Carbon nanotube growth at the tip of SiO$_2$ nanocone

Rajesh Kumar [a,b], Changhoon Choi [c], In-Chul Hwang [a,*], Nagesh Thakur [b]

[a] Department of Chemistry, Center for Superfunctional Materials, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790784, South Korea
[b] Department of Physics, Himachal Pradesh University, Shimla 171005 (H.P), India
[c] POSCO Technical Research Laboratories, Surface Technology Research Group, Gwangyang 545-090, Korea

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ABSTRACT

A well aligned growth of carbon nanotube (CNT) at the tip of SiO$_2$ nanocone using chemical vapor deposition (CVD) method is described. Fe particle at the tip of a nanocone has been observed to work as the catalyst for CNT growth. Initially, a number of self organized SiO$_2$ nanocones were grown via thermal annealing of MnCl$_2$ on Si substrate in the presence of H$_2$ gas. The average diameters of the tip and base of the nanocones were nearly 50 nm and 1 μm, respectively, with length up to 2.4 μm. At the tip of the nanocone a CNT was grown successfully. The CNT grows from the tip of the nanocone where Fe particles accumulate after the reduction of FeCl$_3$ at 950 °C. The accumulation point of Fe particles depends on the orientation of the nanocone tip inside the reaction tube during CVD process. Therefore, the alignment of nanotube at the tip of SiO$_2$ nanocone can be controlled by orientation of the nanocone in the reaction tube.

1. Introduction

CNTs are considered as one of the most attractive material for nanoelectronic applications [1–9] such as nanosensors [10], fuel cells [11], SPM probes [12] etc. Because of its excellent properties like flexible nature, CNT is an ideal candidate for force measurement [13] and imaging surface structures with great depth [14–16]. It also prolongs the life time of imaging probe tip. CNT at the tip of commercial microscopy (such as AFM) can either be attached mechanically [17–20] or grown directly [21]. But attaching CNT at the tip of probe is quite a tedious job because of its nanometer-size diameters. Further due to manipulation at the nanometer scale, it is conceivably difficult to align the angle of CNT at the probe tip. In literature, acrylic adhesive have been used to attach a nanotube at the end of a conventional probe tip. An optical microscope has been used to transfer nanotubes onto the probe tip [22–24]. However, it is difficult to obtain a strong and reliable attachment through this procedure also. It is more rational to grow CNT directly at a commercially available microscopy tip. Previously, to attach a CNT at the tip of microscopy different methods have been used such as chemical vapor deposition CVD [25,26], electric field induced probe attachment [27,28] and magnetic field induced probe attachment methods [29].

In CVD method there is no control over the growth of nanotube at the desired location and its alignment at the tip. While, the electric field induced probe attachment and magnetic field induced probe attachment methods have been found time consuming.

The aim of the present study is to grow a CNT at the tip of pre-grown SiO$_2$ nanocone rather than to grow at the tip of microscopy. Since, it is easier to attach a nanocone having CNT than to attach a bare CNT at the tip of microscopy. It would also provide substantially higher mechanical stability at the tip of microscopy due to micrometer size base diameter of the nanocone.

2. Experimental

The present experiment was performed in two steps; first, SiO$_2$ nanocones were grown on Si substrate and then a controlled growth of CNT at the tip of SiO$_2$ nanocones was achieved. Silicon (100) was pretreated to use it as a substrate to grow SiO$_2$ nanocones, like degreasing was done by acetone and then it was dipped into a diluted HF (10%) solution in order to remove pre-existing native oxide layer on its surface. The substrate was then rinsed under running de-ionized water and finally it was dried in a stream of nitrogen gas. A drop of diameter about 100 μm of 0.02 M solution of MnCl$_2$ (Aldrich, purity 99.99%) prepared in aqueous C$_2$H$_5$OH (C$_2$H$_5$OH:H$_2$O=9:1 vol.) was placed on the substrate. The sampled substrate was subsequently transferred into a quartz tube lying inside a programmable temperature controlled horizontal tube furnace. Ar gas flow was used in order
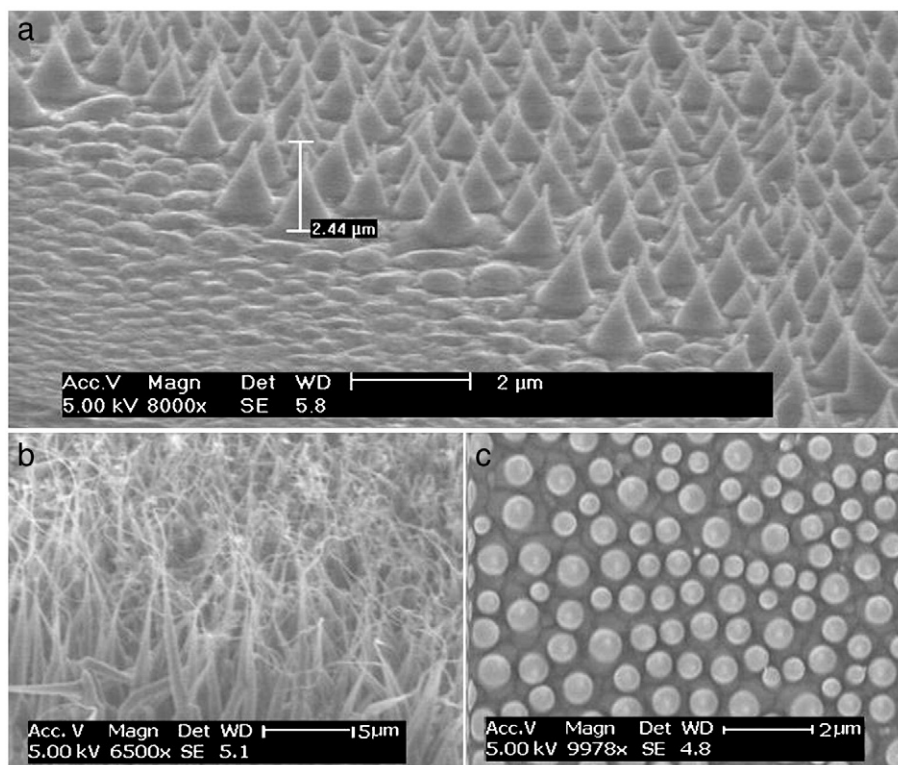
Fig. 1. Field emission scanning electron microscopy (FESEM) images of nanocones grown on silicon substrate at 950 °C. At 45° view (a) shows nanocones grown for 5 h annealing time and (b) shows nanocones grown for 8 h annealing time. (c) Is the top view of nanocones grown for 5 h annealing time.

to dry C_2H_5OH and H_2O solvents from the drop present on Si substrate. After 30 min of Ar flow (100 ml/min) at about 80–85 °C, the temperature was raised to 950 °C and it was maintained for 5 h. Flow of H_2 gas diluted in Ar was used through the reaction tube at a rate of 100 ml/min with already flowing Ar to reduce the $MnCl_2$. The nanocones were grown on the Si substrate for two annealing times of 5 h and 8 h, respectively. These SiO_2 nanocones were characterized by field emission scanning electron microscopy (FESEM) and high

resolution transmission electron microscopy (HRTEM, JEM-2100) installed with energy dispersive X-ray (EDX).

These nanocones on Si substrate were then used to grow CNT at their tip. A 0.1 M solution of $FeCl_3$ (in C_2H_5OH) was coated on a surface of glass slide using spin coating method. The Si substrate having SiO_2 nanocones were then deliberately covered by $FeCl_3$ coated glass slide to transfer a minute amount of $FeCl_3$ at the tip of nanocones. The SiO_2 nanocones with $FeCl_3$ at the tip were transferred again to the reaction

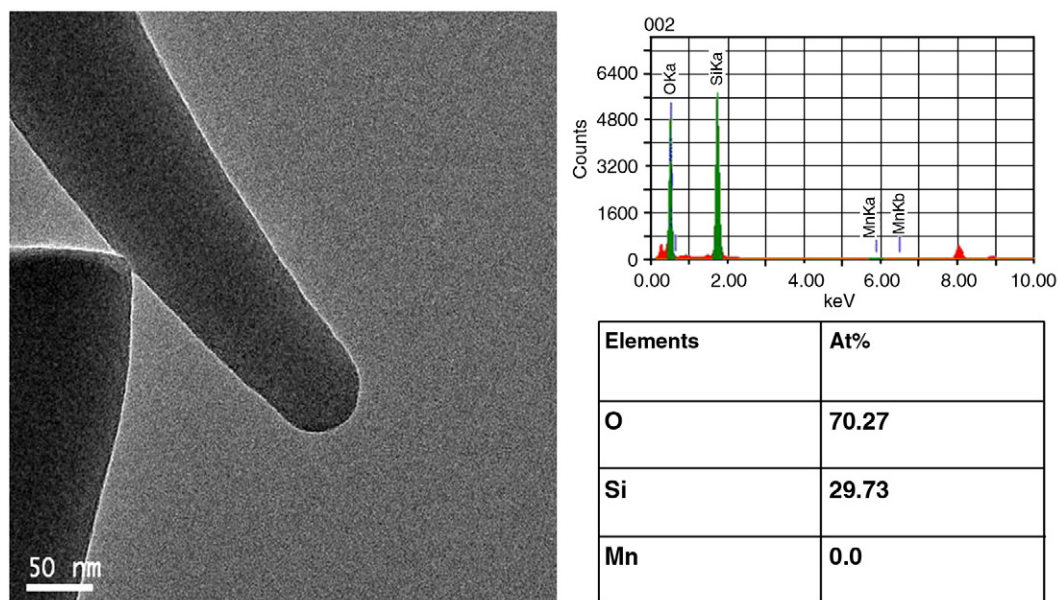| Elements	At%
O	70.27
Si	29.73
Mn	0.0

Fig. 2. TEM image of the nanocone grown at 950 °C for 5 h annealing time, at the top right corner energy dispersive X-rays (EDX) spectrum is shown and the table in bottom right corner shows the atomic% of O, Si and Mn.
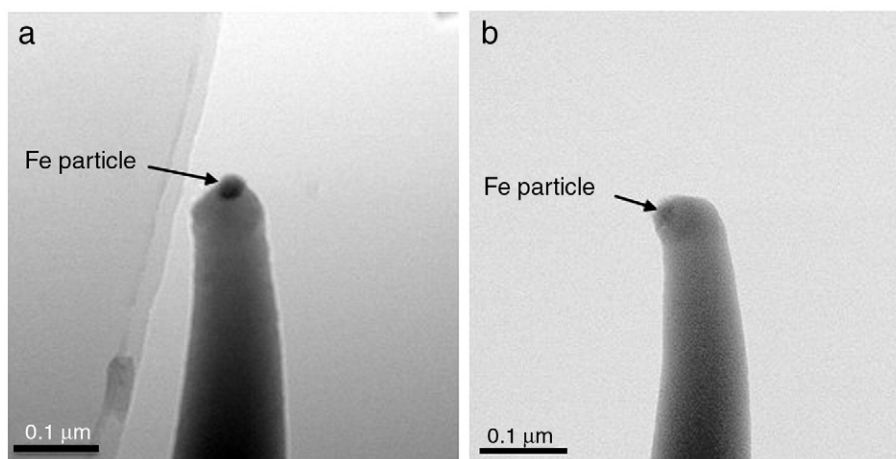
Fig. 3. TEM image of Fe particles at the tip of nanocone, (a) Fe particles are accumulated exactly at the tip of nanocone and in (b) Fe particles are accumulated at some side position of the tip.

tube inside the furnace. In order to grow CNT, a flow of H_2 gas at a rate of 50 ml/min and CH_4 gas at a rate of 50 ml/min was used inside the reaction tube. The temperature was raised to 950 °C and it was maintained for 1 h. Growth of CNT was observed by using two orientations of Si substrate inside the reaction tube. In the first orientation Si substrate was placed in such a way that nanocone tips were aligned in an upward direction and in the second orientation tips were aligned in downward direction. For both orientations, grown CNTs at the tip of SiO_2 nanocones were characterized by FESEM and HRTEM.

3. Results and discussion

The FESEM image of the nanocones grown in first step of experiment, when $MnCl_2$ sampled Si substrate was annealed at 950 °C for 5 h, is shown in Fig. 1(a). This image shows a number of self organized nanocones on the Si substrate. The average diameter of tip and base of the nanocones is found to be nearly 50 nm and 1 μm, respectively, and its length is about 2.4 μm. So far as the mechanism of SiO_2-nanocones formation on Si substrate is concern, the Si surface reacts initially with $MnCl_2 \cdot 4(H_2O)$ and oxidizes into the SiO_2 surface at the high annealing temperature. This leads to the formation of amorphous $MnSiO_3$ (MnO/SiO_2) as a cap of a hump on the Si surface. The grown SiO_2 tends to interact with MnO, resulting in the formation of SiO_2–MnO, while MnO tends to diffuse above SiO_2 with more mobility. Due to a hemispherical cap of $MnSiO_3$, the SiO_2 grows as a nanocone because of the surface tension (the detailed study of SiO_2 nanocone formation has been submitted elsewhere in a separate work). As the annealing time increases, $MnSiO_3$ shell decreases and completely disappears for 5 h of annealing. It has been observed that with an increase in annealing duration from 5 h to 8 h, the length of nanocone increased by more than 5 μm and also its tip becomes thinner and much entangled as shown in Fig. 1(b). Therefore, for the nanocones grown for 8 h annealing time, it is difficult to obtain an accurate measure of the average length and diameter of the tip. Fig. 1(c) shows FESEM image of the top view of nanocones obtained for 5 h annealing time which reveals the circular geometry of the base and bent free tip of nanocones.

A nanocone grown for 5 h annealing time was also characterized by TEM equipped with energy dispersive X-ray spectroscopy (EDX) (Fig. 2). The TEM studies were carried out at an acceleration voltage of 200 kV and a probe current of 1 nA. These studies indicate nanocone as an amorphous structure. The EDX study shows that O and Si constitute the whole nanocone structure (EDX spectrum shown in the top right corner of Fig. 2). The atomic% of elements is tabulated (Fig. 2) having O, 70.27% and Si, 29.73% respectively. This shows Si and O elements with an atomic ratio nearly 1:2 which forms SiO_2. In EDX

characterization, no signal corresponding to Mn catalyst was detected inside a nanocone.

Fig. 3 shows TEM images of Fe nanoparticles (in oxide form) accumulated at the tip of SiO_2 nanocones for two subsequent upward and downward orientations of the tip of nanocones inside the reaction tube during $FeCl_3$ reduction. The position of Fe particles was reconfirmed by EDX point analysis. It was observed that the Fe particles accumulate exactly at the tip when the nanocones were placed in a way to direct the tips downward inside the reaction tube for 1 h at 950 °C (Fig. 3(a)). While in second orientation the nanocones were placed to direct the tips vertically upward (Fig. 3(b)) and the Fe particles accumulated at some side position rather than the exact tip. Fig. 4(a) and (b) is the schematic representation of Fe particles accumulated after the reduction of $FeCl_3$ at the tip for two orientations of nanocones inside the reaction tube. Orientation dependence of accumulation of the Fe particles at the tip of nanocone can be assumed due to the existence of melt form of the nanocone tip during its growth. The tip (SiO_2) of the nanocone as well as the Fe (in the form of oxide) at the tip are expected to be in melt form when annealed for 1 hr at 950 °C after attaching a minute amount of $FeCl_3$ at the tip of nanocone. Hence at the tip of nanocone, both SiO_2 and Fe exist in melt form and obviously Fe has higher density as compared to SiO_2. For upward orientation of the tip, because of higher density of Fe, it does not remain exactly at the tip of cone and flows towards the solid state region of the nanocone and accumulates at slightly lower position than the exact tip. While for downward orientation of the tip, again due to the higher density the Fe accumulates at the exact tip.

In the second step, CVD technique was employed to grow CNT at the tip of nanocone. Fe particle formed after the reduction of $FeCl_3$ at the tip of nanocone acts as the catalyst for the CNT formation, where as the carbon required for CNT growth was supplied from the
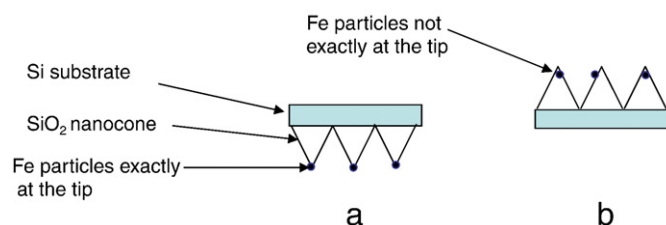

Fig. 4. Schematic representation of Fe particles accumulation formed after $FeCl_3$ reduction at the tip of SiO_2 nanocones inside the reaction tube. (a) The substrate is placed to direct nanocones vertically downward and (b) to direct nanocones vertically upward.
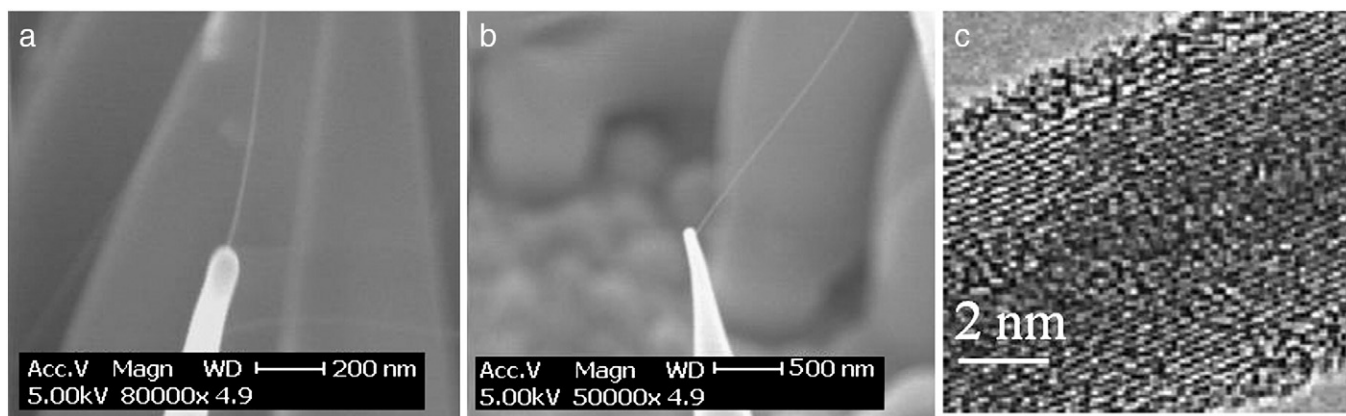
Fig. 5. CNT grown at the tip of nanocone. (a) CNT is vertically above the tip of nanocone and is grown exactly at the tip, (b) shows CNT not exactly at the tip of nanocone and (c) is HRTEM image which shows the CNT as multi wall carbon nanotube.

precursor CH_4. The alignment of CNT at the tip of nanocone also depends upon the orientation of nanocone inside the reaction tube i.e. vertically upward or downward. For downward orientation of the nanocone the CNT was grown right above the tip as shown in Fig. 5(a). But, some bending was observed for upward orientation as shown in Fig. 5(b). The reason is that Fe does not accumulate exactly at the tip for its upward orientation. The CNT was observed to grow few μm above the tip of nanocone for 1 h reaction time. Fig. 5(c) shows HRTEM image of a CNT grown at the tip of a nanocone which is a multi wall CNT of diameter nearly 10 nm.

4. Conclusion

The nucleation position of CNT at the tip of nanocone depends on the accumulation position of Fe particles after the reduction of $FeCl_3$. Fe particles are found to accumulate exactly at the tip of nanocones when Si substrate is placed in such a way that the nanocone tips are oriented downwards inside the reaction tube. Now, the CNT grows from the exact tip and it gets aligned straight. If the nanocone tips are oriented upward inside the reaction tube, the Fe particles accumulate at some side position rather than the exact tip which causes the nucleation of CNT not exactly from the tip of nanocone and in this case CNT also, would not get aligned straight above the tip.

Acknowledgement

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