

# Alignment Characteristic and Mechanism of Carbon Nanotubes Synthesized by Hot Filament Chemical Vapor Deposition in a CH<sub>4</sub>/H<sub>2</sub> Plasma

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## ABSTRACT

Carbon nanotube films have been synthesized on nickel coated silicon wafer substrate using hot filament chemical vapor deposition under various bias and discharge conditions in a CH<sub>4</sub>/H<sub>2</sub> gas mixture. Growth of carbon nanotubes aligned at different angles with respect to the substrate normal has been achieved by applying a negative bias to the substrate holder and initiating a DC plasma discharge between filament and substrate. The nanotubes located far enough from the substrate edges are completely vertically aligned, while the nanotubes around the sample edges are pointing away from the sample center and the alignment angle depends on the distance between the nanotube location and the sample edge. The orientation of the nanotubes appears to be determined by the direction of the electric field lines on the surface of the substrate. Only randomly oriented nanotubes can be obtained when no bias or a positive bias was applied to the substrate holder. The results suggest that the bombardment of ions is the determining factor in the alignment of CNTs.

**Keywords:** aligned carbon nanotubes, hot filament chemical vapor deposition, ion bombardment, plasma

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have attracted great attention in the past decade due to their interesting properties and potential applications. CNTs usually grow as a tangle network of quasi-one-dimensional structures. Unless made to be aligned, many of their unique properties can not be fully exploited. Several methods for growing aligned CNTs were developed in the last few years [1-14]. The alignment of the tubes was achieved by (i) embedding nano-particles of the catalyst in nanopores [1,2], (ii) utilizing very dense tube growth which forces the tubes to align parallel to each other [3-5] and (iii) by growth under plasma conditions and/or by application of a bias voltage to the substrate [6-14]. The alignment orientation was mostly limited to the direction perpendicular to the substrate [1-12]. There was a report in literature demonstrating plasma-enhanced chemical vapor deposition (PECVD) growth of CNTs aligned at ~ 45° to the substrate [13]. Recently, carbon nanofibers aligned at a variable angle to the substrate was achieved using PECVD in a gas mixture of C<sub>2</sub>H<sub>2</sub> and NH<sub>3</sub> when the substrate was located close to the edge of the substrate holder [14].

Most studies have been focused on the vertical alignment of CNTs using PECVD [6-12]. The nanotube growth was found always to occur perpendicular to the local substrate surface regardless of the substrate tilt or shape in a microwave PECVD

process [8]. The electrical self-bias imposed on the substrate surface appears to be the primary mechanism responsible for the conformational alignment. Hayashi *et al.* [7] suggest that force toward the plasma caused by the local electric field in the sheath and negative charge at the top of nanotubes assist them to grow perpendicular to a substrate in a dc discharge. Merkulov *et al.* [14] noticed that the alignment of carbon nanofibers is controlled by the direction of electric field lines during the synthesis process. While researchers agree that CNTs are aligned due to the presence of electric field in a PECVD process. It is not clear whether the mechanism is simple electrostatic attraction of the tubes, preferential etching, or some other effect. In most studies, the growth of aligned CNTs was achieved by negatively biasing the substrate. However, Avigal *et al.* [9] observed that aligned CNTs occurred only when a positive bias was applied to the substrate.

In order to understand the alignment mechanism and to control the orientation of CNTs, detailed investigations of the role of plasma and electric field to the alignment of the CNTs is necessary. Here we report the growth of CNTs using hot filament chemical vapor deposition (HFCVD) in a CH<sub>4</sub>/H<sub>2</sub> gas mixture under various bias and discharge conditions. Aligned CNTs occurred only when a plasma was initiated and a negative bias was applied to the substrate. A gradient radial orientation distribution of CNTs was revealed around the edges of the samples. The results show that the bombardment of ions has substantial effect on the alignment of CNTs and that the bombardment direction of ions determines the alignment orientation of CNTs.

## 2 EXPERIMENTAL METHODS

The CNTs were grown using a hot filament chemical vapor deposition system. Pieces of p-type (100)-oriented mirror polished Si wafers were employed as the substrates. A thin nickel (Ni) film of thicknesses 5 – 50 nm deposited by DC sputtering inside the deposition chamber was used as catalyst. After the catalyst layer was deposited, CNTs were grown on the Ni coated Si substrate by HFCVD. Filament used was coiled tungsten wire of diameter 0.3 mm. The distance between filament and substrate was 8 mm. A DC bias voltage was applied between filament and substrate holder. After the deposition chamber was pumped down to a base pressure of 2×10<sup>-2</sup> Torr using a rotary pump, methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) were introduced. The H<sub>2</sub> flow was maintained by mass flow controller at 50 sccm. The CH<sub>4</sub> feed gas was maintained using a separate mass flow controller. The CH<sub>4</sub> flow ratio (CH<sub>4</sub> : H<sub>2</sub>) was varied from 2 to 25%. When the working pressure was stabilized at 6 Torr, a current was passed through tungsten

filament coil and the dc bias power supply was turned on. Experiments were performed with the substrate holder biased (a)  $-300\text{ V}$  to  $-400\text{ V}$ , corresponding to a discharge current from 0 to 100 mA; (b)  $150\text{ V}$  to  $400\text{ V}$ , a discharge current of 0 to 200 mA, and (c) without bias. The substrate temperature measured using a thermocouple varied from  $400$  to  $650^\circ\text{C}$ . The specimens obtained were characterized by Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). We here note that any pretreatment for the surface of catalyst-metal thin films, i.e. an exposure to  $\text{NH}_3$  gas or ion etching was not necessary for growing CNTs in our case.

### 3 RESULTS AND DISCUSSION

Nanotubes grown without bias voltage, no matter how other parameters were varied as indicated above, are randomly oriented, as shown in Figure 1. In this case, no electric field or plasma was present, the nanotubes grew only by thermal decomposition of  $\text{CH}_4$ .

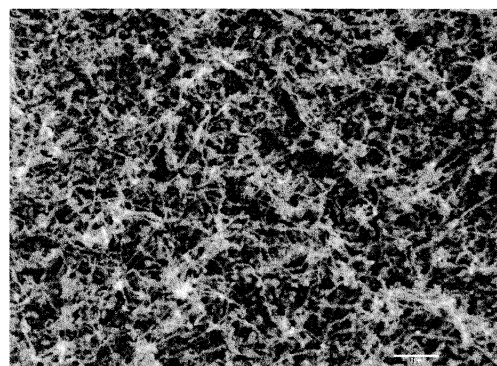


Figure 1: SEM micrograph of carbon nanotubes grown without bias.

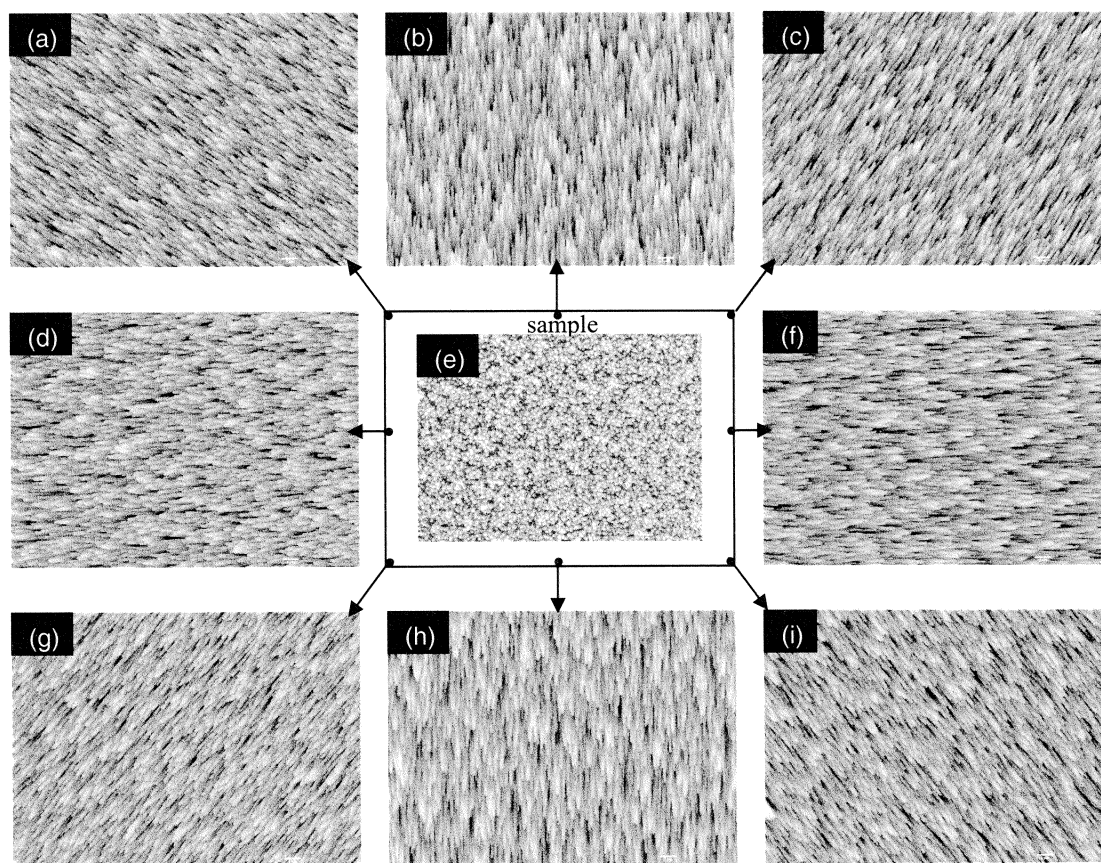


Figure 2: A schematic representation of a sample and SEM images showing the resultant CNTs at different locations around the substrate in the edge region and the center : (a) top-left corner, (b) top edge, (c) top-right corner, (d) left edge, (e) center, (f) right edge, (g) bottom-left corner, (h) bottom edge, (i) bottom-right corner.

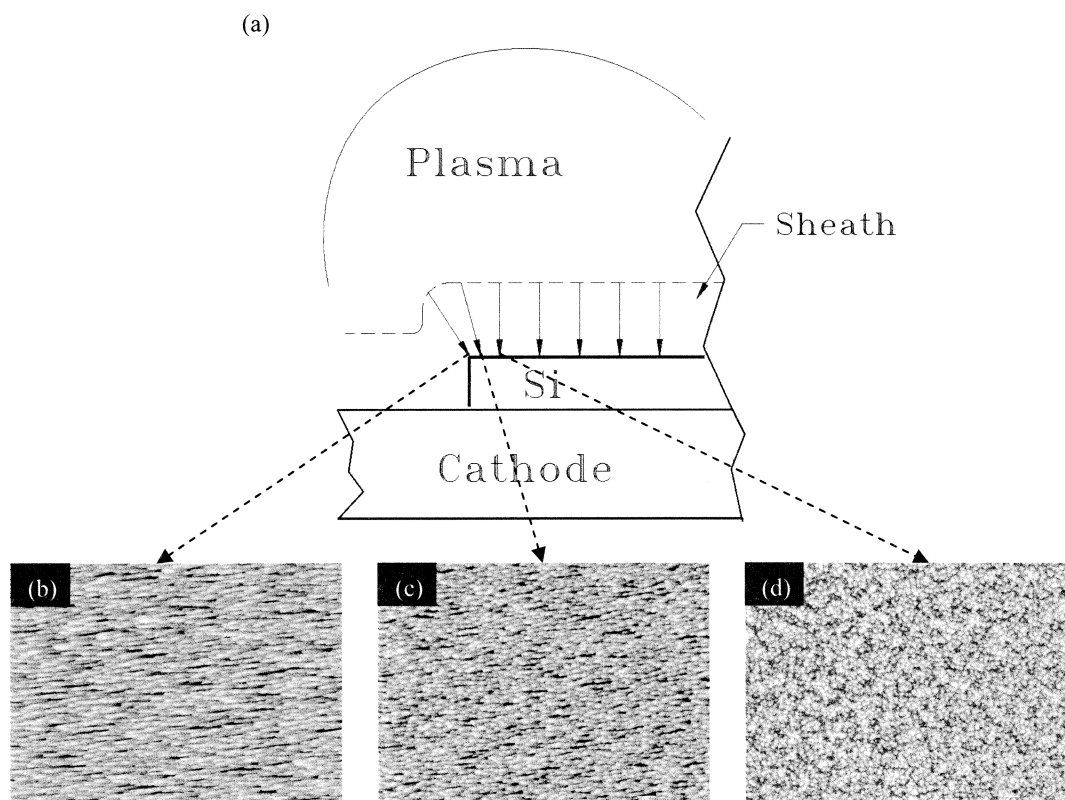


Figure 3: (a) A cut-away view of the substrate and electric field lines in the sheath around the sample and SEM images showing the resultant CNTs located at (b) the edge, (c) 200  $\mu\text{m}$  from the edge, (d) 500  $\mu\text{m}$  from the edge.

Next we created a plasma between the substrate holder and the filament. We prepared samples at various discharge currents varying up to 200 mA. Well-aligned CNT's were obtained when substrate holder was the cathode, even if the discharge current was as small as 25 mA at a discharge voltage of -300 V. SEM images showing the resultant CNTs located at different regions of the sample are shown in Figure 2 and 3. Around the central region of the samples, the nanotubes are perpendicular to the substrate surface, as shown in Fig. 2 (e) and Fig. 3 (d). At the regions around the sample edges, the nanotubes with variable alignment angle and orientation were observed, as shown in Fig. 1(a)-(d), Fig. 1 (f)-(i) and Fig.3 (b), (c). The nanotubes are pointing away from the sample center and the alignment angle depends on the distance between the CNT location and the sample edge. The gradual change of the alignment angle as the location moves from edge to center is illustrated in Fig.3. At the very edge, the nanotubes, as shown in Figure 3 (b), are aligned at a largest angle to the substrate normal. With increasing distance from the edges, the CNTs are aligned closer to substrate normal, as shown in Figure 3 (c). CNTs located far enough from the edges are completely vertically aligned, as shown in Figure 3 (d). When other growth parameters such as gas flow ratio, substrate temperature and Ni film thickness were varied as indicated in section 2, same phenomena were observed.

Figure 4 shows TEM image of a typical carbon nanotube. It clearly shows that the nanotube is centrally hollow tube, not solid fiber. The outside diameter of this carbontube is nearly 50 nm. The inside hollow diameter is nearly 25 nm.

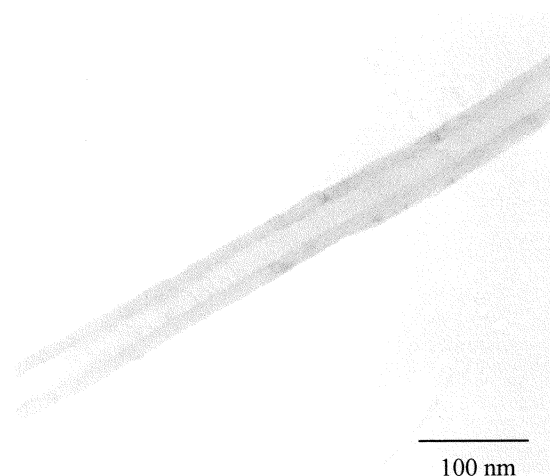


Figure 4: TEM image of a typical carbon nanotube.

Recently, it was described by Merkulov *et al.* [14], and Chen *at al.* [13] what seems to be a plausible and mutually complimenting reason for this alignment. The situation in our experiment is similar. In the presence of plasma between filament and substrate holder, the plasma surrounds all faces of the sample. The substrate surface is bombarded by positive ions along the electric field lines on the sample. The lines of electric field between the sample surface and the plasma are expected to be as shown in Figure 3 (a). The electric field lines around the central regions of the samples are oriented perpendicular to the sample surface. However, the direction of the field lines deviates from the substrate normal at the substrate edges. The closer toward the edge, the greater the angle deviates from the substrate normal. At the very edge, the electric field lines deviate most from the substrate normal. As the distance away from the edge increases, the field line angle deviates from the substrate normal decreases until the lines become completely vertical to the substrate surface. In the presence of the plasma, the conducting nickel particles on tip of each CNT, will be charged to a negative potential, called the floating potential of the plasma. These negatively charged particles would then move towards the anode, away from the cathode, giving rise to growth of aligned CNTs. Thus the alignment orientation of the nanotubes depends both on the direction of the electric field lines as well as the presence of plasma.

This is evident from the fact the well aligned tubes are achieved only in the presence of plasma and with substrate holder as cathode. We prepared samples with substrate holder as anode and the resulting CNTs were randomly oriented. Even a negative bias voltage (−300 V to −400 V) was applied to substrate holder, and if no plasma was generated between filament and substrate holder, the resultant nanotubes were randomly oriented, similar to the case of 0 V bias.

As described by Merkulov *et al.* [14] the flux of ions incident on the substrate could also play an important role in the alignment of CNTs. It is reasonable to assume that the alignment were due to preferential ion etching in the direction perpendicular to the electric-field lines. Because of the preferential etching, the nanotubes perpendicular to the electric-field lines was preferentially etched, consequently, the resultant nanotubes were aligned along the direction of electric field lines.

#### 4 CONCLUSION

Growth of carbon nanotubes using HFCVD under different bias conditions was investigated. Aligned nanotubes can only be synthesized when a plasma was generated and a negative bias voltage was applied to substrate and the orientation of the nanotubes appears to be determined by the direction of the electric field lines. The results show that the bombardment of ions is the determining factor in the alignment of CNTs and that the bombardment direction of ions determines the alignment orientation of CNTs. Consequently, the alignment of CNTs can be well controlled by the bombardment direction of ions.

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