Synthesis and characterisation of ZnO-CNFs hybrid nanostructures for hydrogen storage applications

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Abstract. Zinc oxide carbon nanofibers hybrids (ZnO-CNFs) have been studied for hydrogen storage applications. Zinc Oxide nanoparticles (ZnO NPs) have been deposited using DC magnetron sputtering. We have then grown aligned ZnO nanorods (ZnO NRs) on the ZnO NPs, finally ZnO-CNFs synthesis have been carried out by chemical vapour deposition (CVD), using acetylene (C_2H_2) as a source of carbon. Elastic Recoil Detection Analysis (ERDA) results are presented and show that ZnO-CNFs are promising candidates for hydrogen storage. Results show that the temperature has an effect on the amount of hydrogen absorbed; at lower temperatures hydrogen is detected mostly on the surface and at higher temperatures hydrogen is detected on the surface and on the bulk which yield a higher hydrogen absorption/adsorption. SEM images show that ZnO-CNFs morphology depends on the growth temperature and is correlated to the ZnO NRs morphology.

Keywords: Hydrogen absorption/adsorption, ZnO-CNFs, ERDA, SEM, and EDS

1. Introduction

The world is facing a big challenge on finding the energy resources that are pollution free. Environmental concerns regarding the use of fossil fuels and their predicted exhaustion are globally important issues. The researchers have focus their studies on the energy resource that can replace fossil fuels, these energy resources should be environmental friendly, free of pollution and have high energy efficiency. Hydrogen is a leading candidate to eliminate petroleum dependence, associated air pollutants and greenhouse gases [1, 2]. Hydrogen can substitute fossil fuels in automobile applications, with additional benefit of potentially allowing the production of zero emission vehicles [2]. Hydrogen is the most abundant element in the universe constituting of about 75% of all baryonic mass and it can be found in different kind of materials [3]. Hydrogen can also be produce by splitting water, these process need energy. If hydrogen has to be used as the main source of energy in the world, it needs to be produced and be stored in high quantity. To store hydrogen we need a material that is light weight, safe, low cost and that will store high quantities of hydrogen in a little space. The goal is to pack hydrogen as closely as possible in order to achieve the highest volumetric density by using as little additional material as possible.

Most researchers have shown a higher interest in carbon nanostructured materials for hydrogen application, due to their porous structure. Carbon nanofibers (CNFs) are easily synthesised with different methods; CVD, electro spinning, polymer blend techniques and more other methods [3, 4, 7]. Hydrogen can be absorbed/adsorbed in CNFs in two ways; physisorption and chemisorption. In physisorption, hydrogen is absorbed and stored in the pores of CNFs by weak Van der Waal forces. In chemisorption, hydrogen is chemically bonded into carbon forming the weak covalent bonding. The morphology of CNFs is controlled by the substrate/catalyst which was grown onto. In this research work, vertically aligned ZnO NRs were used as the substrate to grow ZnO-CNFs, which could be used for hydrogen storage application.

There are three available onboard automobile hydrogen storage methods: (a) gas compressed to high pressures [1, 6] (b) the use of a cryogenic liquid at temperatures near to its boiling point (20.3 K) [1, 6] and (c) reversible metal and chemical hydrides [1, 6]. 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 [5, 6]. Hydrogen stored as metal and chemical hydrides adds significant weight, cost, and thermal complexity to onboard storage systems [6]. The presence of ZnO NRs in CNFs will alter the properties of CNFs and we believe it will enhance the hydrogen absorption. The method of hydrogen profiling (ERDA) shows that our ZnO-CNFs can absorb/adsorb hydrogen since hydrogen is detected in both bulk and the surface of the sample.

2. Experimental Procedure

2.1. Synthesis of ZnO nanoparticles

ZnO NPs were deposited on the silicon (111) wafer substrate using dc reactive magnetron sputtering (AJA Orion 5 sputtering system). Substrates were chemically washed. The deposition chamber was evacuated to a base pressure of 10^{-5} Torr by oil-diffusion-pump and turbo-pump combination. High purity (99.995%) argon and oxygen were used as sputtering and reactive gases. Zinc metal of 99.999% purity was used as sputtering target. The flow ratio of argon to oxygen was controlled at 2:1. The sputtering pressure, which is a total pressure of argon and oxygen, was set to 3×10^{-3} Torr. The sputtering power was set to 70 W. The sputtering time was varied from 15 minutes to 60 minutes. After each deposition the samples were annealed at a substrate temperature of 300 ºC for further oxidation. Annealing time and pressure was 60 minutes and 3×10^{-3}Torr. Zinc target was pre-sputtered in argon-oxygen atmosphere for 5 minutes to remove the surface oxide layer.

2.2. Synthesis of ZnO NRs

ZnO NRs were grown on ZnO NPs using the hydrothermal process [7]. The hydrothermal solution was prepared by dissolving $ZnCl_2$ on distilled water and hydrolysed with NH_3 (25%). Solution was transferred to autoclave bottles with silicon wafer vertically aligned. The autoclave bottles with substrates were put on the incubator, the temperature was set to 90 ºC. 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 suddenly after the required time to stop the process, then were washed with distilled water thoroughly to remove impurities on the surface of ZnO NRs and dried on the incubator for 5 minutes.

2.3. Synthesis of ZnO-CNFs

Chemical vapour deposition (CVD) was used for the nucleation of ZnO-CNFs using a dc reactive magnetron sputtering. High purity (99.995 %) of acetylene (C_2H_2) was used as the source of carbon. The flow rate of C_2H_2 was controlled at 10 sccm. Substrate temperature was varied from 500 ºC to 800 ºC to investigate the effect of temperature on the nucleation of ZnO-CNFs. ZnO NRs were used as a catalyst aligned and to control the morphology of ZnO-CNFs. CVD pressure was kept at 3 ×

10^{-3} Torr and time was kept at 40 minutes for all the samples.

3. Results and Discussions

3.1. ZnO NPs analysis

Figure 1a-c shows SEM images of ZnO NPs deposited at 15 minutes, 30 minutes, and 60 minutes respectively. The average diameter of the particles sizes increases from 6.73 – 37.60 nm, at 15 minutes the average size was 6.73 nm, at 30 minutes it was 16.71 nm, and at 60 minutes the average diameter was measured to be 37.60 nm. It was observed that, as the deposition time changes, the colour of the film change. The change in the colour of the sample can allow us to use these ZnO NPs for other application i.e as a decorating coatings but on this work are used as seeding for ZnO NRs.

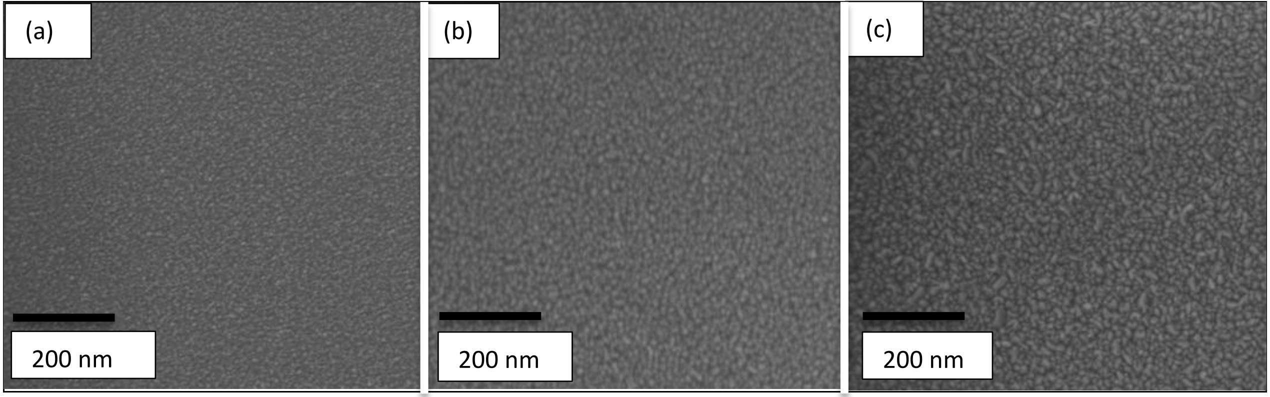

Figure 1: SEM images of ZnO NPs grown at different deposition time.

3.2. ZnO NRs analysis

Since ZnO NPs were used as a seeding for the growth of ZnO NRs, the effect of ZnO NPs on the synthesis of ZnO NRs was investigated.

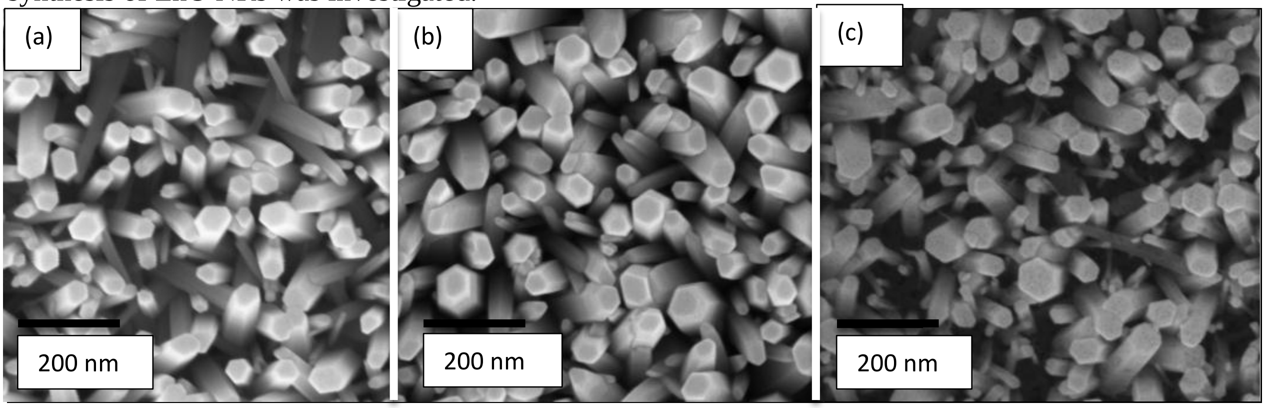

Figure 2: SEM images showing the effect of ZnO NPs grown at different deposition times on the growth of ZnO NRs. (a) 15 min, (b) 30 min and (c) 60 min.

Figure 2 shows the SEM images of ZnO NRs, that were synthesised at ZnO NPs sputtered at different deposition times. ZnO NRs were all synthesised for 2 hours at different seeding of NPs. Figure 2a shows SEM image of NRs grown on 15 minutes sputtered ZnO NPs, their average diameter and the length of these NRs were found to be 60.34 nm and 129.72 nm respectively. Figure 2b shows the NRs of 30 minutes sputtered NPs and their average diameter and length was found to be 75.40 nm and 105.90 nm respectively. Figure 2c show ZnO NRs of 60 minutes sputtered NPs, their average diameter and length was measured to be 90.31 nm and 114.05 nm respectively. The result show that the diameter of NRs increases with the increase in particles size of NPs.

3.3. Analysis of ZnO-CNFs

The effect of temperature on the nucleation of ZnO-CNFs was investigated using SEM imaging and EDS to study the chemical composition. Figure 3 show SEM images of ZnO-CNFs deposited at 500 ºC, 600 ºC, 700 ºC, and 800 ºC. Figure 3a shows that ZnO-CNFs take the morphology of ZnO NRs; only small amount of carbon is formed on the surface of NRs, this is confirmed by EDS result as shown in table 1.

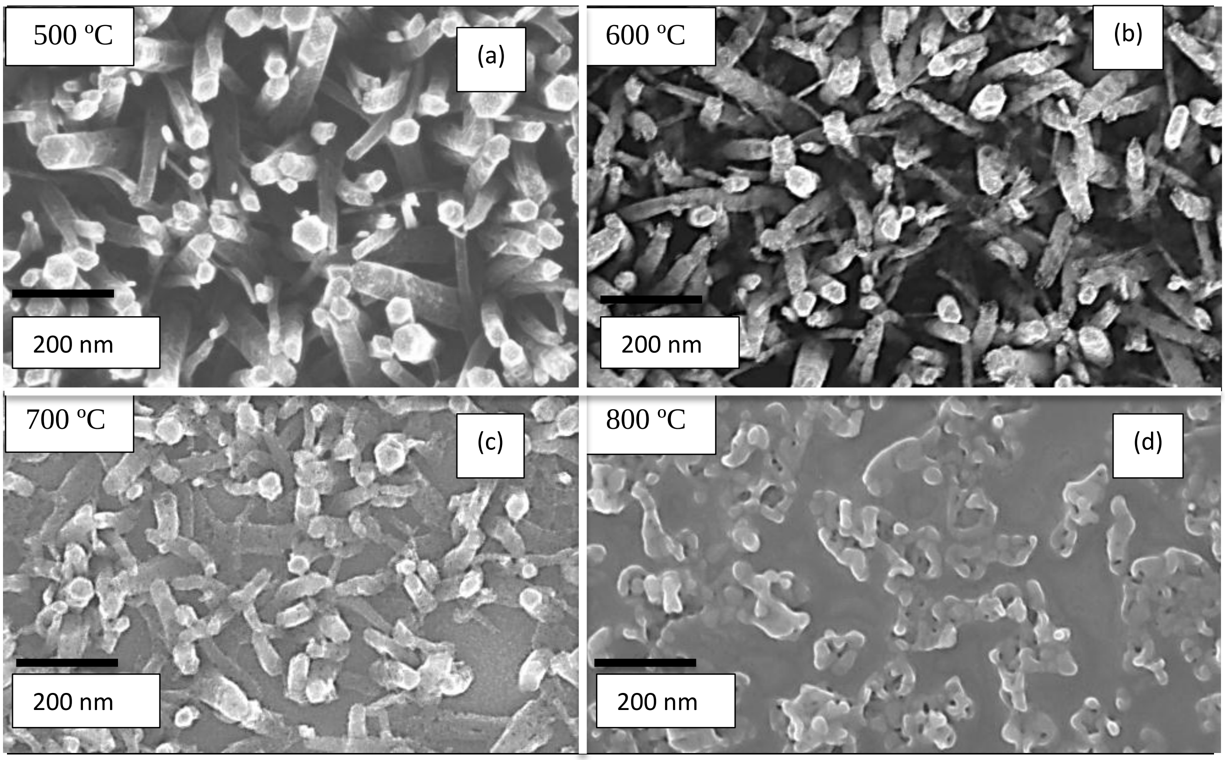

Figure 3: SEM images of ZnO-CNFs synthesised at different temperatures.

Figure 3b & 3c shows that when the temperature is increased (600 ºC & 700 ºC respectively), the hexagonal structure of ZnO NRs is lost and ZnO-CNFs take the shape of NRs. Figure 3d shows that at high temperatures ZnO-CNFs meltdown and loses the aligned morphology. EDS result show that carbon concentration increase with the increase in temperature (500 ºC-700 ºC) see table 1. At high temperatures (800 ºC+) the content of carbon drops and Zinc and oxygen content increases. The process of CVD involve braking down of C_2H_2 into C* and H*. H* will be attracted to oxygen of ZnO NRs, to form $H_2O_{(g)}$ causing vacancies on the NRs and $H_2O_{(g)}$ is pumped out the system. C* will grow on that vacancies forming a weak covalent bonding with Zn (temporal bonding), as the concentration of C increases on the system C-C bonds are formed which are very strong covalent bonding. Zinc melts at 419.5 ºC; hence when it loses it bonds (with oxygen, and with carbon) it will start to melt, living carbon building in the NRs taking the morphology of ZnO nanorods. As the temperature increases the reaction rate also increases, up until the process will be faster; hence Zn melts before C-C bond is form. CNFs need a catalyst to grow, thus the morphology of CNFs is controlled by a catalyst used. On figure 3d, ZnO-CNFs do not have a perfect morphology because the catalyst was melting down and it followed that structure.

Table 1: EDS table of Result, showing chemical composition in atomic %.

Elements	ZnO NP At. %	ZnO NR At. %	ZnO-CNFs 500 ºC At. %	ZnO-CNFs 600 ºC At. %	ZnO-CNFs 700 ºC At. %	ZnO-CNFs 800 ºC At. %
C			31.29	75.16	84.21	35.11
O	59.74	66.76	45.84	20.74	14.75	63.23
Zn	40.26	33.24	22.87	4.10	1.04	1.66

ERDA method was used to study hydrogen adsorption/absorption on the samples. Samples were named as following; S9 deposited at 700 ºC, Ze deposited at 600 ºC, S8 deposited at 500 ºC, and silicon wafer which is the substrate.

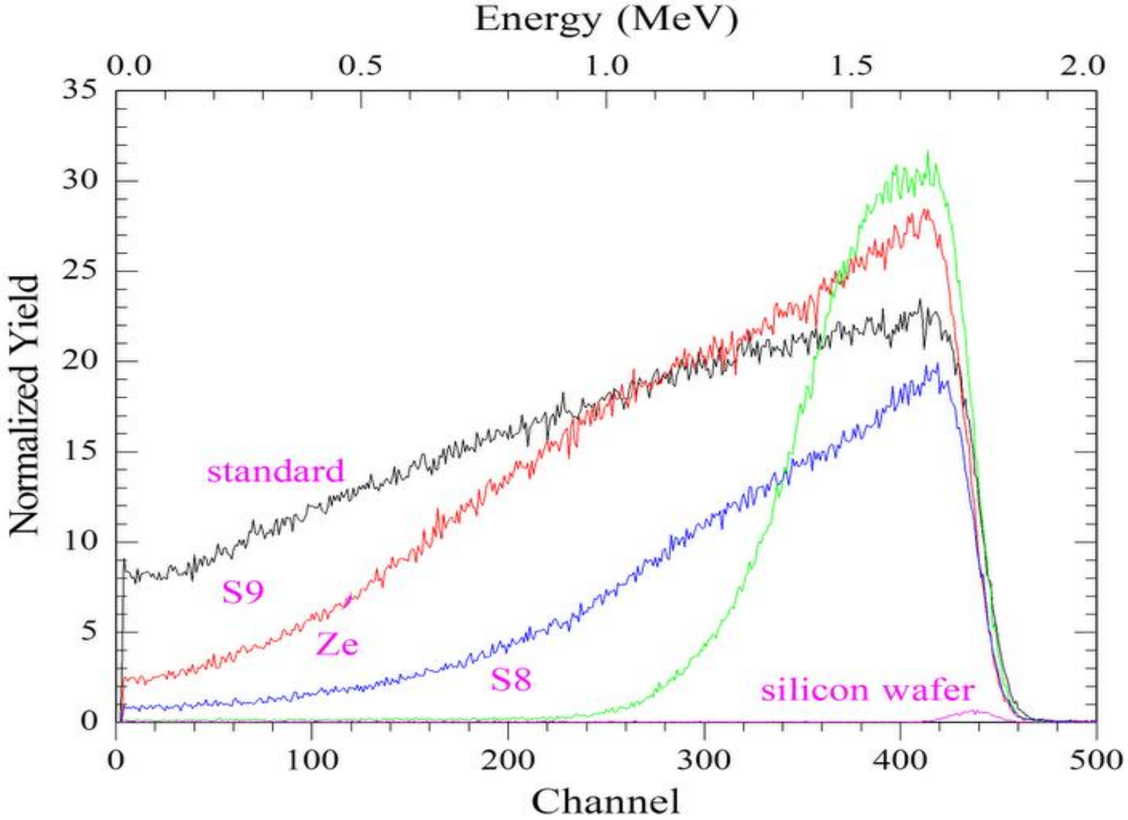

Figure 4: ERDA result, showing hydrogen absorption/adsorption.

The samples were compared to a standard material (kapton), a stable polyimide which has a very high concentration of hydrogen. In kapton hydrogen was detected in the bulk and also on the surface, on silicon wafer it was only detected on the surface. In the sample prepared at lower temperature (500 ºC), hydrogen was detected mostly at the surface figure 4 (sample S8). The reason hydrogen is detected on the surface is because carbon was only formed on the surface of the ZnO NR see figure 3a and table 1. As the temperature increases, we started to detect hydrogen on the surface and in the bulk (figure 4 sample Ze deposited at 600 ºC), since we still have more content on ZnO we still detect less amount of hydrogen. At 700 ºC we start to detect more hydrogen on the surface and in the bulk sample S9 figure 4, these is due to the increase of carbon content on the sample, since we have 84.21 At.% of carbon. These tell us that by increasing the content of carbon on the sample the content of hydrogen increases, since it was absorbed /adsorbed by carbon only not by ZnO NRs.

4. Conclusion

ZnO NRs were grown ZnO NPs sputtered at different deposition time on silicon wafer substrate. Using SEM, it was shown that the size of ZnO nanoparticles increases with the increase of the deposition time and ZnO NRs growth depends on particles size of ZnO NPs. ZnO NPs also shows an interesting properties of changing colour with the change in time, which can be used to use them as a decorating coatings. SEM result showed that ZnO-CNFs morphology was controlled by ZnO NRs. Using ERDA it was determine that ZnO-CNFs have high absorption/adsorption of hydrogen at temperatures around 700 ºC than lower temperature around 500 ºC.

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