum specific area for carbon is 1315 m².g⁻¹ (single-sided graphene sheet) and the maximum amount of hydrogen that can be adsorbed is 3 wt. % [12]. The hydrogen storage capacity of 1.1 wt.% for Zr-MOF at 77 K and pressure up to 1 bar and the BET surface area of 241 m².g⁻¹ was reported [13]. The hydrogen isotherm for ZnO-CNFs sample annealed at 700 °C is shown by
Figure 5.14. The hydrogen storage capacity is very low compared to that found in the literature as it was found to be 0.044 wt.% at 77 K and pressure up to 1 bar. The hydrogen storage capacity is directly proportional to the specific surface area (BET surface area) of the material at 77 K and pressure approximately 1 bar [14]. In order to increase the hydrogen uptake, the BET surface area of the material needs to be improved. In our case we use silicon wafer as a substrate in the synthesis of ZnO-CNFs; in most of the literatures consulted they use powder sample. The substrate used contributes to the mass of the sample during the analysis, this will have the effect on the results. Typically 0.1 – 0.3 g of the sample mass is required for the analysis; which in our case, >95% of the sample mass is the substrate; which makes the samples to be extremely small; this might be one of the reason the hydrogen storage capacity is extremely low. ERDA results are the one that can give us a better conclusion since they are not affected by the substrate.
5.7. References


The aim of this research work was to investigate hydrogen sorption in ZnO-CNFS. The first goal was to synthesise ZnO NPs at different deposition time to get different particle sizes, using direct current reactive magnetron sputtering. The second goal was to use ZnO NPs as the seeding for growing ZnO NRs using the hydrothermal process, to study the effect of seeding in the growth of ZnO NRs. The third goal was to grow ZnO-CNFS by chemical vapour deposition using ZnO NRs as the catalyst. ZnO-CNFS were characterised using SEM, XRD, EDS, and Raman spectroscopy and tested for hydrogen absorption/adsorption. Different particle sizes were observed from ZnO NPs, the particle sizes were directly proportional to the deposition time. The effect of seeding on the growth of ZnO NRs was observed. ZnO NRs grown on different seeding resulted in different diameters, length distribution and they were all vertically aligned. The crystal structures for ZnO NRs and ZnO NPs were found to be that of hexagonal wurtzite structure for both. ZnO NRs were more crystalline than ZnO NPs. The D–mode and the G–mode in ZnO-CNFS was observed. The D–mode by theory, is always observed in disordered graphitic carbon resulting in both \( sp^2 \) and \( sp^3 \) hybridisation. The G–mode by theory, correspond to graphitic carbon resulting in \( sp^2 \) hybridisation. From this observation we conclude that ZnO-CNFS are graphitic. The single crystalline structure of ZnO-CNFS was observed which almost correlate with the peaks of the catalyst. The structure of ZnO-CNFS was driven by the structure of ZnO NRs.

For hydrogen sorption (absorption/adsorption), the hydrogen concentration profiling method (ERDA) was used to test for hydrogen in the samples. ERDA is able to trace the hydrogen profile of the sample and we can tell whether is on the surface or the bulk. Hydrogen sorption was not observed on the silicon substrate. Hydrogen sorption (both surface and bulk) was possible on two samples prepared at 600 °C and 700 °C, sample at 700 °C with higher hydrogen content. The samples at 500 °C and 800 °C were only able to absorb (surface only) hydrogen, sample at 500 °C with higher hydrogen content. From results obtained we can be able to conclude that ZnO-CNFS can be used for hydrogen sorption (absorption/adsorption). We also observe the effect of annealing temperature on the hydrogen sorption, which allows us in future to focus only to the two temperatures which showed a high yield of hydrogen sorption. Further analysis was investigated using ASAP 2020 HD analyser; which allowed us to determine the BET surface area and hydrogen storage capacity. The hydrogen storage
capacity obtained was 0.044 wt.% for sample annealed at 700 °C at 77 K and pressure up to 1 bar and the BET surface area for the sample was 7.9 m².g⁻¹. It was observed that the sample mass is mostly the substrate which had a huge effect on our finding; we found ERDA result more reliable since the substrate has no effect on the analysis. The high hydrogen storage capacity reported was mostly on the powder samples, we wanted to take a different root and test hydrogen storage on the thin films and with our method we were able to control the growth direction and the morphology of ZnO-CNFs.