Controllable Sequential Low Temperature Plasma Assisted Growth of Vertical Multi-wall & Single-wall CNTs

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ABSTRACT

By investigating the effects of growth parameters of carbon nanotubes (CNTs), we have arrived at small diameter, single/multi-wall nanotubes at low temperatures. Synthesis of CNTs was performed using the gas mixture of methane (CH_4) and hydrogen (H_2) in a DC-PECVD reactor. To avoid Nickel (Ni) grain agglomeration we developed a new method of hydrogenation consists of several sequences of CH_4 flow to temporally passivate the grains to keep the sizes unchanged. Sweeping different conditions for the CH_4 sequences interesting results were obtained. Immediately after the two-step pretreatment, CH_4 was introduced into the chamber to initiate the growth of CNTs. The 10 nm effective reduction in CNT diameter was reported in the final results.

Keywords: CNTs, PECVD, hydrogenation, S/M/WNT

1 INTRODUCTION

Distinctive CNT properties such as electrical, magnetic, non-linear optical and mechanical features make carbon nanotubes as a potential candidate for wide areas of applications [1-2]. Indeed, for most of the known applications, it is highly needed to control over their diameters, lengths and orientations, which are critical parameters for the physical properties of CNTs [3-4].

There are several suggested approaches to control the CNT diameter during the plasma enhanced chemical vapor deposition (PECVD) growth. A straightforward method is to restrict the catalyst grain sizes in pre-growth treatment [5]. In some systems, Ammonia (NH3) has often been used as an environmental gas for PECVD growth of CNTs. It is stated that the pretreatment of catalyst particles with NH_3 plasma results in a thin nitride layer on the catalyst surface, which suppresses catalyst deactivation by decomposing excessive carbon [6] and either prevent the grains to be agglomerated and form bigger particles.

Based on this idea, we have devised a new sequential pretreatment method to replace ammonia with the previously involved hydrocarbon gas. Synthesis of CNTs was performed using the gas mixture of CH_4 and H_2 in a DC-PECVD reactor. The physical properties of samples were investigated by HR-SEM and Raman spectroscopy.

2 FABRICATION PROCEDURE

Prior to CNT growth a thin Ni layer 1-8 nm was deposited. The synthesis of CNTs was performed at 700 °C using the gas mixture of CH_4 and H_2 in a DC-PECVD reactor. The main feature of the system is a DC-plasma generator which enhances the dissociation and growth of carbon nanotubes from the hydrocarbon source as well as causes the CNTs to grow vertically, in the direction of the electric field. The vacuum in the quartz reaction chamber is achieved and maintained at a level of 10^{-4}Torr by a turbo-mechanical and rotary dual-stage pump, and mass flow controllers are used to control the level of the supplied gasses. A computer allows programming the growth in a sequential manner.

A dual-step pre-growth treatment of the surface was performed. First, the surface of the sample was treated with a hydrogen blow at a flow rate of 20 sccm for 15 min with the substrate temperature maintained at 700 ℃. This step was followed by a 5 min treatment of hydrogen plasma (plasma current of 40 mA) at the same temperature of the growth in order to create nano islands of Ni. It was observed that the initial Ni island formation was critical in the final growth properties of the nanotubes.

Immediately after the two-step pretreatment, methane (CH4) was introduced into the chamber with a flow rate of 12 sccm for 12 min in order to initiate the growth of CNTs. The flow hydrogen gas remained constant at 8 sccm. Growth of the CNTs was performed over substrate temperatures ranging from 550 to 700 -C and at a pressure of 1.6 Torr. The size, shape and density of CNTs were determined by high-resolution scanning electron microscope (HRSEM) and Raman spectroscopy. The sample series were divided in two categories; a) Si wafers with normal H_2 plasma treatment, and b) Si wafers with sequential pre-growth treatment.

In the normal case the total growth process can be shown as Fig. 1(a, d-e). The main difference with these two types occurs in nano-size island formation. In the first type after 15 min. annealing treatment nano islands are formed ,

to activate the islands to initiate the growth we expose it to hydrogen plasma for 5 minutes, but in this period the islands begin to agglomerate together and form the bigger grain which consequent in bigger diameter for CNTs.

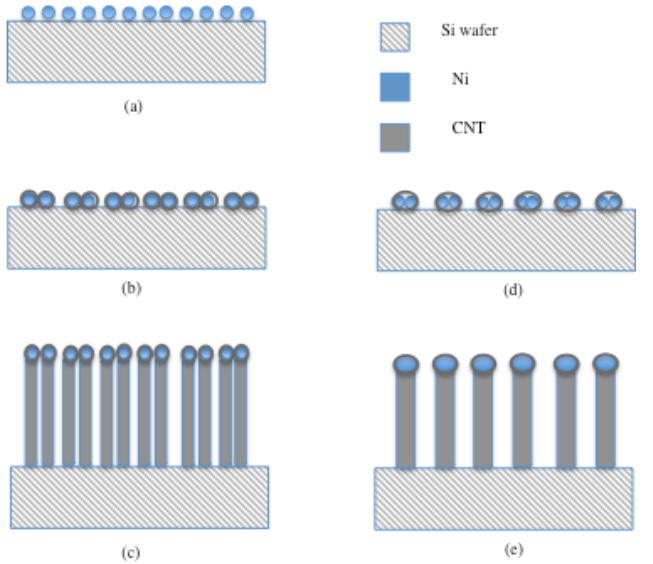


Figure 1: The fabrication process of vertical CNTs. (a) Ni grain formation after 15 min. annealing, and (b), (c) sequential process; Nano-island passivation and CNT growth (d), (e) Normal process; Nano-size island agglomeration and CNT growth.

To prevent the island agglomeration we run a sequential pre-growth treatment, which includes periodic pulses of methane during the hydrogen plasma treatment. The pulses are shown in Fig. 2. In this case after 15 min. annealing the nano islands are formed but to prevent their agglomeration, methane flow forms a carbonic layer around the grains that can be the start of CNT growth so the final diameter decreases.

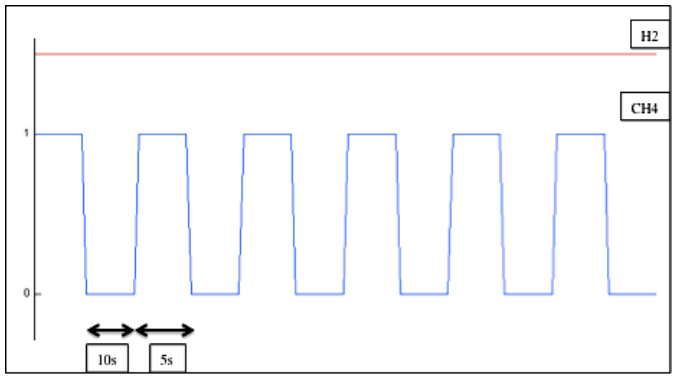


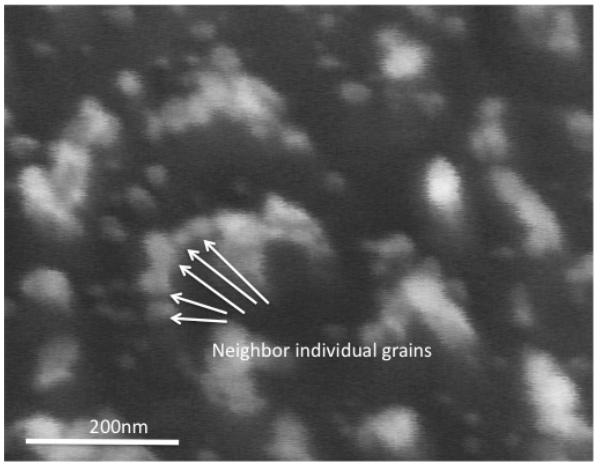
Figure 2: The gas flow diagram of sequential pretreatment containing CH_4 periodic pulse and continuous flow of H_2.

To compare these two methods Fig. 1 schematically describes the process. Part d-e is related to normal case, as it is shown the neighbor Ni grains gathered together and shaped a bigger one that result in a single CNT. Part b-c illustrates the sequential process which passivates the neighbor grains leads to growth of individual CNTs from each of the neighbor grains.

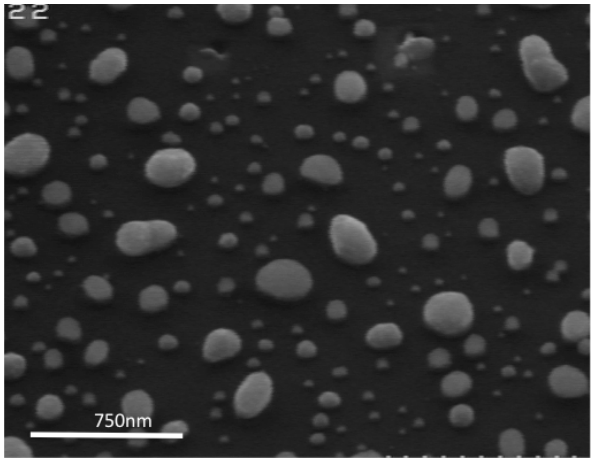
3 RESULTS AND DISCUSSION

3.1 Nickel nano-island formation

The physical structure of CNTs has been investigated using a field emission scanning electron microscopy (FESEM) unit. The SEM images of Fig. 3 correspond to the formation of Ni nano-islands on Si wafer with 1nm Ni deposited layer. Ni deposition was done at 100℃ with ebeam deposition. As it can be seen, Ni grain sizes decreases from initial average value of 40-50 nm for normal method to 5-20 nm for the sequential process. The sequential methane flow was repeated for 25 sequences.



(a)



(b)

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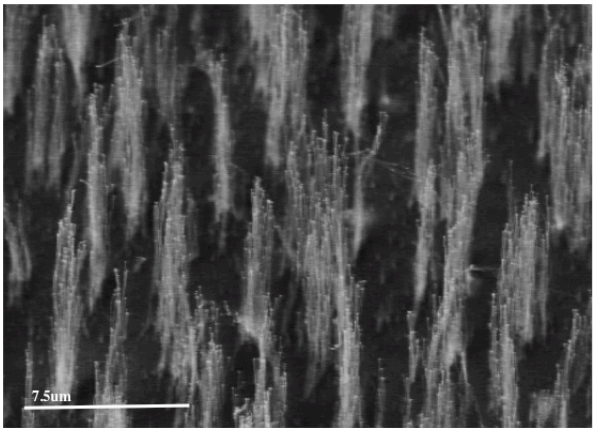
Figure 3: Ni nano-island formation, (a) Sequential method (b) Normal method. Arrows in the top figure show how the neighboring islands do not merge to form greater sizes.

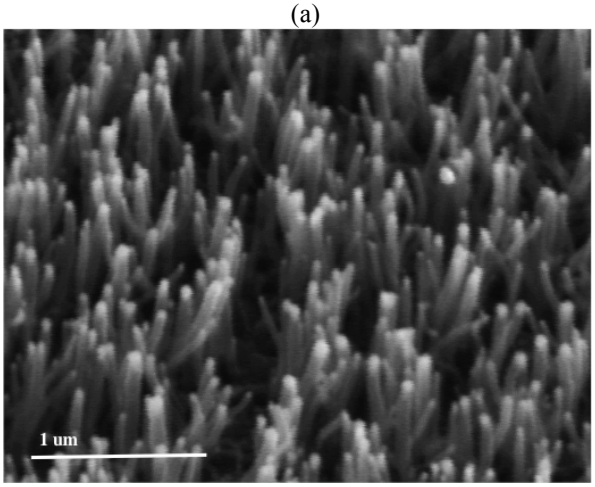
3.2 CNT growth

CNT growth step starts immediately after the two-step pretreatment. Methane (CH_4) and hydrogen were introduced into the chamber for 12 minutes with constant flow of 12 and 8 sccm respectively to initiate the growth.

As we except there was a significant reduction in CNT diameters for the sequential pre-treatment samples. Another remarkable point was the CNT growth rate which shows a good improvement in sequential mode. It was observed that the major CNT height is formed in initial period of growth step that was about 5 seconds. While an equivalent height in normal process was achieved after 12 minutes.



(a)



(b)

Figure 4: CNT growth on Si wafer with 3nm Ni layer, (a) Sequential method (b) Normal method.

The SEM images of Fig. 4 show the CNT growth for the two processes, it can be seen that the average diameter for normal growth is about 30-40 nm, which the value for sequential growth is about 8-15 nm.

On the other hand, vertical arrays of CNTs are made of SWNTs with the diameters of 1.4-2.0 nm according to the Raman spectra RBM peaks (Fig. 5). The significant peaks detected around 120-350cm-1, and the very low-intensity D band in Raman spectra of vertical CNTs indicates that predominately semiconducting SWNTs were synthesized [7].

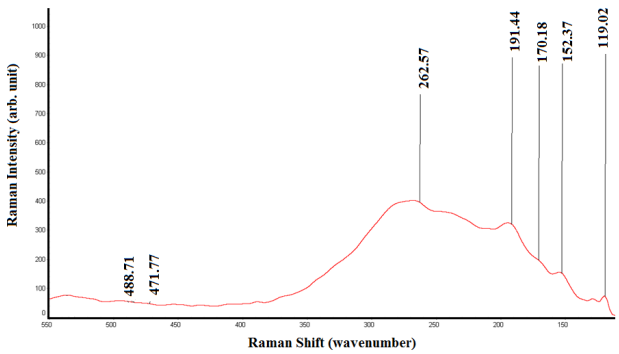


Figure 5: Raman Spectra of RBM mode of SWNT sample, showing significant picks in 120-350 cm^{-1}

SEM images show an effective average of 10 nm reduction in CNT diameters for same catalyst layer thickness. Fig. 6 shows the formation of narrow nanotubes, which seems to agree with the data obtained from Raman spectroscopy.

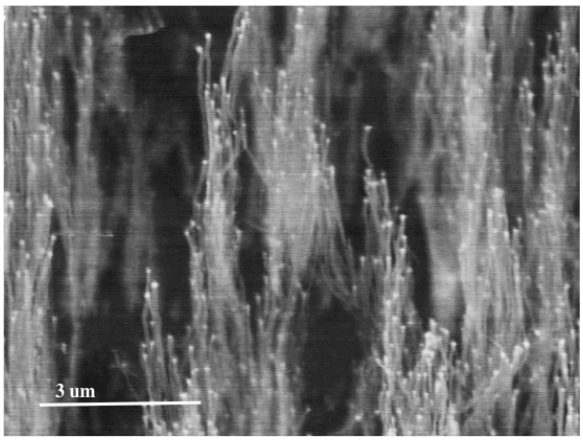


Figure 6: SEM images of CNT growth after sequential pre-growth treatment includes 8-15 nm CNTs.

4 CONCLUSION

A dual-step pre-growth treatment of the surface was performed. First, the surface of the sample was treated with a hydrogen-blow for 15 min. with the substrate temperature at 550-700°C, followed by a treatment of hydrogen plasma. This step was performed in two ways; in a normal process a constant flow of H_2 was introduced to chamber and in a sequential one this constant flow was combined by a

periodic pulse of methane flow at the same temperature of the growth in order to create Ni nano-islands. To avoid Ni-grain agglomeration we developed a new method of hydrogenation consists of several sequences of methane flow to temporally passivate the grains to keep the sizes unchanged. Sweeping different conditions for the methane sequences interesting results were obtained. Immediately after the two-step pretreatment, CH_4 was introduced into the chamber for 12 min. to initiate the growth of CNTs. An effective average of 10 nm reduction in CNT diameters for same catalyst layer thickness was observed in final achievements.

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