Growth and characterization of carbon nanotubes on ZrN thin film surfaces

T G Nyawo[1] and O M Ndwandwe[1]

[1]Department of Physics and Engineering, University of Zululand, Private Bag X1001,
KwaDlangezwa, 3886, South Africa.

Email: tgnyawo@gmail.com

ABSTRACT In this study catalyst of Fe nanoparticles of different sizes have been sputter deposited on Al_2O_3, ZrN thin film surfaces at different values of pressure so as to vary their sizes. Carbon nanotubes (CNTs) have then been grown on ZrN by Chemical Vapour Deposition (CVD) using acetylene as a source of carbon. The growth of CNTs on ZrN has been compared to their growth on Al_2O_3. It has been found that it is easier to grow CNTs on Al_2O_3 than on ZrN under the same conditions. Various methods of promoting CNT growth on ZrN have been investigated. The resulting nanostructures have been characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Rutherford Backscattering Spectrometry (RBS). Such structures may find potential use in field emission displays and gas sensors.

1. Introduction

Materials that may be used as field emitters in a field emission display must have unique properties. Some of these properties are chemical inertness, high electrical conductivity, high melting point and a high aspect ratio. Carbon nanotubes have been studied extensively in the past and are being considered for the next-generation of materials to be used in cold cathode devices [1 – 4]. Various methods have been employed to grow carbon nanotubes. These include arc-discharge, laser vaporization and Chemical Vapour Deposition (CVD) [5]. CVD is the most convenient method from which it is easy to obtain good quality CNTs on a large scale if appropriate growth conditions are chosen [6]. The interest in ZrN films stems from their excellent physical and chemical properties. ZrN films are well known for their high hardness, high melting point and good resistance to corrosion [7]. ZrN is a good reflector of radiation in the IR region of the electromagnetic spectrum and has thus been used for thermal insulation purposes [8].

In this paper we report on the growth and characterization of CNTs on sputter deposited ZrN films and compares these results to CNTs grown on Al_2O_3. We also introduce various methods that may be used to promote growth of CNTs on the surface of ZrN films. We could not find any previous work where an attempt has been made to grow CNTs on ZrN films despite the obvious practical applications of such structures.

2. Experimental procedure

Silicon wafers were chemically cleaned using methanol, followed by acetone, then trichloroethylene, then acetone, and finally methanol. These were then rinsed in distilled water.

In order to deposit ZrN, silicon wafers that had been cleaned were dried and loaded in AJA's Orion 5 Sputtering System and the chamber evacuated to a chamber pressure of better than 4 x10^{-7} Torr. The sputtering target used for the deposition of ZrN was a disk of 2 inch diameter and 0.250 inch thickness made of high purity (99.5%) Zr metal. Argon was used as a process (sputtering) gas. Nitrogen was introduced to act as a reactive gas so as to form ZrN. The flow rate of argon was varied between 6 sccm and 10 sccm. Nitrogen flow rate for the deposition of ZrN was varied between 2 sccm and 4 sccm to obtain the desired Zr:N ratio. Deposition of ZrN was done for time periods varying from 1 hour to 2 hours. All ZrN depositions were done at room temperature. The sample was rotated so as to obtain a film of uniform thickness. The target to sample distance was kept at 34 cm. DC magnetron sputtering was used to deposit the films. The power on the magnetron(s) during all depositions was 200 W. To obtain Al_2O_3, Al was sputter deposited in an oxygen atmosphere. Magnetron power used was 100 W and the duration of the deposition was 30 minutes.

3. Results and discussion

In order to find layer thicknesses of deposited films we used Rutherford Backscattering Spectrometry (RBS). Figure 1 shows RBS spectra of ZrN films deposited using DC sputtering at a magnetron power of 200 W for 1 hour 30 minutes at a chamber pressure of 3x10^{-3} Torr using gas flow rates of 10 sccm for argon and 3 sccm for nitrogen. Argon was used as a process gas in order to sputter Zr atoms from a Zr target and nitrogen was introduced as a reactive gas, let in, in the vicinity of the silicon substrate onto which Zr ions were deposited. We describe this sample on figure 1 as not oxidized. We then deposited a second sample under the same conditions. The second sample was deliberately oxidized for 20 minutes in a chamber evacuated to a pressure of 3x10^{-3} Torr in oxygen that was flowing at 2 sccm at a temperature of 200 ^{o}C. Spectra in figure 1 were obtained by scattering alpha particles of energy 3.05 MeV on the surface of the sample. At this energy the yield obtained from the scattering of alpha particles from oxygen is enhanced because of a higher scattering cross-section. We call this effect the oxygen resonance. This enables us to follow even small changes in the level of oxidation of the sample.

3.1 RBS results

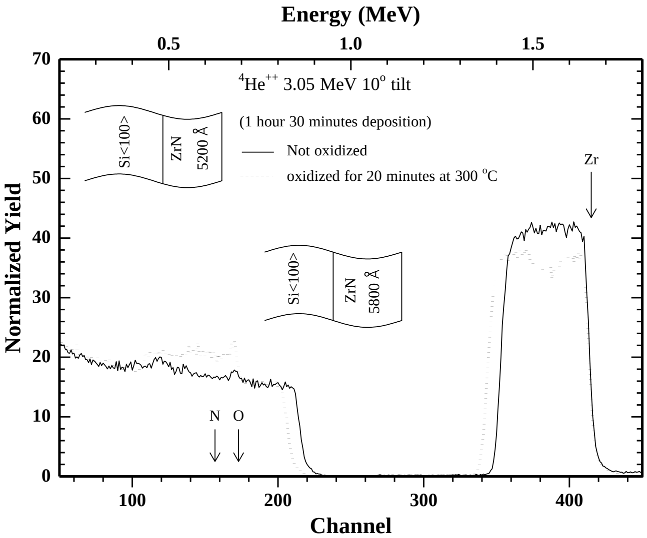


Figure 1: RBS spectra of sputter deposited ZrN samples. The sample labeled 'not oxidized' was sputter deposited without letting in any oxygen into the chamber. The other sample was deposited similarly but was afterwards annealed at 200 ^{o}C for 20 minutes in flowing oxygen.

We simulated the RBS spectrum shown as 'not oxidized' in Figure 1 using RUMP [9] and found that the thickness of the film is 5 200 Å. The oxidized film was found to have a thickness of 5 800 Å. The spectrum shows clearly that the oxidized sample has more oxygen when compared to the unoxidized sample. Our aim was not to find the exact amounts of oxygen in the samples, but rather to have a comparison. Such a comparison, was hoped, would give us an answer whether it is easier to grow CNTs on an oxidized ZrN surface or not.

To grow CNTs on the surface of the ZrN film we first deposited Fe nanoparticles on the film using unbalanced DC magnetron sputtering. In order to obtain Fe nanoparticles of different sizes, we varied the pressure inside the chamber while keeping other variables constant. The argon flow rate was 8 sccm, magnetron power was 130 W, while the duration of the deposition was 2 minutes. We then used an Atomic Force Microscope (AFM) to characterize the nanoparticles of Fe. Figure 2 shows the AFM results for a sample where Fe was deposited for two minutes, using magnetron power of 130 W at a pressure of $9x10^{-3}$ Torr. Samples where Fe nanoparticles were deposited at various pressures showed that both density and size of the nanoparticles depend on pressure.

3.2 AFM results

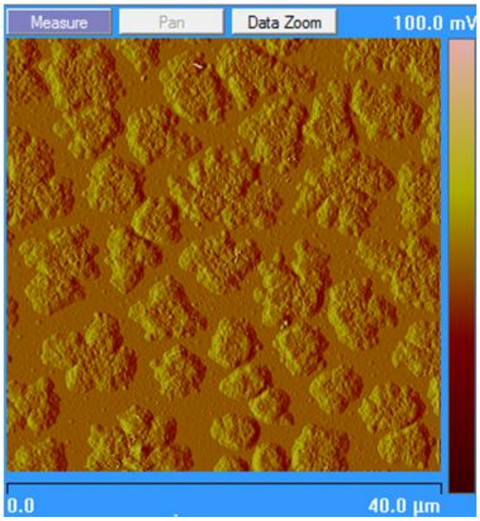


Figure 2 (S4): AFM image of Fe nanoparticles deposited on a silicon substrate by DC magnetron sputter deposition at a power of 130 W at a argon flow rate of 8 sccm and a chamber pressure of $9\text{x}10^{-3}$ Torr for a duration of 2 minutes.

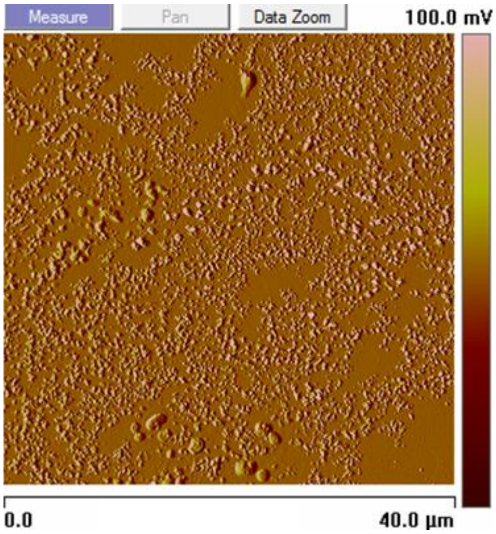


Figure 3: AFM image of Fe nanoparticles deposited on a silicon substrate by DC magnetron sputter deposition at a power of 130 W at a argon flow rate of 8 sccm and a chamber pressure of $1.5\text{x}10^{-2}$ Torr for a duration of 2 minutes.

Figure 3 is an AFM image showing Fe nanoparticles that were deposited at a pressure of $1.5\text{x}10^{-2}$ Torr at magnetron power of 130 W using an argon flow rate of 8 sccm for a duration of 2 minutes. All Fe depositions were done at room temperature. It is seen that the Fe particles in figure 3 are smaller than those in figure 2. We then set out to measure the size of the Fe particles in figure 3. To measure the linear density of particles we drew a straight line (sectioning) as shown in figure 4. We then counted the number of peaks on this line over a distance of 8 μm. We found 9 peaks and calculated the linear density to be 1.12 peaks per μm. Measuring linear density many times in different directions showed that the average linear density for Fe particles deposited at $1.5\text{x}10^{-2}$ Torr is 1.1 peaks per μm.

Figure 5 is an AFM image of Fe nanoparticles deposited at a chamber pressure of $1.5\text{x}10^{-2}$ Torr using unbalanced DC magnetron sputtering at a power of 130 W for a duration of 2 minutes. Peaks were chosen and their vertical heights measured (see red line). The height of the particle marked red on the image in figure 5 was found to be 40.6 nm while its diameter was found to be about 1.1 μm. The average diameter taken over 30 particles was found to be close to 0.44 μm.

We repeated the process of measuring linear density and diameter for Fe particles deposited at a pressure of $9\text{x}10^{-3}$ Torr. The summary for all such AFM measurements is given in table 1.

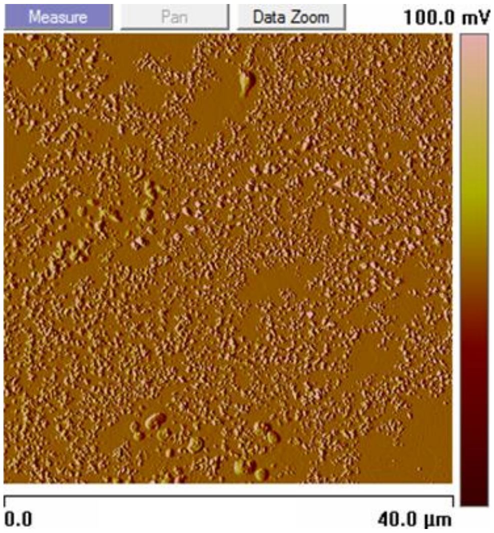
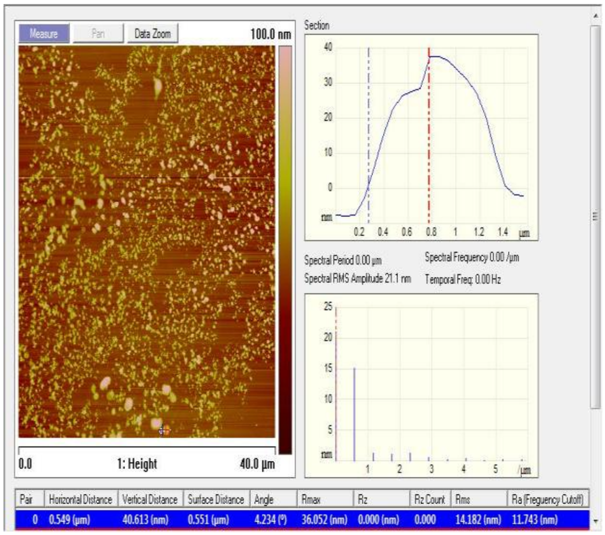


Figure 4: (linear peak density): This shows a calculation of linear density of the peaks. The number of peaks on a length of 8 μm is shown to be 9 or 1,12 peaks per μm. Drawing such lines in different directions gives linear density along those directions. The average linear density of peaks may then be calculated.



Spectral Period 0.00 µm
Spectral Frequency 0.00 /µm
Spectral RMS Amplitude 21.1 nm
Temporal Freq: 0.00 Hz

Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)
0	0.549 (µm)	40.613 (nm)	0.551 (µm)	4.234 (°)	36.052 (nm)	0.000 (nm)	0.000	14.182 (nm)	11.743 (nm)

Figure 5: AFM image (Fe on ZrN) of a sample prepared at a chamber pressure of 1.5×10^{-2} Torr. The distance between the blue and red lines on the image on the left have been placed on top of a particle so as to measure its diameter. The peak is shown on the top right and its diameter has been found to be 1.19 μm and the vertical height has been found to be 40.6 nm.

Table 1: A summary of AFM results giving both average linear density and average particle diameters at different pressures.

Chamber Pressure	Average height	Average linear density	Average diameter
9×10^{-3} Torr	28.08 nm	0.46 peaks/μm	4.46 μm
1.5×10^{-2} Torr	24.28 nm	1.1 peaks/μm	0.44 μm

3.3 SEM results

Many attempts were made to grow CNTs on the surface of ZrN, but most failed. We then put a ZrN film on an Si substrate sample together with an Al_2O_3 on Si sample in the same chamber in order to find out whether there is any effect of the substrate on the growth of CNTs (under the same growth conditions). We then deposited Fe nanoparticles on the surface of both samples. The AFM results are shown in figure 4 and figure 5. We then raised the temperature to 700 ^{o}C and let in C_2H_2 so as to grow the CNTs on the surface of the samples (without breaking vacuum). Figure 6 is an SEM image of CNTs grown on Al_2O_3. We could find only a few CNTs on the surface of the ZrN film that had been put together with the Al_2O_3 film in the same chamber (SEM images of ZrN film after attempts to grow CNTs are shown in figure 7). These images show clearly that it is much easier to grow CNTs on the surface of Al_2O_3 compared to growing them on the surface of ZrN under the same conditions. We do not yet understand why there is such a difference between the two surfaces.

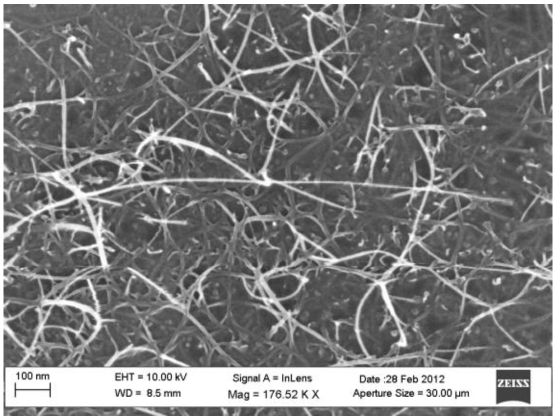


Figure 6: Carbon nanotubes grown on the surface of Al_2O_3 on silicon. Nano-Fe particles had been deposited on the Al_2O_3 surface to act as catalysts for the CNT growth.

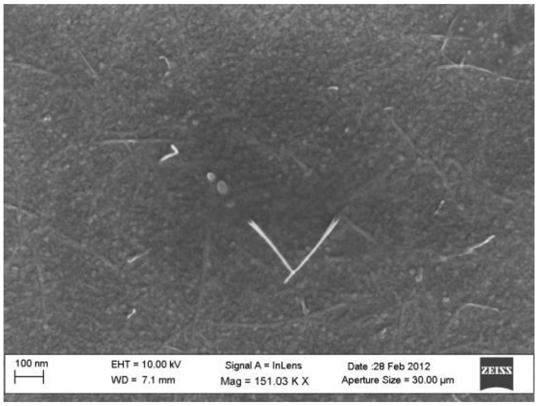


Figure 7: CNTs on the surface of a ZrN film on Si. The same amount of catalyst Fe was deposited on this ZrN as in the Al_2O_3 film shown in Figure 6. There however seem to be more CNTs on the Al_2O_3 film when compared to those on the ZrN film.

In order to increase the density of CNTs we oxidized the ZrN film slightly by raising the temperature to 200 ^{o}C, bleeding in oxygen into the chamber after deposition of ZrN, and keeping the sample in the chamber for 20 minutes. The chamber pressure was kept at $3x10^{-3}$ Torr during the oxidation process. The SEM image shown in figure 8 shows that oxidizing the surface of the ZrN film slightly promotes the growth of CNTs. Repeating the same experiment several times conclusively convinced us that it is easier to grow CNTs on oxidized ZrN films when compared to growing them on unoxidized ZrN films. Figure 1 compares RBS data of an oxidized film at the oxygen resonance energy of 3.05 MeV using alpha particles to that of an unoxidized film. Figure 8 is an SEM image of the surface of the oxidized film after CNTs had been grown on it. Compare figure 8 to the case where the ZrN surface has not been oxidized, figure 7.

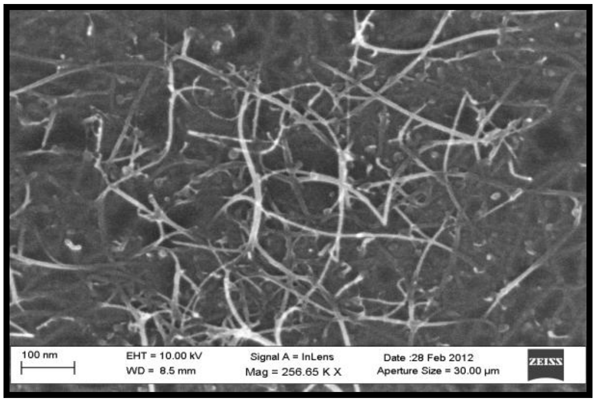


Figure 8: SEM image of the surface of an oxidized ZrN surface. The conditions under which these CNTs were grown are the same as those used when growing those shown in Figure 7. The only difference is that the surface of the ZrN film in Figure 7 was not oxidized.

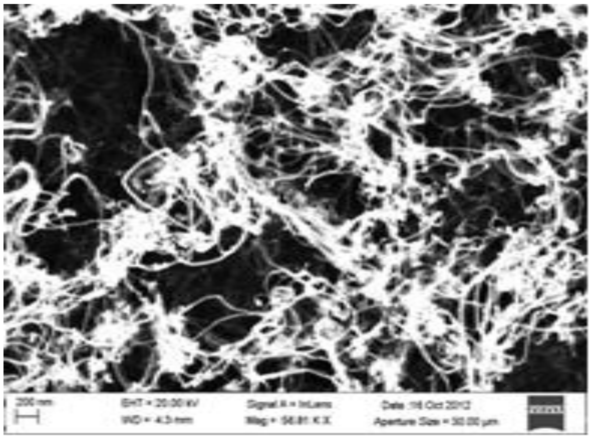


Figure 9: This SEM image shows CNTs on the surface of a ZrN surface. No attempt was made to oxidize the ZrN film. The CNTs were grown in a chamber kept at $3x10^{-3}$ Torr in the present of water vapour. The conditions under which these CNTs were grown are the same as those used when growing those shown in **Figure 7**.

Figure 9 shows an SEM image of CNTs obtained on the surface of ZrN using C_2H_2 as a source for carbon at a temperature of 700 ^oC and by introducing water vapour in the chamber in which the CNTs were grown. The water vapour seem to promote the growth of CNTs. Comparing the image in figure 9 to that of figure 7 shows that it is possible to increase the number of CNTs by introducing water vapour in the chamber. Figure 7 shows a situation where there was no deliberate introduction of water vapour.

4. Conclusion.

In this work ZrN thin films have been deposited on silicon substrates. Several attempts to grow CNTs on these surfaces showed that it is not easy to grow them on ZrN surfaces. CNTs were then grown on Al_2O_3 surfaces to test whether the conditions for the growth of CNTs were suitable. Placing both types of surfaces (ZrN and Al_2O_3) in the same chamber enabled us to compare the effect of these two surfaces on the growth of CNTs under the same conditions. The results obtained showed clearly that CNTs grow much more readily on the surface of Al_2O_3 compared to that of ZrN.

An attempt was then made to enhance the growth of CNTs on ZrN. First, the surface of the ZrN film was oxidized and the extent of its oxidation compared to that of a sample which had not been deliberately oxidized using resonant alpha scattering at an energy of 3.05 MeV. At this particular energy the scattering cross section of alphas on oxygen is larger compared to other scattering energies making it easier to compare the extent of oxidation in the two films. It was found that CNTs grow easily on the oxidized ZrN film when compared to the film that had not been oxidized. Oxidation of the ZrN surface therefore enhances the growth of CNTs on it. The growth of CNTs on the surface of ZrN was found to have been enhanced by the existence of moisture inside the chamber. Moisture (water vapour) has been found to increase the growth of CNTs on ZrN.

Future work

We would like not only to increase the number of CNTs on the surface of ZrN, but must grow them such that they are vertically oriented in order to make a viable field emitter. The process still need fine tuning by measuring the optimal amount of moisture for CNT growth as well as an optimal oxidation level.

Acknowledgements:
We thank the (SA) National Research Foundation for financial assistance through the Local Equipment Travel/Training & Synchrotron Grant UID No. 80465 of April 2012. We also thank iThemba LABS for their hospitality and the use of their Ion Beam Analysis equipment. Assistance from the University of Zululand Research Committee through Grant S67/93 of 2012 and 2013 is acknowledged.

References:

[1] Sung Mi Jung, Hyun Young Jung, Jung Sang Suh, Carbon 46(2008)1973-1977.

[2] Zhu L, Sun Y, Hess D W, C.P. Wong, Nano Letters 6(2) (2006)243-247.

[3] Wang Q H, Setlur A A, Laurenhaas J M, Dai J Y, Seeling E W, Chang R P H, Applied Physics Letters 72(22) (1998)2912-2913.

[4] der Heer W A, Chatelain A, Urgate D, Science (239)(1995)1179-1180.

[5] Choi W S, Choi S H, Hong B, Lim D G, Yang K J, Lee J H, Materials Science and Engineering, C26(2006)1211-1214.

[6] Bertoni G, Cepek C, Romanato F, Casari F C S, Bassi S A L, Bottani C E, Sanchrotti M, 42(2004)423-460.

[7] Lamni R, Martinez E, Springer S G, Sanjines R, Schmid R P E, Levy F, Thin Solid Films, 447-448(2004)316-321.

[8] Pichon L, Girardeau T, Straboni A, Lignou F, Guerin F P, Perriere J, Applied Surface Science 150(1999)115-124.