Low-temperature Growth of Vertically Aligned Carbon Nanotubes on a Glass Substrate Using Low Power PECVD

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Abstract. In the traditional PECVD method for growing carbon nanotubes (CNTs), the electric field is an important parameter. Its role is to orient CNT growth and dissociate the H-C bond from hydrocarbon gases. Therefore, high energy ions, molecules, and radicals as plasma elements can affect the verticality of CNTs. In this paper, a new configuration for an electric field for the growth of field-oriented and long CNTs on a glass substrate at temperatures below 400°C is reported. Simulation and experimental data show that CNTs are grown at a considerably lower voltage than traditional methods. Using this method, growing vertical CNT on such low-cost substrate glass is more possible for CNT-based devices and bio-applications where price is important.

Introduction

Carbon nanotubes (CNTs) have been the center of attention for many researchers mainly because of their unique electronic and mechanical properties, but also because of their specific applications, such as field effect transistor [1], solar cell [2], field emission devices [3-6], sensors [7], and in bio-applications [8]. One of the most important areas of research on CNTs is their synthesis method. Among the numerous methods developed for the synthesis of CNTs, arc-discharge [9], laser vaporization [10], pyrolysis [11], thermal chemical vapor deposition [12], and plasma-enhanced chemical vapor deposition (PECVD) [13] are the most common.

PECVD is the most common method of CNT synthesis because of its ability to grow vertically-aligned CNTs. However, growing CNTs using PECVD typically involves temperatures higher than 500°C. Such temperatures and the high intensity of plasma in the growth region which is used to decompose gases atoms and determine growth direction, can damage the substrate and CNTs growth. Therefore, the choice of a substrate material could be limited [13-15].

Various methods have been utilized to produce CNTs at low temperatures, including the two-zone reactor [16], microwave plasma enhanced chemical vapor deposition (MPECVD) [17], and AC-DC-PECVD techniques which we introduced in our previous report [18]. With these methods, limitations on choice of substrate have been eliminated, but a high applied voltage for dc bias is needed, which causes high plasma intensity. This condition causes damage to the substrate because of high energy ion bombardment. Ion-induced damage can be considered as plasma intensity damage [19], so plasma intensity damage remains as a challenging problem.

In our previous work [18], an AC-DC-PECVD method was developed using a two-stage plasma technique for low-temperature growth of CNTs on glass substrates. We used the AC plasma as remote plasma in the first stage to decompose atoms of gases into ions, electrons, and radicals. These particles were brought to the second stage, in which, by applying the DC plasma, CNTs were grown directly on the substrate. This two-stage method is the most suitable technique for growing CNTs at low temperatures. However, AC plasma can cause substrate damage because of high energy ion bombardment [19]. This can also affect the direct (DC) plasma which leads to changes in the vertical alignment of CNTs. The intensity of the DC region is an important parameter in determining the shape and geometry of CNTs on the substrate. Controlling the intensity of DC
plasma in this method is difficult, and poor control of intensity can adversely affect the CNTs growth direction resulting in CNTs with poor alignment.

In this paper, we report a low-temperature DC-PECVD method for growing vertically aligned CNTs on silicon oxide and glass substrates at 400°C using acetylene (C2H2). In this modified method, the remote (AC) plasma, which was used in AC-DC-PECVD, and consequently all its adverse effects have been eliminated. The DC plasma anode plate and the distance between the anode and cathode plates are utilized to create radicals which play the main role in CNT growth and cause the creation of uniform plasma in the growth region. These conditions remove all adverse plasma effects and lead to the synthesis of long and vertically aligned CNTs at low growth temperatures.

Experimental

**CNT synthesis setup.** Fig. 1 (a) shows the schematic diagram of the modified PECVD system which is used for CNT growth in this work, and Fig.1 (b) illustrates the schematic diagram of plate configuration in the AC-DC-PECVD system which was used in our previous work [18]. In the modified configuration, the anode and cathode structures are the main features. A horizontal quartz reaction chamber and a turbo-mechanical pump provided vacuum inside the reaction chamber. More details about this system are provided in ref [18]. As is clear from Fig.1, the modified PECVD system differs from the AC-DC-PECVD system in that its AC power generator is eliminated and the configuration of the anode and cathode plates is different. Modified PECVD uses only a DC power supply to generate DC plasma. As shown in Fig.1 (a), the system comprises two separate plates, the cathode plate and the substrate plate, which are connected electrically outside the reaction chamber. The cathode and anode plates are perpendicular.

![Fig.1 Schematic diagram of (a) the PECVD system for carbon nanotube growth on a glass substrate, and (b) plate configurations of the AC-DC-PECVD system.](image)

**CNT synthesis procedure.** The typical RCA cleaning method was used to clean the glass and silicon substrates before synthesis. A 10 nm thick Ni thin-film was deposited on the substrates by electron-beam evaporation to act as catalyst for PECVD growth. H2 gas at a flow rate of 100 sccm was used during the growth process as the carrier gas, and acetylene as the source gas was introduced to the reaction chamber at a flow rate of 25 sccm. With this method, we were able to grow CNTs at 400°C for 20 minutes. The grown CNTs were characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The traditional PECVD method and the modified
method were simulated by the commercial 3D electrical field and particle calculation software package CST STUDIO SUITE.

Results and Discussion

Experimental data. To compare the effect of plasma damage on substrate and vertically aligned CNTs, we synthesized CNTs at high temperatures (650°C) using the traditional PECVD method, at low temperatures (400°C) using AC-DC-PECVD, and finally by utilizing our proposed modified DC-PECVD method. Fig. 2 shows the SEM images of various samples grown at different temperatures using different configurations of PECVD. In this part of the work, silicon was used as the substrate because of the high temperatures used in the growth process. Fig. 2 (a) shows vertically aligned CNTs grown using PECVD at a temperature of 650°C with a plasma power of 2.5 W/cm². For this sample, plasma damage on the substrate was negligible, because silicon is as hard a material as the substrate. When the temperature was reduced to 550°C and 400°C, significant negative effects of temperature decrease on CNT growth were observed. Bends in the carbon nanotube and amorphous carbon were seen. This effect is clear in the SEM images shown in Figs. 2 (b) and 2 (c). Optimum CNT growth was achieved at 650°C while the plasma power was 2.5 W/cm². However, the fact that the growth process occurs at high temperatures makes this method suitable only for specific substrates (such as silicon) which have high melting points.

Fig. 2 SEM images of CNTs grown using PECVD on Si substrate at various temperatures of (a) 650°C, (b) 550°C, (c) 400°C with plasma power of 2.5 W/cm².
As mentioned earlier, the AC-DC-PECVD method was used for low-temperature CNT growth. In this technique, active radicals that are produced by the AC plasma and the heating process play a key role, because the mean free path of the active radical permits the growth of CNTs in low-temperatures [18-20]. Fig. 3 shows the SEM image of CNTs grown at 400°C on a glass substrate using this method. In these images, 1000V AC plasma was used to produce active radicals. As is clear from the figure, CNT growth was vertically oriented, and the height of CNTs was about 2µm. The effect of AC Plasma on the vertical alignment of the CNTs can also be observed in the figure. The curvature in the CNTs, which can be seen in Fig. 3(a), was caused by the AC plasma on the DC plasma which directly causes CNT to grow. Because the distance between the AC plasma region and the DC plasma is dependent on the mean free path of active radicals [18], this distance is not more and it is fixed. This effect can be observed as a bend in the shape of the CNTs, as shown in Figs. 3(a) and 3(b).

![Fig. 3 SEM image of CNTs grown at 400°C on a glass substrate using the AC-DC-PECVD method: (a) high magnification image; (b) low magnification image.](image)

As previously mentioned, the intensity of the AC plasma affects the low-temperature growth of CNTs. AC power is an important parameter which makes the active radicals for CNT growth. Unfortunately, however, the AC plasma intensity can damage vertically aligned CNTs and the substrate. Fig. 4 shows the SEM micrograph of various CNT samples grown at 400°C with different AC plasma intensities. In these images, the adverse effects of AC plasma intensity are quite clear. Fig. 4 (a) shows CNTs grown with a plasma power of 5.5 W/cm². As is clear from Fig. 4 (a), the growth is complete, but the plasma affected the vertically aligned CNTs by causing them to become curved. So, the AC plasma power was decreased to eliminate its adverse effect. Figs. 4 (b) and 4 (c) show the SEM micrographs for a sample obtained with lower plasma power (3.5 W/cm² and 1.5 W/cm², respectively). As can be seen from these images, the growth is not perfect, more impurity was observed, and there are still curvatures in the CNT structures. Active radicals are created by AC plasma; thus, when the AC plasma power decreases, there are not enough active radicals in the region to promote the growth of CNT. In these samples, growth was not perfect, because the amount of active radicals for CNT growth depends on AC plasma power in this method [18]. For the sample in Fig. 4 (d), the AC plasma power was increased to 8 W/cm² in order to produce more active radicals, and its destructive effect on the glass substrate is obvious in the figure.

To eliminate the adverse effects of plasma intensity, a new method is introduced in this work. As illustrated in Fig. 1(a), the anode plate is exposed to higher temperatures than the cathode plate. At the anode plate, gases are decomposed into ions, electrons and radicals. The distance between the anode and the cathode plate allows the radicals to be transferred to the lower temperature region uniformly with low plasma intensity at the cathode plate. This condition at the cathode plate leads to the growth of long and fully vertically aligned CNTs without the damage caused by plasma on the substrate and CNTs.

Fig. 5 shows SEM micrographs of CNTs grown using our proposed method at the temperature of 400°C on a glass substrate with a plasma power of 1.2 W/cm² (240 V and 20 mA). These images
indicate the uniform distribution of CNTs as well as their vertical alignment. The height of the CNTs is about 2µm, and there is no impurity or damage to the substrate and CNTs. The vertical alignment of the carbon nanotubes is clear from the cross-sectional SEM image of CNTs. Furthermore, there is no curve in the CNT structure, so the effect of plasma on the shape and geometry of the CNTs has been eliminated.

![SEM micrographs of CNTs grown at 400°C on glass substrates with different AC plasma intensities.](image)

**Fig. 4** SEM micrographs of CNTs grown at 400°C on glass substrates with different AC plasma intensities of (a) 5.5 W/cm², (b) 3.5 W/cm², (c) 1.5 W/cm², (d) 8 W/cm².

![Cross-Sectional and top view SEM micrograph of CNTs grown at 400°C using our proposed method.](image)

**Fig. 5** (a) Cross-Sectional and (b) top view SEM micrograph of CNTs grown at 400°C (1.2 W/cm²) using our proposed method.

Finally, Fig. 6 shows the effects of plasma intensity on the quality of the CNT shape. These two SEM images show samples obtained under identical conditions in terms of temperature, gas flow and time, and different plasma configurations. Fig. 6(a) shows results from the AC-DC-PECVD method, and Fig. 6 (b) shows results from the modified PECVD method. It seems that the modified method caused a decrease in CNT wall damage and increased the verticality and length of the CNTs.
because of the plasma affects. Therefore, using the modified configuration of plasma, all adverse effects of AC plasma were eliminated, and long vertically-aligned CNTs could be grown.

Fig. 6 SEM micrographs of long and vertically-aligned CNTs grown at 400°C using the (a) AC-DC-PECVD method, and (b) modified method.

To investigate the quality of grown CNTs, Raman spectrometry was used. Raman spectrometry is a nondestructive tool used for the morphological characterization of carbonaceous materials. Fig. 7 compares Raman spectra of CNTs grown using the modified PECVD and AC-DC-PECVD methods. Two prominent bands are seen in the Raman spectroscopy of the CNTs: The D band around 1350 cm\(^{-1}\) and the G in the vicinity of 1580 cm\(^{-1}\). The D band originates from a hybridized vibrational mode related with graphene edges, and it refers to the presence of some disorder in the graphene structure. The G band is related to the ordered carbonaceous structures. Raman spectroscopy of the CNTs defines the ratio of the D-band intensity to the G-band intensity for determining the quality of the CNT structure. This ratio is known as the R-value [21].

The Raman spectra of the CNTs grown using AC-DC-PECVD show a D/G ratio of about 1.23, representing the high amount of defect density in their structure. This ratio in CNTs grown with the modified method is 1.01, which indicates the high quality of the CNTs. It can be said that eliminating AC plasma causes a decreased effect to CNT structure.

Other bands shown with Raman spectroscopy were at the low frequency end of the spectrum and are known as Radial Breathing Mode (RBM) bands. These bands at MWCNTs are not prominent, because the outer tubes control the inhalation mode. The more major D band in MWCNTs is...
predictable to a certain extent, given the multilayer configuration, and it refers to more disorder in the structure [21-22].

**Simulation data.** To understand the effect of plasma damage, the traditional PECVD method and our proposed modified PECVD method were simulated using CST STUDIO SUITE software. In this simulation, we designed the vacuum chamber and anode/cathode plates in accordance with Fig.1 (a). To simulate plasma, the electric potential of each plate was defined like the experimental CNT growth process conditions. Anode and cathode voltages were adjusted to 240 volts and near zero, respectively.

Fig. 8 shows the direction of the electrical field and radical movement for our modified method and the conventional PECVD method. The obtained simulation results for our proposed method (Fig. 8 (a)) indicate that electrical field lines move from the anode plate to the cathode plate. This configuration suggests that radicals, which are created at the anode plate, move toward the cathode plate. These conditions also exist for the traditional PECVD method. But to create this state, different conditions must exist. For example, plasma intensity and temperature growth is different with the modified method. The electrical field direction affects the movement of the radical which is clear from the simulation results shown in Fig.8. The presence of active radicals at the cathode plate will result in CNT growth. The amount of active radicals depends on the electrical field direction and plasma intensity.

Fig. 8 Simulation of the electrical field direction during CNT growth process for (a) the modified PECVD method (maximum electrical field is shown in red (39658 \( V/m \))) and (b) the conventional PECVD (maximum electrical field is shown in red, 35125 \( V/m \)).

Figs. 9 (a) and 9 (b) clearly illustrate the distribution of electric potential. In these figures, the maximum electrical potential (240 v) is shown in red and the minimum is shown in blue. In the conventional PECVD method, the potential is higher than in the proposed method which causes more damage to the CNTs and the substrate. As is clear from Fig. 9 (a), the distance between the anode and cathode plates in our proposed method causes all adverse effects of electrical potential at the cathode plate region to be eliminated by creating a uniform distribution of electrical potential, which leads to CNT growth with minimal damage and few impurities. In contrast, as is obvious from the potential distribution shown in Fig. 9 (b), the electrical potential is not uniform in the
conventional PECVD setup. In the conventional PECVD method, we had to use a high intensity of plasma during the heating process in order to decompose gases for the synthesis of CNTs. This condition leads to the non-uniform distribution of electrical potential inside the CNT growth region.

![Simulation results of electrical potential distribution for (a) the modified method and (b) conventional PECVD.](image)

**Summary and Conclusion**

We have successfully implemented a method for the low-temperature growth of vertically aligned carbon nanotubes of various sizes and lengths on glass substrates using a new configuration of anode and cathode plates in a PECVD reactor. The presence of the anode plate is essential to create active radicals needed for forming CNTs and to remove all adverse effects of AC plasma and high intensity plasma. The modified configuration of the electric field plates in the PECVD technique causes the new procedure for low temperature growth of CNT and growth of vertically aligned CNT with low plasma intensity damage to the substrate and CNTs. Using a 10 nm thick Ni seed layer, we grew vertically aligned CNTs up to 3µm in height and less than 200nm in diameter.

The simulation and experimental data show that CNTs will grow at very low voltages with respect to the traditional methods, and the new electric field structure is suitable for growing long CNTs. We have also been able to grow controllable structures on glass substrates suitable for field emission purposes, such as displays and electron emitters. The growth of high density and vertically aligned CNTs on a glass substrate can make them a good candidate for gas detection, sensors, and bio-applications.

**References**


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