

## Effect of ammonia gas etching on growth of vertically aligned carbon nanotubes/nanofibers

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**Abstract:** The etching effect of ammonia (NH<sub>3</sub>) on the growth of vertically aligned nanotubes/nanofibers (CNTs) was investigated by direct-current plasma enhanced chemical vapor deposition (DC-PECVD). NH<sub>3</sub> gas etches Ni catalyst layer to form nanoscale islands while NH<sub>3</sub> plasma etches the deposited amorphous carbon. Based on the etching effect of NH<sub>3</sub> gas on Ni catalyst, the differences of growing bundles of CNTs and single strand CNTs were discussed; specifically, the amount of optimal NH<sub>3</sub> gas etching is different between growing bundles of CNTs and single strand CNTs. In contrast to the CNT carpet growth, the single strand CNT growth requires shorter etching time (5 min) than large catalytic patterns (10 min) since nano dots already form catalyst islands for CNT growth. Through removing the plasma pretreatment process, the damage from being exposed at high temperature substrate occurring during the plasma generation time is minimized. High resolution transmission electron microscopy (HRTEM) shows fishbone structure of CNTs grown by PECVD.

**Key words:** carbon nanotube; ammonia etching; nickel catalyst; plasma enhanced chemical vapor deposition (PECVD)

### 1 Introduction

Carbon nanotube (CNT) is one of the most anticipated nano-materials because of its small dimension and excellent mechanical, electrical, thermal, and chemical properties[1–3]. Various synthesis methods were developed, such as laser ablation, arc discharge, and chemical vapor deposition (CVD)[4–5]. Each synthesis method has its own advantages over other methods, and finds its own potentials in terms of quality and productivity.

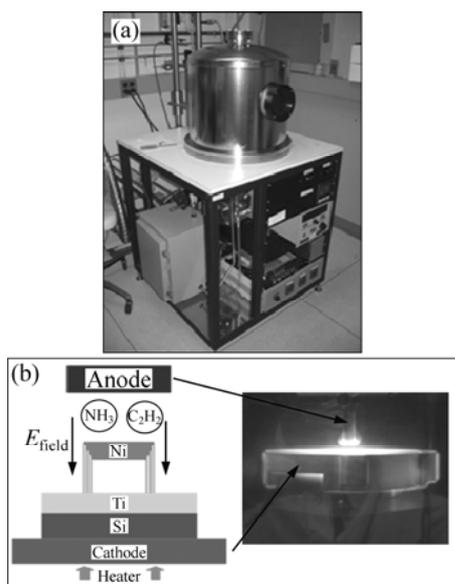
In the recent decade, plasma enhanced chemical vapor deposition (PECVD), has been widely used to grow CNTs vertically[6]. PECVD's capability of growing aligned CNTs at relatively low temperature makes it possible to grow aligned CNTs in an array and single strand configuration together with various catalytic pattern generation techniques. The controlled synthesis of carbon nanotubes/nanofibers (CNTs) by PECVD is an essential step for realizing many functional

nano devices and technologies[7]. However, the vertical CNT growth mechanism remains unclear although there are many studies on the CNT growth by PECVD[8–9].

NH<sub>3</sub> pretreatment before plasma generation may be the key control parameter in the CNT growth with the form factors of islands in catalyst layers[10]. In this work, the effect of NH<sub>3</sub> gas etching on the growth of CNTs in forest form and a single strand array was investigated, and different roles of NH<sub>3</sub> gas in both forms of CNT growth were discussed.

### 2 CNT growth in PECVD

Vertically aligned CNTs are grown on a patterned Ni sample using a home-built PECVD shown in Fig.1(a). It is generally accepted that CNTs can be grown by three steps: the decomposition of the hydrocarbon gas (in this work, acetylene (C<sub>2</sub>H<sub>2</sub>) was used over a catalytic metal (nickel (Ni)), the diffusion of the carbon atoms through the bulk and the surface of the islands of catalyst layer, and subsequent precipitation of the carbon atoms beneath



**Fig.1** Home-built PECVD (a) and schematic of CNT growth by plasma (b)

the islands in the tube form of graphene layers (see Fig.1(b))[10–12].

With the mechanism of the CNT growth by electric field, CNTs were grown in PECVD. To investigate the effect of  $\text{NH}_3$  etching, two types of Ni catalyst samples were prepared: one for a forest of CNTs and the other for single strand CNTs. For growing a bundle of CNTs, a rectangular marker was patterned in to  $30\ \mu\text{m} \times 300\ \mu\text{m}$  size through the photolithography processes. Before

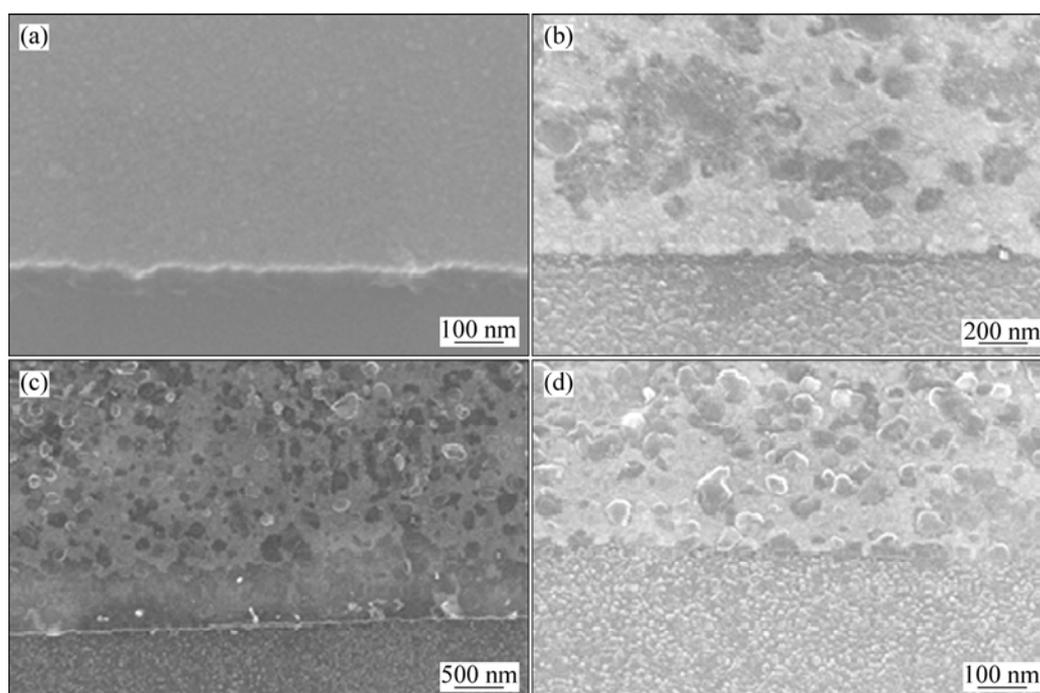
depositing a nickel (Ni) catalytic layer, 25 nm-thick titanium (Ti) layer was deposited on a Si wafer to promote the adhesion of Ni to the Si wafer and prevent catalyst silicide formation at the high temperature during the CNT growth. To investigate the effect of  $\text{NH}_3$  etching on single strand CNTs, Ni dots (100–200 nm in diameter) were patterned on a p-type B doped Si wafer (100).

Each prepared sample was loaded in a PECVD chamber evacuated by rotary and turbo-molecular pumps to a base pressure ( $<1.33 \times 10^{-4}$  Pa) to eliminate impurities and water vapors. When the desired pressure reached, the sample was heated to  $580\ ^\circ\text{C}$ , and at this temperature only  $\text{NH}_3$  gas without igniting plasma was introduced at  $160\ \text{cm}^3/\text{min}$  to make the islands of Ni catalyst. Then,  $\text{C}_2\text{H}_2$  was introduced into the chamber for 1 min, and the plasma was ignited for the CNT growth simultaneously while  $\text{NH}_3$  was introduced. CNTs were grown at a gas mixture of highly purified (99.99% purity)  $\text{C}_2\text{H}_2$  and  $\text{NH}_3$ ,  $50\ \text{cm}^3/\text{min}:160\ \text{cm}^3/\text{min}$ . After the CNT growth time, the plasma was turned off, and the heater was cooled down slowly to prevent the CNT damage from the sudden change of temperature.

### 3 Results and discussion

To verify the etching effect of the  $\text{NH}_3$  gas, the surface of Ni catalyst layer with 15 nm in thickness after  $\text{NH}_3$  introduction for different time was examined.

Fig.2(a) shows a FESEM image before  $\text{NH}_3$  introduction, and Figs.2(b)–(d) show the results after



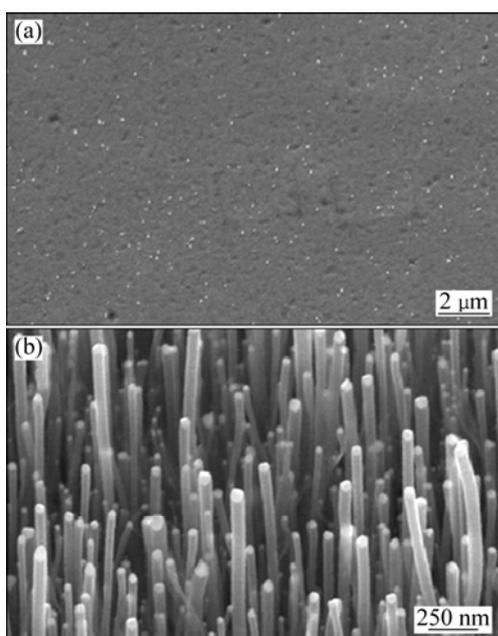
**Fig.2** FESEM images of Ni catalyst layer with thickness of 15 nm before  $\text{NH}_3$  introduction (a) and after  $\text{NH}_3$  introduction for 5 min (b), 10 min (c) and 15 min (d)

NH<sub>3</sub> introduction for 5, 10, and 15 min. As the NH<sub>3</sub> introduction time increases, it is found that catalyst islands are formed by the NH<sub>3</sub> etching process. As shown in Fig.2(b), a wide excavated area is formed after 5 min. After NH<sub>3</sub> introduction for 10 min, islands for the CNTs growth are formed on the catalyst layer. Over 15 min, Ni islands still exist.

To check the role of the substrate temperature, Ni catalyst layer was annealed for 10 min without NH<sub>3</sub> gas. However, there is no Ni island even with 1 h heating. These experimental results confirm the role of NH<sub>3</sub> gas as an etchant. Without heating substrate, however, the catalyst islands are not formed even during NH<sub>3</sub> gas introduction. From this phenomenon, it is expected that high substrate temperature leads to the increase of the surface energy and the mobility of Ni atoms. Finally, it will help Ni thin film to be cracked for forming islands.

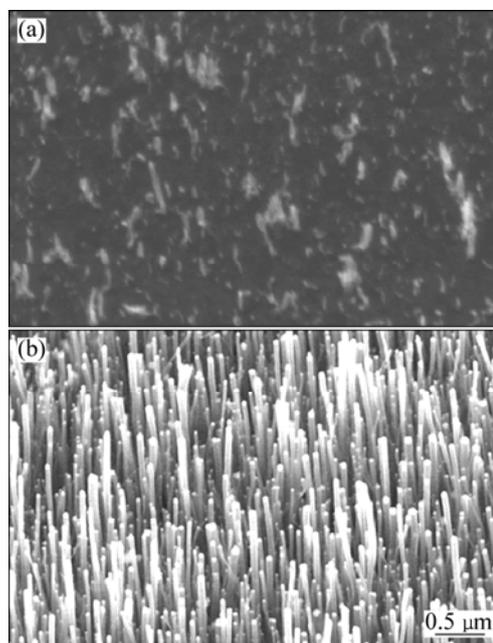
Fig.3 shows CNT growth results from different etching times before generating the plasma to grow CNT. As shown in Fig.3(b), CNTs are grown well after forming islands by NH<sub>3</sub> etching effect. This result further confirms that the island formation by NH<sub>3</sub> etching is essential for the CNT growth. In general, NH<sub>3</sub> pretreatment for catalyst island formation by etching is achieved by NH<sub>3</sub> plasma for 10–40 min[12–13]. However, the high substrate temperature occurring during plasma exposing for a long time can give damage to the other component when CNT applied devices are made. By reducing the plasma ignition time, the selection of materials will be more flexible in the design of a device.

Growing single strand CNTs differs from growing a



**Fig.3** CNTs growth results from different etching time before generating plasma to grow CNT: (a) 5 min; (b) 10 min

bundle of CNTs as individual nano dots work like the islands formed by NH<sub>3</sub> etching process. With reference to several previous papers for film thickness to grow CNT forest and single strand CNTs[13–14], a thin Ni film (15 nm) is applied with NH<sub>3</sub> for 5 min before growing CNTs. However, there is no CNT on Ni catalyst film. Fig.4(a) shows FESEM image of CNT growth in carpet film with a thickness of 15 nm. As shown, CNTs are grown sparsely on carpet film. After increasing NH<sub>3</sub> etching time to 10 min, CNT forest and single strand CNTs are grown. Fig.4(b) shows the well grown CNTs on the carpet film. From these results, it can be seen that the balance between the thickness of catalysts and the NH<sub>3</sub> etching time is one of the most important parameters in growing CNTs by PECVD.

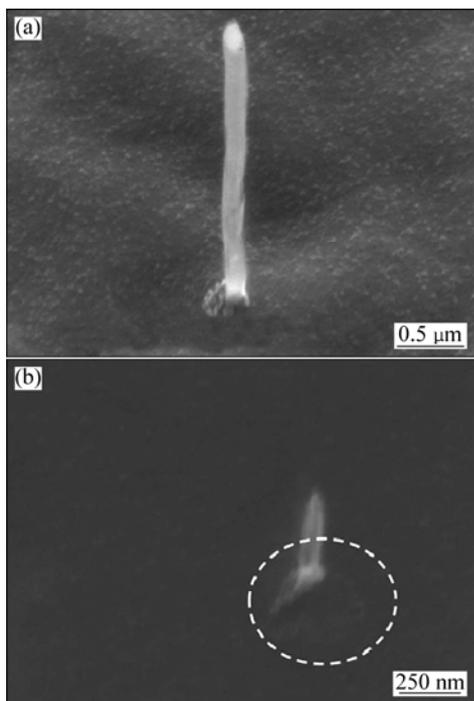


**Fig.4** FESEM images of grown CNTs after NH<sub>3</sub> etching for 5 min (a) and 10 min (b) on thin film

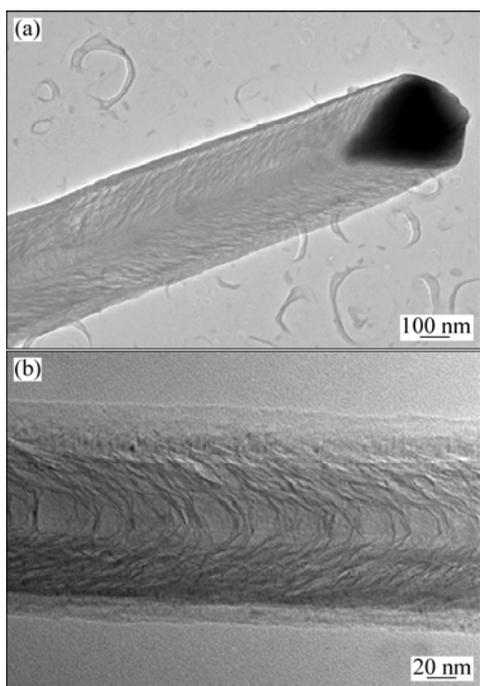
Under the same conditions, single strand CNT was grown on single nano dot. Fig.5(a) shows the vertically aligned single strand CNT on single nano dot with a thickness of 15 nm. In this case, the shorter NH<sub>3</sub> gas etching time of 5 min is required as the Ni dots are already formed before the growth process. As shown in Fig.5(b), however, well grown single strand CNT cannot be obtained. In the middle of the white dot circle, the trace of Ni dot is shown instead of CNTs. It is the evidence of over-etching by NH<sub>3</sub>. To investigate the necessity of NH<sub>3</sub> etching in single nano dots, the growth of CNTs on the single nano dots without NH<sub>3</sub> introduction was tried, but vertically aligned single strand CNTs cannot be obtained.

From this experimental result, it is expected that NH<sub>3</sub> pretreatment in gas phase has not only the role in

generating catalyst islands by etching effect, but also the unknown role in growing single strand CNTs on single nano dots. High resolution transmission electron microscopy (HRTEM) images of CNT's top and body show fishbone structures with multiple layers parallel to the outer surface of the Ni catalyst surrounded by disordered outer layers along the CNT axis, as shown in Fig.6.



**Fig.5** FESEM images of grown CNTs after  $\text{NH}_3$  etching for 5 min (a) and 10 min (b) on single nano dot



**Fig.6** HRTEM images of CNT with fishbone structures: (a) Top; (b) Body

## 4 Conclusions

1) With different  $\text{NH}_3$  gas inserting time into the chamber, Ni catalyst islands are formed over 10 min  $\text{NH}_3$  introduction time. Under this condition, well vertically aligned grown CNTs are obtained. By removing the plasma pretreatment process, the damage of the substrate from being exposed at high temperature for a long time by plasma ignition can be minimized and flexible substrate choices in making CNTs integrated devices can be obtained.

2) Through the comparison with a large area patterned sample and single nano dot, it is found that a single nano dot needs shorter  $\text{NH}_3$  etching time than a large area patterned one to grow CNTs as a single dot forms catalyst island already.

3) Different  $\text{NH}_3$  etching times are optimized for a bundle of CNTs and single strand CNTs, and successful growth of vertically aligned single strand CNTs is achieved repeatedly.

4)  $\text{NH}_3$  in the gas state, not in plasma state, has the etching effect and is one of the most important factors that should be considered in CNTs growth by PECVD. This finding of  $\text{NH}_3$  etching effect in the gas phase introduces the well grown CNTs to a wide range of opportunity for the integration into MEMS and NEMS devices.

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