Novel Branched Nanostructures of Carbon Nanotubes on Si Substrates Suitable for the Realization of Gas Sensors

Y. Abdi, S. Mohajerzadeh, M.H. Sohrabi, M. Fathipour and M. Araghchini

Nano-Electronic Center of Excellence
Thin film Lab. and Nanoelectronic lab, ECE Department,
University of Tehran, Tehran, Iran, Email: mohajer@ut.ac.ir

ABSTRACT

A novel tree-like nanostructure of carbon nanotubes is reported through the multi-stage growth of vertically aligned nanotubes. The growth of branched structures is feasible by means of a hydrogenation treatment of already grown carbon nanotubes on silicon substrates. Subsequent growth of CNTs would lead to the evolution of tree-like nano-structures. Such branched nano-structures are useful for the formation of gas sensors as well as field emission devices and displays.

Keywords: hydrogenation, carbon nanotubes, nickel seed, tree-like, vertical growth.

1 INTRODUCTION

Carbon nanotubes are of great importance due to their exceptional electrical and mechanical properties. Such one dimensional structures have been considered as promising candidates for ballistic field effect transistor fabrication, gas sensors, field emission devices and displays and also as additive for improving the mechanical properties of polymers and cements. They can be used as sharp tips for AFM applications as well as for nano-writing and nano-lithography [1-2].

The growth of carbon nanotube has been feasible using a variety of techniques among which one can identify chemical vapor deposition and specially, plasma enhanced chemical vapor deposition as one of the most promising methods to realize electronic-grade structures. The presence of plasma during the growth, not only lowers the processing temperature, it also leads to a vertical alignment of CNTs which can be further used for the formation of composite structures using an oxide or polymer matrix.

In this paper we report a new structure in which the growth of carbon nanotubes is achieved on top of already grown CNTs. The initial growth happens on (100) silicon substrate whereas the subsequent growth is achieved on top of the vertically grown nanotubes, using the trapped nickel at the top side of CNTs as the seed for the second and third growth. Scanning electron microscopy has been widely employed to study the growth. Also a preliminary sensing element for oxygen has been realized. Apart from gas sensing elements, the newly presented nano-structures can find applications for the formation of nano-actuators and motors where the branched structure assimilates the rotating element of the nano-metric system.

2 EXPERIMENTAL

The fabrication of branched structures started with the deposition of 5-8 nm thickness of Ni layer by e-beam evaporation system onto a (100) silicon substrate with a P-type doping of $1X10^{15}$ cm^{-3}. Ni was used as a catalyst of growth and can be patterned using standard photo-lithography. If features smaller than 0.5µm are needed standard optical lithography cannot be exploited. To achieve such features we have developed a hydrogenation assisted nano-island formation where small clusters of nanotubes can be formed with no need to a nanolithography technique [3].

As the second step, vertical nanotubes were grown using plasma enhanced chemical vapor deposition (PECVD) on Si wafers. This process was carried out at the temperature of 650ºC and at a pressure of 1.6 torr of acetylene/hydrogen gases. The ratio of acetylene/hydrogen flows during the process was kept at 1 to 4. Well-aligned nanotubes with a diameter of 50 to 150 nm are regularly obtained. Most recently we have been able to achieve nanotubes with diameters below 10nm using a reduced plasma power during the hydrogenation step and by increasing the hydrogen percentage during the growth of CNTs in the C_2H_2/H_2 mixture.

In Figure 1 we have collected some of the SEM images of the samples prepared for this study. Parts (a) and (b) of Fig. 1 depict two of the scanning electron microscope images of the patterned and grown nanotubes on Si with desired features. The evolution of a circular ring as seen in part (a) of this image is a result of direct photo-lithography of a small round and solid spot of nickel as the seed for the growth of CNTs and a proper hydrogenation to hollow out the circle and to form a ring. To obtain the image of Fig.(1.b), we have used a back-scattering mode of SEM imaging. As shown in this image, Ni particles are placed on top of nanotubes, as expected from a tip-growth mechanism. The idea of the growth of branched-nanostructures originates from using such Ni particles for the subsequent growth of CNT branches on top of the original nanotubes. The process flow is schematically shown in Figure2. Hydrogen plasma was used to create small Ni nano-particles on tip of nanotubes. To protect the nanotubes, they were coated by TiO_2 layer. Deposition of TiO_2 was carried out in CVD reactor in presence of oxygen gas and $TiCl_4$ vapor at a temperature of 220ºC and at atmospheric pressure.

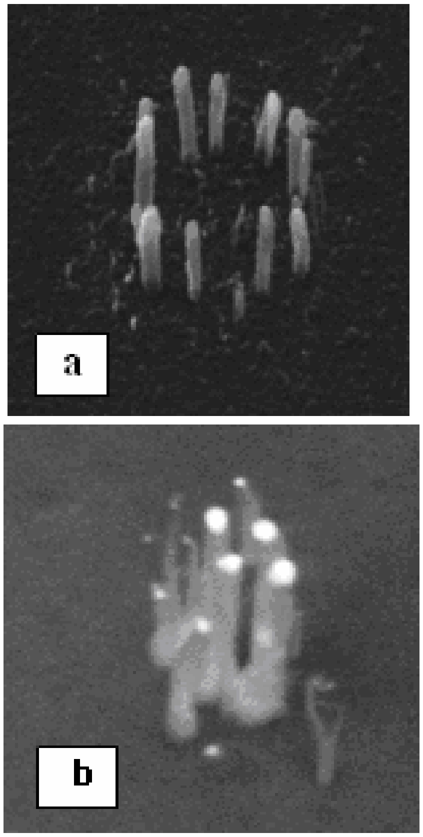


Figure 1: A collection of various CNTs grown on Si substrate patterned prior to the growth. (a) Circular growth, (b) a small cluster of CNTs where its image indicate the presence of Ni at the tip side.

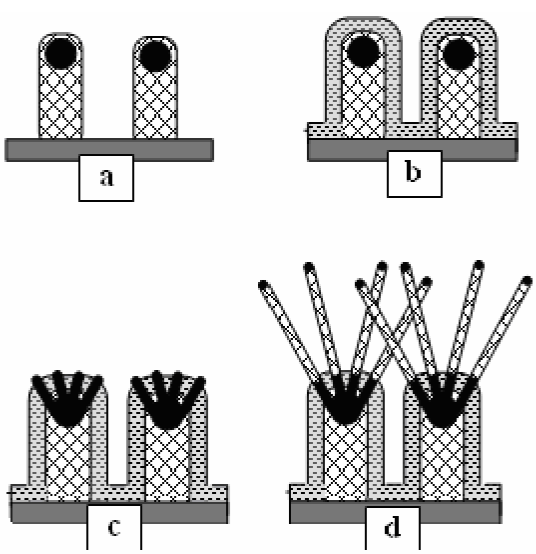


Figure 2: The evolution of branched structure from vertically aligned carbon nanotubes (a). Coating with titanium oxide (b), hydrogenation bombardment (c) and the subsequent growth (d).

TiO_2-coated nanotubes were placed in the PECVD reactor and at a temperature of 650ºC and a plasma power density of 5.5 W/cm^2, the hydrogenation processing of the sample has been carried out. The pressure of the chamber was kept at 1.5 torr during the hydrogenation step. After 15 minutes of hydrogenation, the tip side of nanotubes is expanded and small particles of Ni appear. These Ni nano-particles act as catalyst seed for the growth of secondary nanotubes on original structures. The hydrogenated samples were immediately exposed to the acetylene gas in the same reactor and the growth of branches on nanotubes was achieved.

3 RESULTS AND DISCUSSION

Figure 3 demonstrates the SEM results of the process which was schematically presented in the previous section as a step by step manner. Parts (a) and (b) of this figure correspond to the growth of individually placed nanotubes before and after coating with the TiO_2 layer. Part (c) of this figure shows the TiO_2-coated nanotube after hydrogen bombardment. As shown in this part, Ni catalyst comes out through the titanium-oxide layer. Part (d) shows an image of the nanotubes after subsequent growth has been accomplished.

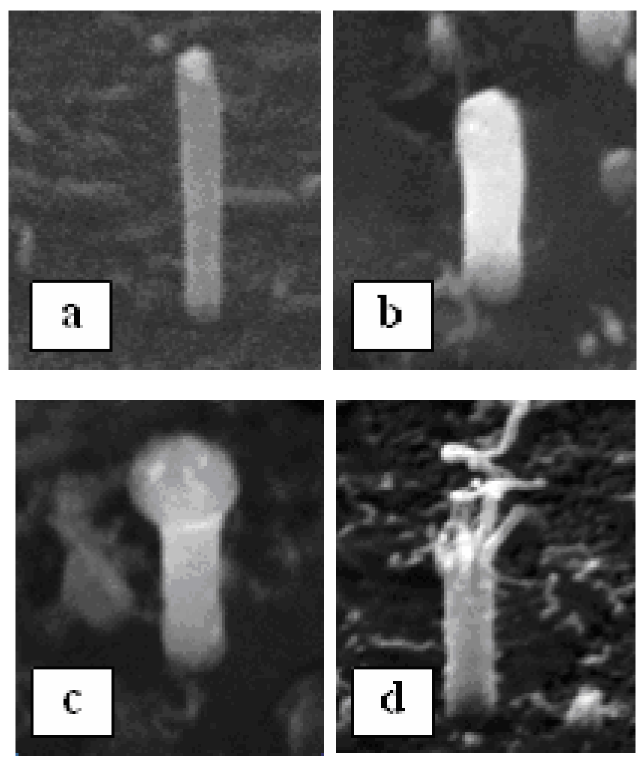


Figure 3: (a) Individually placed CNTs on Si, (b) coated with TiO2, (c) hydrogenation of the specimen leading to an expansion of the tip side and (d) the growth of a second growth.

Because the size of newly evolved nickel spots is much smaller than the original seeds, the secondary nanotubes with smaller diameters can be grown on top of initial nanotube, as shown in part (d).

A collection of tree-like nano-structures is also presented in Fig. 4. Two top images in this figure show the creation of individually placed branched nanotubes on top of individual CNTs on the silicon substrate. The image at the bottom depicts a corner of a large cluster of CNTs formed in a branched like manner. By controlling the plasma power density in hydrogenation step, samples with different diameter of branches were obtained.

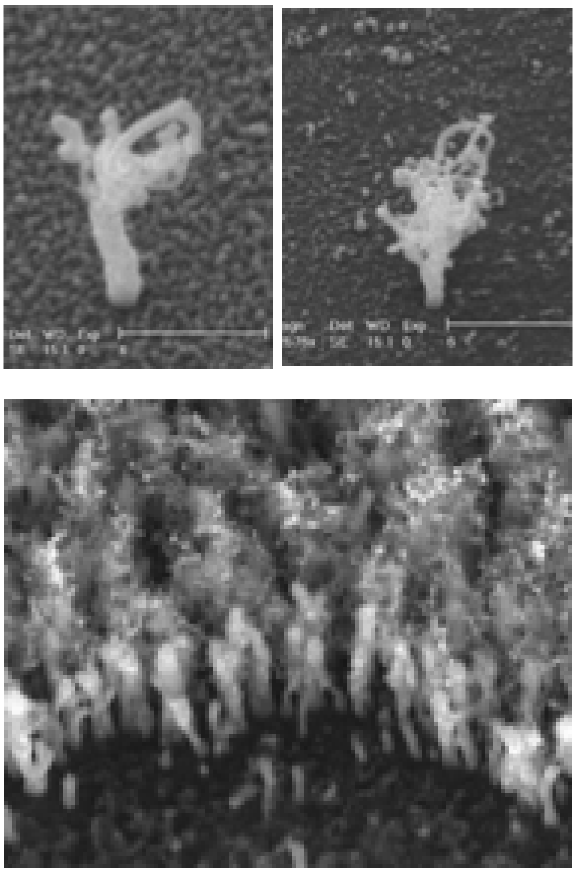
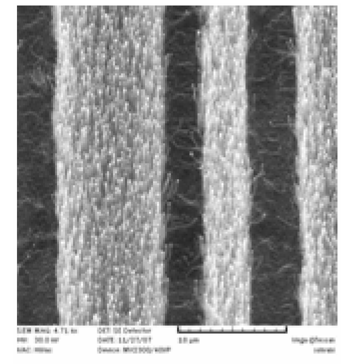


Figure 4: SEM images of tree-like structures with different diameter of branches. The bottom image shows a cluster of CNTs in a branched-like structure.

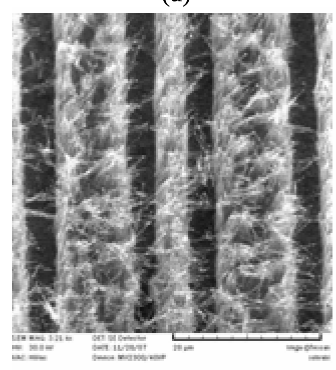
3.1 GAS SENSORS

For the fabrication of the gas sensor based on such nano-structures, Si substrates were first doped by phosphorous in designated areas to form P-N junctions at desired places. Then Ni layer was deposited and patterned to form interdigital structures suitable for gas sensor fabrication. The exposed areas of the silicon substrate were vertically etched away to create recession in those regions and to avoid short-circuiting the parallel fingers of the interdigital structure. This step is carried out using a reactive ion etching technique assisted by hydrogen/oxygen passivation. By using the process which was mentioned before, tree-like structures were grown on these interdigital patterns.

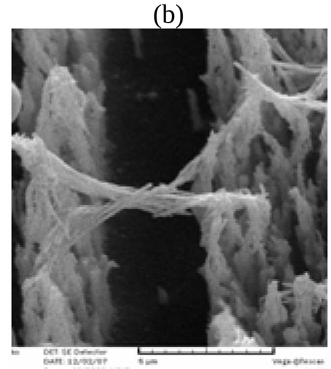
Figure 5 represents the SEM images of the sensor structure. Parts (a) and (b) show nanotubes and tree-like structures on comb-like fingers, respectively. As shown in the figure in some places, branches were joined together. So the fingers of the interdigital structure are electrically connected together through these branches. It must be born in mind that the electrical isolation of parallel fingers in the original interdigital structure has been ensured by a P-N junction isolation.



(a)



(b)



(c)

Figure 5: The formation of interdigital structures for the gas sensor fabrication. (a) as-grown CNTs, (b) tree-like formation and (c) a higher magnification view showing the connection of neighboring fingers.

In order to perform the gas sensing experiment the sample is placed in a chamber which is being purged by nitrogen as an inert ambient. By introducing oxygen gas to the chamber, the electrical conductivity of the structure shows a considerable reduction. Oxygen incorporation can passivate the carbon bonds and lower the electrical conductivity of the sensor. Since the sensing mechanism is mainly due to the oxygen presence at the surface of the device, this structure can also be used for sensing the reducing gases such as hydrogen and carbon monoxide.

Figure 6 represents the sensing characteristic of the structure. This measurement has been carried out at room temperature and oxygen gas was introduced after 20s. As seen from this figure, not a significant increase is observed in the electrical resistance of the sample.

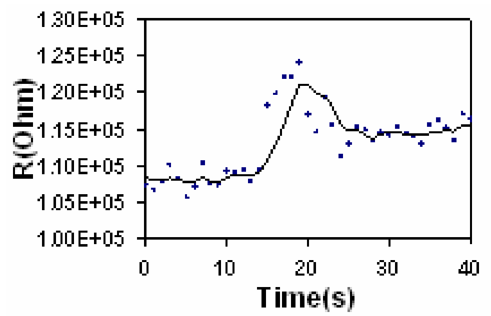


Figure 6: The resistance-time behavior of the sample at room temperature. Not a significant result is observed under such conditions.

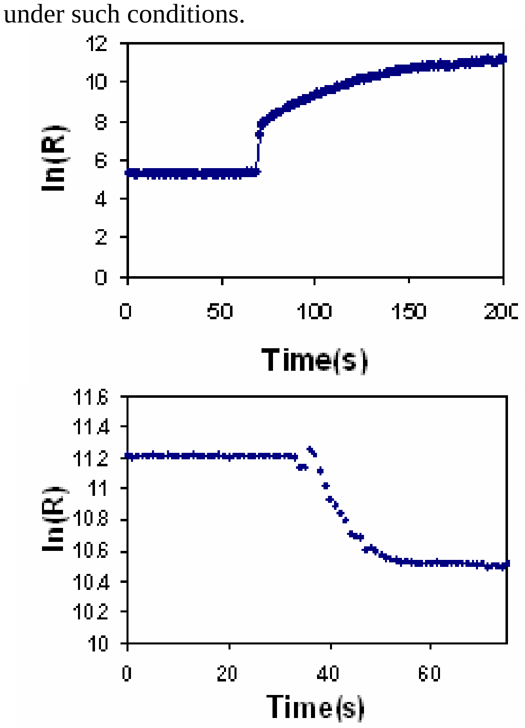


Figure 7: The response of the sensor to gas incorporation at a temperature of 200°C (top) evidencing a sharp and quick response. (bottom) The recovery of the sensor at the same temperature.

For better functionalizing the nanostructures the measurement was carried out again at 200 ºC. Results of this measurement are shown in figure 7. Part (a) of the figure demonstrates that by introducing the gas, the resistance of the sensor was increased. Part (b) shows the electrical characteristic of the sample during the recovery period.

4 CONCLUSIONS

We have successfully fabricated new branch-like nano-structures of carbon nanotubes on silicon substrates using a hydrogenation-assisted sequential growth. The evolution of such nano-structures has been possible by a second growth of carbon nanotubes on top of the original vertically aligned structures. The coating of the nickel seed which is placed at the tip side of the CNTs by a titanium oxide layer and its expansion by a hydrogenation process leads to a leach of nickel through the protective layer and allows the formation of newly evolved nano-size islands of nickel on the very tip side of the original CNTs. These new sites can be used as the seed for the growth of thinner nanotube and in the form of a branched tree-like structure. The realization of such nano-structures on parallel lines of an interdigital structure has been used as a device for gas sensing application.

This work has been supported with a grant from Ministry of Industry and Mines of Iran and partial support from Research Council of the University of Tehran. Technical assistances of Mr. J. Koohsorkhi and Dr. M.D. Robertson are greatly acknowledged.

REFERENCES

[1] J.-M. Bonard, M. Croci, C. Klinke, F. Conus, I. Arfaoui, T. Stockli, A. Chatelaine, Carbon 40 (10) (2002) 1715.

[2] M.I. Milne, K.B. Teo, G.A. Amaratunga, P. Legaganeux, J. Mater. Chem. 14 (6) (2004) 933.

[3] Y. Abdi, S. Mohajerzadeh, H. Hoseinzadegan, J. Koohsorkhi, Appl. Phys. Lett. 88 (2006) 053124.