SYNTHESIS OF VERTICAL GROWN BAMBOO TYPE CARBON NANO TUBES

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ABSTRACT

Bamboo type nanotubes were synthesized by acetylene gas in a hydrogen plasma environment using Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) equipment with C_2H_2/H_2 as source gases. The Bamboo type nanotubes was arranged vertically with the TiN barrier layers and the Ni catalyst were used in an experiment on the growth of carbon nanotubes (CNTs) on Si wafer. The specified temperature annealing has done on the H_2 environment to enhance the particle formation. The metal particle size is closely related to the diameter of the nanotubes, when carbon nanotubes are synthesized on transition metal-coated substrates by the thermal Chemical Vapor Deposition (CVD) method. In order to investigate the optimal conditions for growth of Bamboo type CNTs, the nickel (Ni) thin films were annealed at various temperatures under hydrogen atmosphere. The growth rate of carbon nanotubes was most remarkable after annealing at 700 °C.

Keywords: Carbon nanotubes, MPECVD, Ni thin films, reaction time.

INTRODUCTION

Since the first surveillance of CNTs [1], general researches have motivated on the synthesis of CNTs with high application. Numerous synthetic methods such as arc discharge [2–4], laser vaporization [5, 6], pyrolysis [7], and plasma enhanced or thermal CVD [8–15] were engaged. Synthesis of well-aligned CNTs on a large area is necessary for one of various applications, electron emitter of field emission displays. The arc discharge and the laser vaporization techniques can produce the large amount of CNTs, but it is very difficult to control the alignment and size [4, 5]. These methods also require distillation process to dispersed pure CNTs from other particles. Many research groups have engaged the CVD method for the drive of large scaled fabrication of CNTs [8–15]. It is shown that the CVD technique can synthesize the CNTs with high purity, high yield, selective growth, and good vertical alignment. In this study, we report the vertically aligned multi walled CNTs growth on a large area of silicon oxide (SiO_2) substrate by using MPECVD method. The surface of catalytic cobalt Nickel (Ni) film deposited on the SiO_2 substrate is improved by wet hydrogen fluoride (HF) and/or subsequent hydrogen (H_2) gas etchings. Acetylene (C_2H_2) gas was used to produce CNTs. Despite many successful syntheses, the growth mechanism is still not completely understood. Therefore, we discuss a possible mechanism for the CNT growth.

EXPERMENTAL AND THEORETICAL METHODS

We have grown carbon nanotubes using a MPECVD method, which has been believed to be the most promising candidates for the synthesis of vertical aligned CNTs due to the low temperature and the large area growth possibilities [16]. The well aligned multi wall CNTs have been attracted for the use of vacuum microelectronics especially in field-emission tip. Vertically oriented CNTs were successfully synthesized by MPECVD with C_2H_2 / H_2 as source gases. Additionally, the TiN barrier layers and the Ni catalyst were used in an experiment on the growth of CNTs on Si wafer. The TiN barrier layer was deposited on the Si wafer using sputtered method, and the thin Ni film was deposited using E-beam evaporation method (Thickness: TiN 100nm / Ni 20nm). It has been well known that the metal particle size is closely related to the diameter of the nanotubes, when carbon nanotubes are synthesized on transition metal-coated substrates by the MPECVD method. For the reason, the specified temperature annealing has done on the H_2 environment to enhance the particle formation. Figure 1 shows the modified Ni film surface on various temperatures and Table 2 indicates the corresponding roughness.

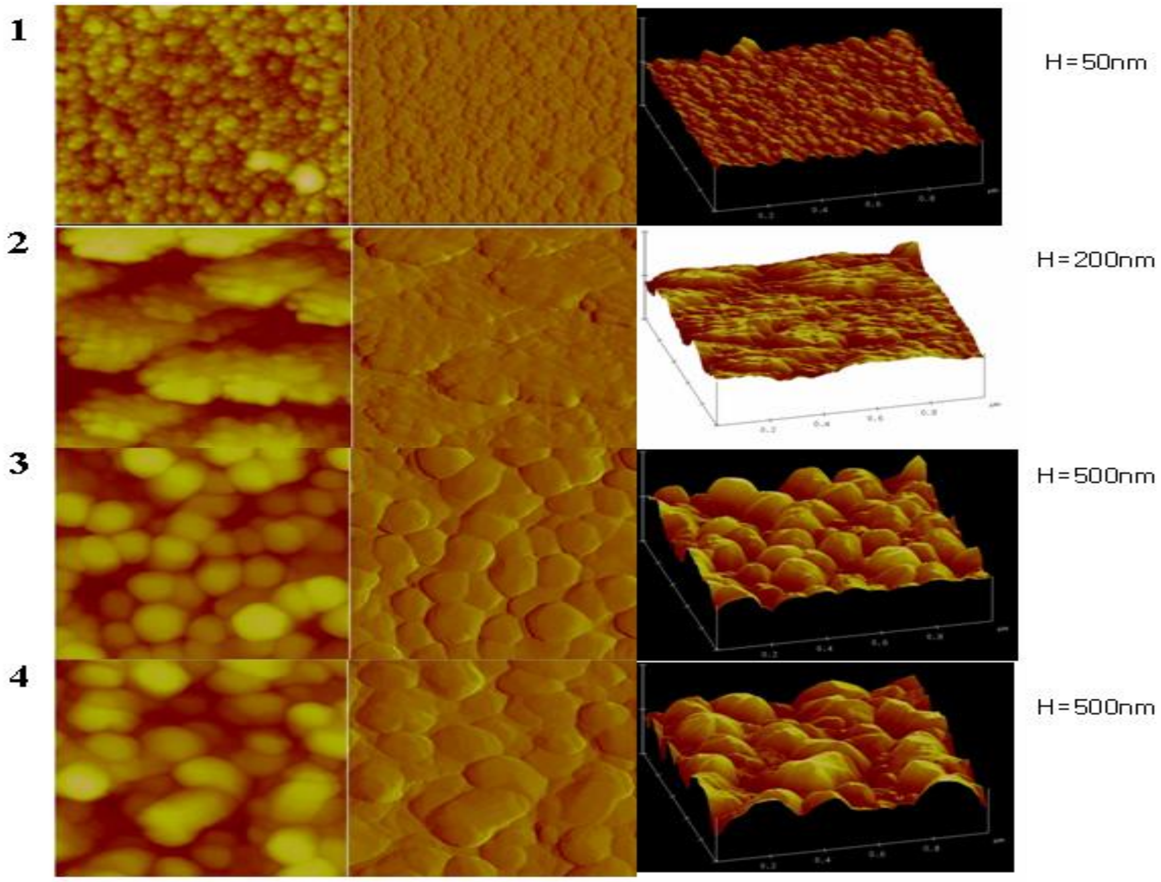

Figure 1. Ni thin film modification at various temperatures.

Table 1. Ni thin film roughness variation. Scale (10nm x 10nm).

	Ra(nm)	Temp. (°C)	Gas (sccm)	Heating time (min)
1	2.171	-	-	-
2	9.526	650 ℃	H_2 80	10
3	23.391	700 ℃	H_2 80	10
4	26.437	750 ℃	H_2 80	10

When we annealing at high temperature, the surface roughness has a tendency to increase. This phenomenon can be stated by 'Ostwald ripening' [17]. Prior to coalescence there is a collection of islands of varied size, and with time the larger ones grow or "ripen" at the expense of the smaller ones. The desire to minimize surface free energy of the island structure is the driving force. To figure the relations between the roughness and CNTs growth out, we annealed the Ni / TiN / Si substrates at various temperatures (Table 1) and we grew the CNTs on the same roughness test conditions except adding carbon source (Table 2).

Table 2. CNTs growth on Ni thin film at various temperatures. (After anneal 10 min at the same reaction temperature)

	Reaction Temp. (°C)	Gas source C_2H_2/H_2 (sccm)	Reaction Press. (Torr)	Reaction time (min)	Growth rate (nm/min)
1	650°C	6 / 80	2.5	30	56
2	700°C	6 / 80	2.5	30	133
3	750°C	6 / 80	2.5	30	66

The highest CNTs growth rate worked at 700°, despite of the large size of the coagulated metal islands (about 200 nm), compared to CNTs diameter (30 nm). We expect that the inequality in metal surface at high temperature promotes nuclei of CNTs.

RESULTS

For the synthesis of CNTs, MPECVD system was employed and compared with simple CVD system. The Ar plasma ignited at 0.1 Torr with flow Ar 80 sccm, 400 W thereafter H_2 80sccm flow into the chamber and made hydrogen plasma environment. Before the plasma ignition, thermal furnace heated at 650 °C and sustained set temperature and acetylene 6 sccm flew the chamber about 10 min at 10 torr to make CNTs synthesis condition. After 10 min reaction, the CVD system and the MPECVD system shows considerable difference in CNTs length. The CNTs growth rate in the MPECVD is 3.5 μm / min but 0.4 μm in CVD system. In a hydrogen plasma mood, the acetylene reduced to methane like monomer species.

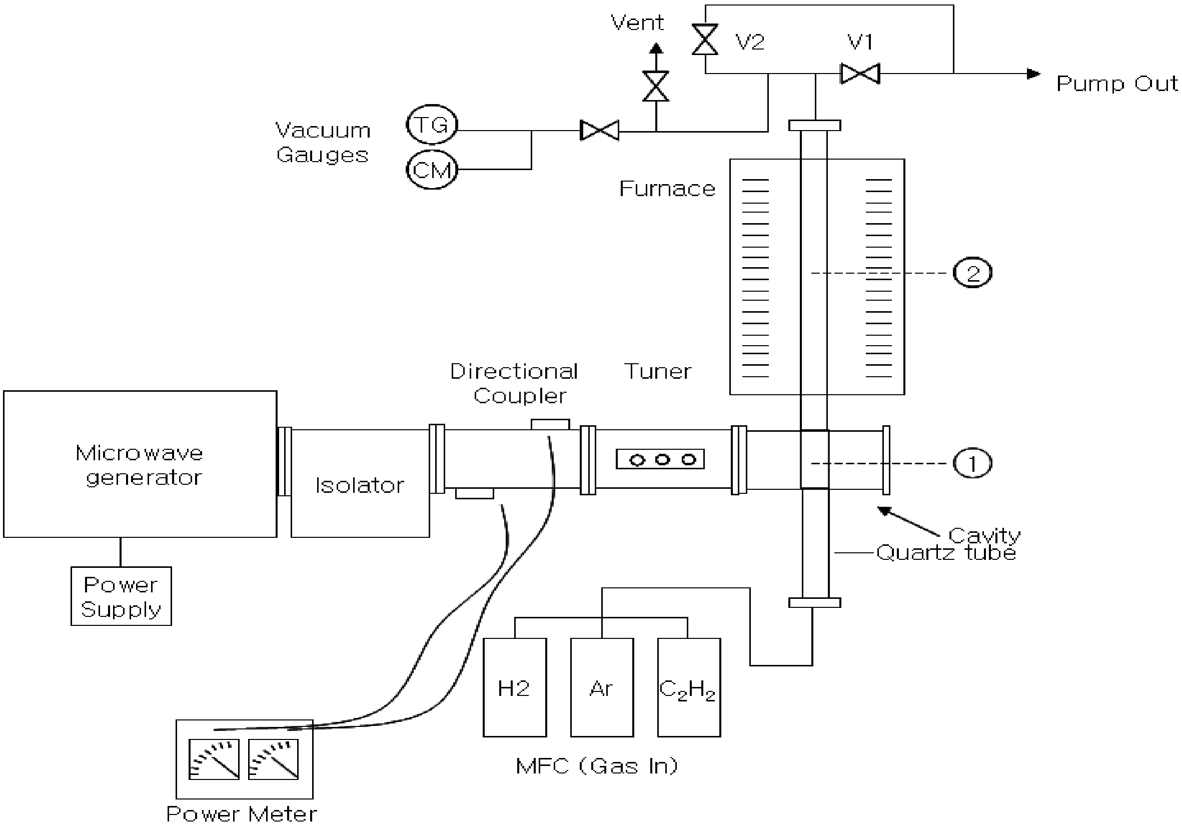

Figure 2. MPECVD system. Cavity for petal-like graphite synthesizes (1), and cavity for CNTs growing (2).
***. TG: Thermocouple Gauge.**
CM: Capacitance manometer.

SEM was employed for the analysis of the morphology and density of Ni filled CNTs. Figure 3 (1–3) shows the FE-SEM images of carbon nanotubes synthesized at 650 ℃, 700 ℃ and 750 ℃. The CNTs were synthesized on the Si (1 0 0) substrates using Ni catalyst and the high aspect ratio nanostructures had randomly oriented spaghetti-like morphology in this cases. In many cases, small bright catalyst particles were detected at the tip of the multiwall CNTs. This suggests that the tip growth mechanism is likely to be responsible for the CNT synthesis under the present conditions for the catalysts.

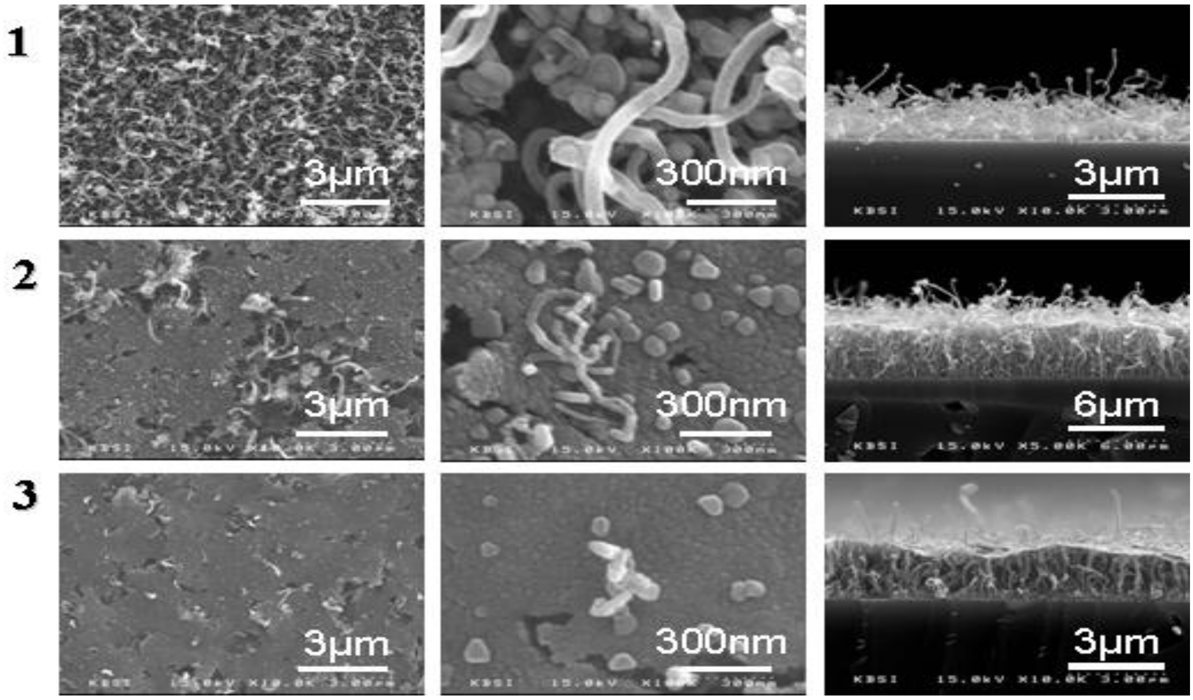

Figure 3. SEM images of CNTs synthesis on Ni thin film. Top view (left), and its magnified image (center) and the sectional view (right).

Figure 4 shows comparison of CNTs growth between MPECVD and CVD system. Comparing two synthesis methods, it can be seen that the CNTs synthesized 60 ㎛ height by MPECVD . In addition, the shape of the CNTs grown is better in length and vertical growth.

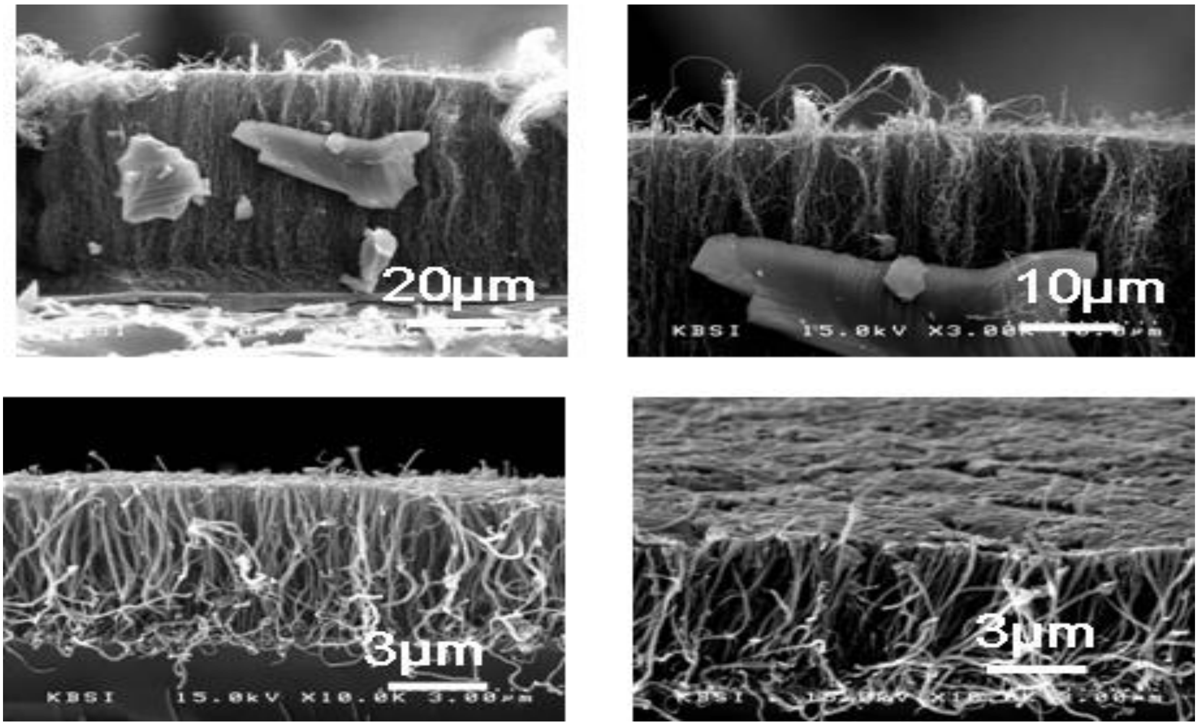

Figure 4. Comparison of CNTs growth between MPECVD (upper) and CVD (bottom) system. (Reaction condition: 10 Torr, 10 min, 650° C, 400 W)

The conditions of this experiment were performed under a pressure of 10 Torr, a pressure of 650 degrees, and a DC power of 400 W for a reaction time of 10 minutes. The CNTs grown in the MPECVD system collected with razor blade and sonicated about 1 hour in ethanol and then copper grid dipped in the solution for STEM (Scanning Transmission electron microscope unit, JEOL JEM 2011, Voltage range 80~200kV) analysis. From TEM image we know that the CNTs are metal particle incorporated in CNT strand end (Figure 5). The diameter of the synthesized CNTs was 30 nm and the typical growth pattern of bamboo type was observed.

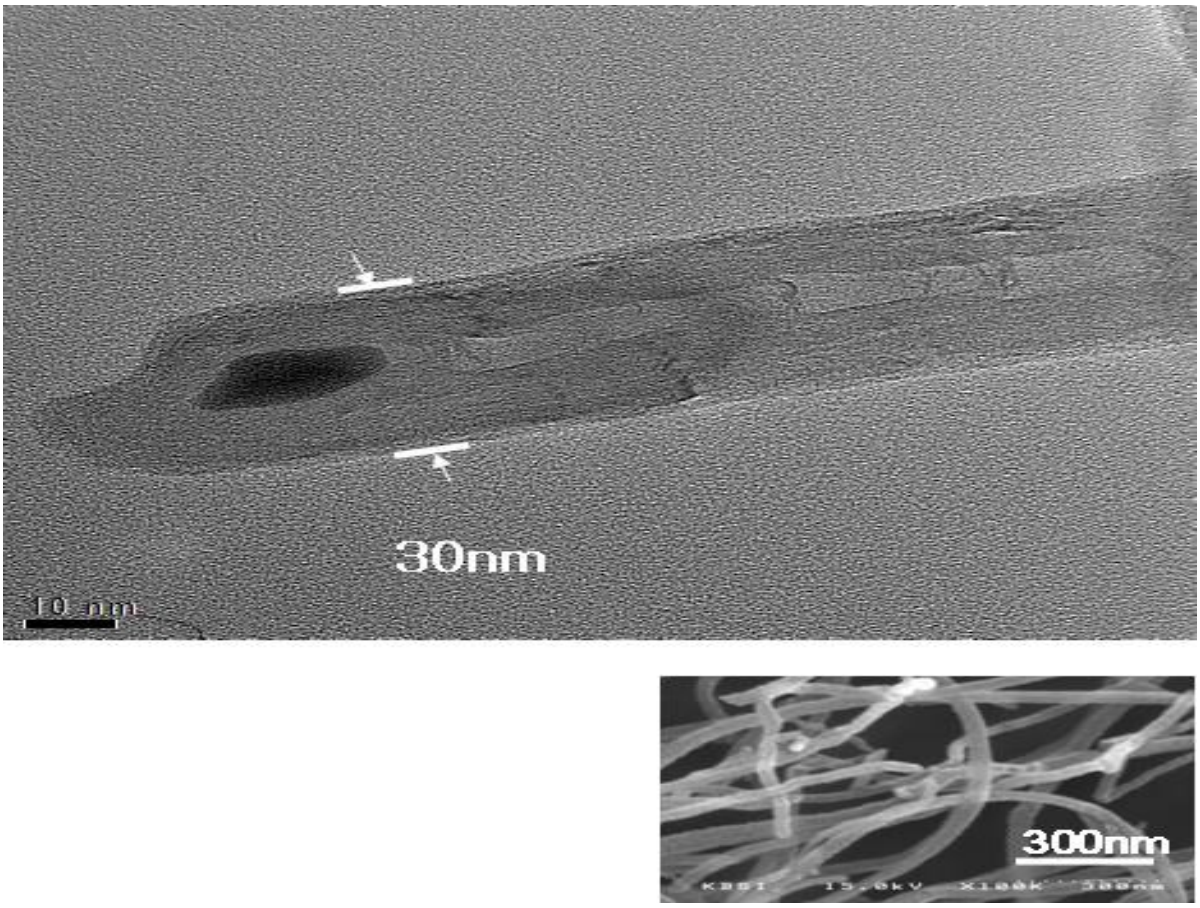

Figure 5. TEM image of bamboo-type multiwall CNTs and its corresponding SEM image.

Dennis W. Hess et al suggest the method of XPS analysis on vertically grown CNTs [18]. If the CNTs chase the tip growth mode, incorporated metal binding energy peak should be observed. By considering the XPS data (Figure 6), that there are not $Ni_{2}p3/2$(852.7 eV) but C1s (284.65 eV) and O1s (532.65 eV) peak appear.

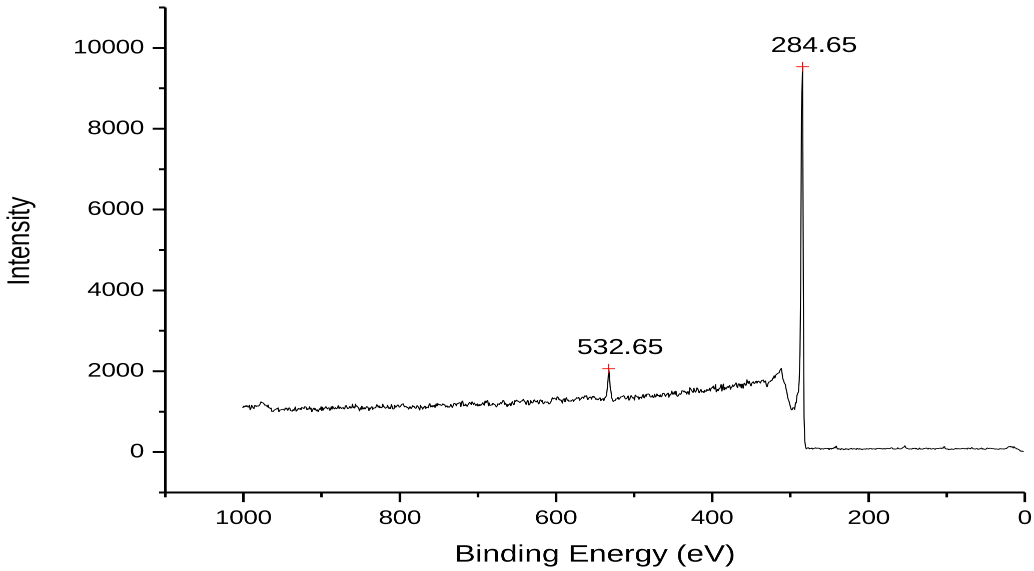

Figure 6. XPS data of bamboo type MWNTs. (Al Kα source, non-monochromated 1486.6 eV)

DISCUSSION

Many fractures of multiwall CNTs seem from the plasma impact. Two different growth modes can be suggested based on the interaction of the catalyst with its support as described by Baker [19]. The interaction of the catalyst with the support can be characterized by its contact angle at the growth temperature, analogous to "hydrophobic" (weak interaction) and "hydrophilic" (strong interaction) surfaces. Thus, the surface interaction between the catalyst and its support is an important consideration which dictates the growth mode (Figure 7). The tip growth model was suggested to explain the SEM images of CNTs (Figure 4). Also, we can identify the structure of CNTs by TEM image analysis with Figure 5. The hollow tip with any Ni catalytic particles, as seen from Figure 5, is inconsistent with the tip growth model. When the MPECVD method was used for the CNT synthesis, the catalytic particles usually remain at the tip of CNTs, which was justified by the tip growth model. Therefore, in order to explain the hollow tip of CNTs as well as the bamboo structure, the tip growth model would be rather suitable. In the growth reaction of CNTs, the diffusion of carbon in the catalyst metal has been believed to be the rate-determining step. The growth rate of CNTs can be described by an Arrhenius equation that the activation energy is the diffusion energy of carbon in the metal. Support for this model comes from experiments on the kinetics of growth of CNTs on the γ-Ni metal from acetylene at 1000 ℃, yielding the activation energy of 142 kJ mol^{-1}, which is close to the activation energy for diffusion, 148 kJ mol^{-1} [20, 21]. So we concluded that the bamboo-typed MWNTs growth follows the tip-growth mode. It seems to be the high interaction between nickel thin film and titanium nitride buffer layer.

ISSN 2398-1385

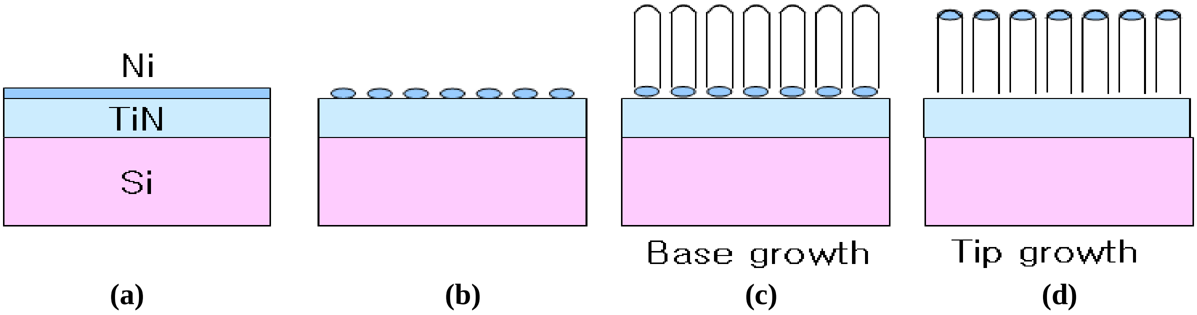

Figure 7. Growth mode of CNTs. The multilayer thin film, Ni: 20 nm TiN: 100 nm (a) after the annealing (b), base growth mode (c) and tip growth mode (d).

CONCLUSIONS

We have grown the vertically well aligned bamboo type multi walled CNTs on a large area of Ni deposited SiO_2 substrates using the MPECVD method. The diameter of CNTs is 30 nm and the length is about 60 μm length. The multi walled CNTs have the hollow tip and the bamboo structure that the hollow compartments are separated with the graphite layers. The multi walls are in good crystalline phase. The tip growth mechanism is suitable for the CNTs grown by MPECVD. We suggest that surface and bulk diffusions of carbons play an important role in determining the structure of CNTs. The vertically aligned multi walled CNTs grown on the Ni deposited substrate can be applicable to the many fields.

ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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