Directed Growth of Carbon Nanotubes Utilizing Plasma Induced Surface Charging Voltage

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ABSTRACT

In this work, we present a method for directed lateral growth of carbon nanotubes (CNTs) between electrodes on a substrate during an in-situ Radio Frequency – Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) CNT growth process, by utilizing plasma induced charging inherent in a Radio Frequency (RF) plasma process. The die consists of a pair of electrodes on insulator with lithographically patterned iron (Fe) catalyst islands on the edges. One electrode is electrically connected to the substrate by a platinum (Pt) plug while the adjacent electrode is electrically isolated. CNT growth was performed using RF-PECVD. Due to spatial non-uniformity in the plasma, the electrodes charged up to a different DC voltage each during the plasma process, a phenomenon known as plasma induced charging. A self-generated electric field is thus established during the growth between the isolated electrode with respect to the adjacent electrode to direct the lateral growth of CNTs.

Keywords: carbon nanotube, directed growth, plasma induced charging, electric-field.

1 INTRODUCTION

Carbon nanotubes exhibit many impressive and useful electrical properties, and hold great promise for utilization in future generations of integrated nano-circuits [1-2]. However, a prerequisite to achieve such integration is the ability to assemble individual CNT at the desired location, with the desired orientation to form a controllable and well-organized assembly. Electric-field assisted assembly of CNTs constitutes a commonly used approach to achieve such a goal. This approach exploits the high polarizability property of CNTs [2] to control the orientation of the CNTs via an electric field that is applied externally. This approach can be further classified into two subgroups, namely (a) controlled assembly of CNTs by post-growth technique or (b) by an *in situ* growth technique.

Electric-field assisted assembly of CNTs by post-growth techniques allows one the flexibility to choose the CNT synthesis method. Various widely-known synthesis methods include electric arc discharge, laser vaporization and chemical vapor deposition [2-4]. However, a major drawback of these synthesis techniques is that they produce nanotubes which are in bundles on a substrate. Sonification of the nanotubes in solution is often employed to separate these bundles into individual nanotubes. These isolated nanostructures suspended in solution are then dispersed onto a device substrate with prefabricated electrodes. Through the application of an external electric field onto these electrodes via micrometer/millimeter sized electrical contacts, controlled alignment and assembly of these nanotubes in the direction of the electric field have been demonstrated [5-6]. However, post-growth assembly of nanotubes in solution has limitations, including poor solubility of nanotubes in solution and a significant amount of undesirable nanotube impurities in suspension [7]. Moreover, the process is strongly dependent on the evaporation time of the solution [8]. The tedious and time-consuming processing steps also make this approach difficult to apply to nanotube assembly on a large scale.

In the *in situ* controlled growth technique, lithographically-defined catalyst islands are patterned onto isolated electrodes connected to micrometer/millimeter sized contact pads. An external electric field is applied between these isolated electrodes via these contact pads during thermal CVD growth of nanotubes. Nanotubes have been shown to orientate themselves in the direction of the electric field during growth and if the growth duration is long enough, these nanotubes can bridge pairs of electrodes [7,9]. This method suffers the same limitation as that faced by the post-growth assembly, namely, the need for an externally applied electric field to control the nanotube assembly. Thus, sufficiently large-sized contact pads need to be fabricated on the substrate to allow for ease of external electrical contacts. Though previous works using this method can demonstrate the proof-of-concept by using a pair of electrodes, this method might pose a significant challenge for large-scale assembly of nanotubes where a significant number of internal contact pads and external electrodes are needed for electrical interfaces which will render this method difficult to implement.

In this work, we present a method for directed lateral growth of CNTs between electrodes on a substrate during an *in situ* CNT growth process by utilizing a self-generated

electric field that is created by plasma induced surface charging inherent in RF plasma processing.

2 EXPERIMENTS

2.1 Measurement of Plasma Induced Charging Voltage in RF System

Plasma induced surface charging on isolated electrodes on a substrate is a common phenomenon in RF plasma processing. Due to a spatial non-uniformity of the plasma, the electrodes at a finite distance from each other on a substrate charge to a different voltage [10-12]. This charging voltage is commonly known as plasma induced charging voltage. Several authors have conducted experiments to verify its presence through different measured induced voltages across a wafer during RF plasma processing using either programmable EEPROM devices, such as a CHARM wafer or by real-time probe devices, such as a SPORT wafer [13-14].

We used a method similar to the SPORT technique [13] to verify the presence of plasma induced charging voltage on the substrate and to measure its magnitude in our RF plasma reactor system.

Our home-built RF-PECVD system used for CNT growth is as shown in Figure 1. The system comprises a cathode (also acts as the sample stage) which is a custom-made boron-nitride resistive heater (GE Advanced Materials) that has been coated with carbon for grounding purposes and connected via electrical feedthroughs to an external power supply. The heater is also directly connected to a RF generator operating at 13.56 MHz through a matching network and a DC blocking capacitor. In this configuration, the chamber walls forms the anode which is grounded to the chassis. Gas feeds lines for the gases, namely, C_2H_2 and NH_3, are connected via the chamber walls, with flow rates controlled by external mass flow controllers. The substrate temperature during the process can be monitored real-time through a sapphire window on the chamber using an on-axis pyrometer (Minolta TR-630). The whole system was pumped with a rotary pump with downstream pressure control.

Figure 2 shows the cross-sectional view of the sample used for the measurement of the plasma induced charging voltage. The sample is a silicon-on-insulator (SOI) die of dimension 5mm x 5mm, consisting of two highly p-doped (p++) silicon (Si) electrodes electrically isolated from each other. A Pt-filled plug connects one electrode to the conductive Si substrate. The typical process for CNT growth was carried out to simulate the actual condition. NH_3/C_2H_2 gas was flowed into the chamber at a flow rate of 60 sccm / 9 sccm, respectively, with a processing pressure of 2.9 mBar and a growth temperature of 620 °C while measuring the potential difference across the two electrodes in real-time using the SPORT technique.

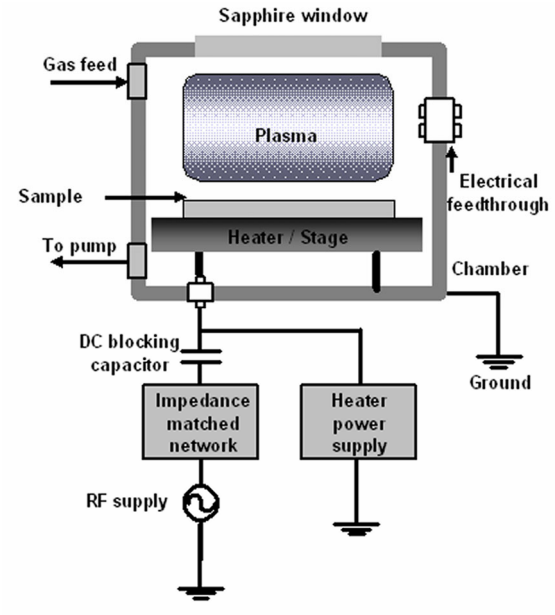

Figure 1. Home-built RF-PECVD system configuration for CNT growth.

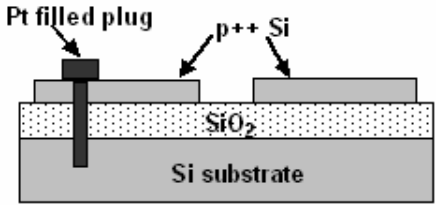

Figure 2. Cross-sectional view of the sample used to measure plasma induced charging voltage.

2.2 Sample Preparation

In order to illustrate the directed growth of CNTs during an *in situ* RF-PECVD CNT growth process using the plasma-induced surface charging voltage, the following experiment was conducted.

Another SOI die of dimension 8mm x 10mm was used. The detailed process flow to fabricate this die is shown in Figure 3. The die consisted of a 3μm thick highly doped (p++) silicon (Si) layer which functions as an electrode layer on a 2μm thick silicon dioxide (SiO_2) layer which functions as an insulation layer [Fig. 3(a)]. The die was patterned and etched to delineate pairs of p++ silicon electrodes isolated from the substrate by the silicon dioxide layer. For illustrative purposes, two pairs of electrodes are

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shown, namely the "predefined electrodes" and the "control electrodes" [Fig. 3(b)]. One electrode from the "predefined electrodes" was electrically connected to the silicon substrate by a Platinum (Pt) plug while the adjacent electrode, spaced 8μm apart, was electrically isolated. Both electrodes from the "control electrodes" were also spaced at 8μm apart, and were each electrically connected to the substrate by Pt plugs. The Pt plugs were defined using a focused ion beam (FIB) (FEI Quanta 200-3D). The p++ electrode dimensions are 5μm x 30μm. [Fig. 3(c)]. Iron (Fe) catalyst islands were patterned on the top edges of all the electrodes by electron-beam lithography, metallization and liftoff [Fig. 3(d)].

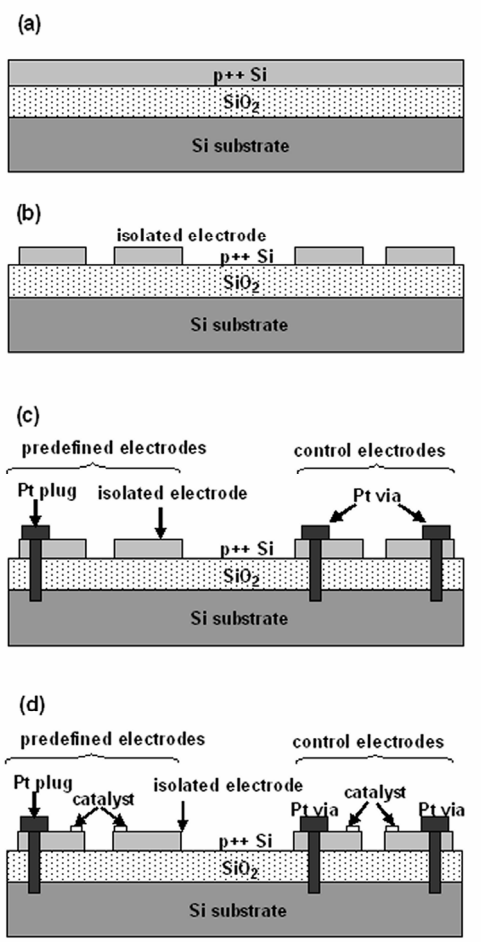

Figure 3. Schematic diagram process flow to fabricate "predefined electrodes" and "control electrodes" to illustrate directed lateral growth of CNTs using plasma induced surface charging.

This sample was mounted onto the stage heater of the RF-PECVD system as shown in Figure 1, with the substrate in direct contact with the heater stage through conductive carbon paint. CNT growth was performed using RF-PECVD at an RF power of 50W while simultaneously flowing NH_3 and C_2H_2 gas composition with a flow rate of 60sccm/13sccm at 3.2mBar process pressure. The growth temperature was maintained at 700°C with growth duration of 10min. After growth, the die was observed using a field-emission scanning electron microscope (FE-SEM) (Phillips XL30 FEG).

3 RESULTS AND DISCUSSION

Figure 4 shows the measured plasma induced charging voltages across the two electrodes of the sample shown in Figure 2 at varying RF power using the SPORT technique. A potential difference of -110V to -165V exists at an RF power of between 20W to 40W during the process. This measurement thus verifies that surface charging leading to a potential difference between an isolated electrode with respect to the substrate exists during RF plasma processing in our reactor system. The magnitude of this potential difference is proportional to the applied RF power.

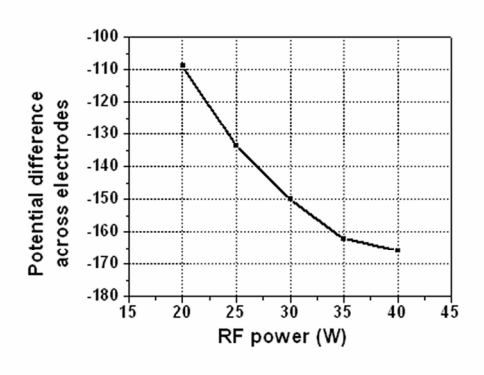

Figure 4. Measured potential difference across the two electrodes at varying RF power using the SPORT technique to verify the presence of plasma induced charging voltage present in our reactor system.

Figure 5 illustrates the directed lateral growth of CNTs utilizing this plasma induced charging voltage. Straight growth of CNTs was observed between the "predefined electrodes" of the sample shown in Figure 3d. Since previously measured plasma induced voltages in Figure 4 indicates a negative potential drop between the isolated electrode with respect to an adjacent electrode electrically contacted to the silicon substrate during RF plasma processing, an electric field is postulated to exist between the two electrodes at a finite distance of 8 μm from each other during RF plasma processing in our system. A ball-park figure of the magnitude of this electric field is above 20V/um considering a potential difference above 160V and a gap of 8μm at this process condition. The observed nanotube growth direction in the direction of the electric field, with the almost perpendicular orientation of the nanotube between the electrodes, illustrates the validity of this postulation.

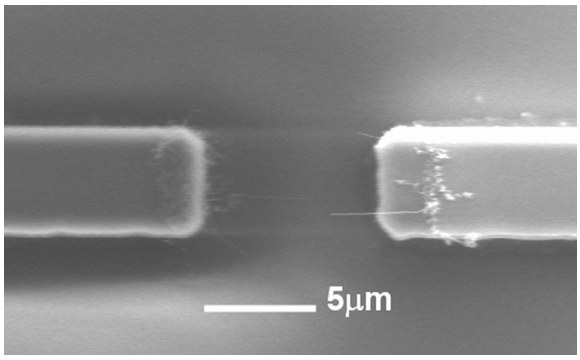

Figure 5. SEM image shows aligned growth of CNTs in the direction of the self-generated electric field formed between the "predefined electrodes".

In contrast, for the "control electrodes" as shown in the SEM images in Figure 6, the as-grown carbon nanotubes did not exhibit any preferred alignment and grew randomly from the edges of the electrodes. This is as expected since the two "control electrodes" are tied to the same electrical potential by the plugs during plasma CVD growth.

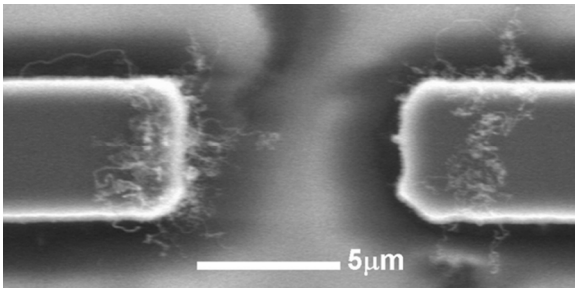

Figure 6. SEM image shows random orientation of the CNTs grown between the pair of electrodes on the control experiment where no electric field exists.

The present work thus provides an alternative method for directed growth of CNTs utilizing electric-field assisted assembly. Conventional methods using *in situ* growth assembly or post-growth assembly suffer from limitations such as the need for an externally applied electric field and subsequently the need for large-size electrode pads, and non-scalability of the process. In contrast, the present technique does not require large-size contact pads on the substrate. If a network of CNT assembly is required, elaborate and messy external contacts and electrical feedthroughs to the process chamber are not required since there is no need to apply any external biasing. More importantly, conventional scalable semiconductor processes can be utilized in this technique, making it a viable approach for large-scale integration.

4 CONCLUSION

In summary, we have presented a technique for directed growth of CNTs between adjacent electrodes using plasma induced surface charging in an RF plasma to create a self-generated electric field between predefined electrodes. This method provides an alternative technique for the directed growth of carbon nanotubes to enable controlled and organized assembly of carbon nanotubes for future integrated nano-circuits.

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REFERENCES

[1] M. Terrones, *Annu. Rev. Mater. Res*. **33**, 419, 2003.
[2] H. Dai, *Acc. Chem. Res.* 35, 1035 (2002).
[3] O. Zhou, H. Shimoda, B. Gao, S.J. Oh, L. Fleming and G. Z. Yue, *Acc. Chem. Res.* **35**, 1045 (2002).
[4] E. T. Thostenson, Z. F. Ren and T. W. Chou, *Compos. Sci. Technol.* **61**, 1899 (2001).
[5] X. Q. Chen, T. Saito, H. Yamada and K. Matsushige, *Appl. Phys. Lett.* **78**, 3714 (2001).
[6] Z. Chen, W.C. Hu, J. Guo, and K. Saito, *J. Vac. Sci. Technol. B* **22**, 776 (2004).
[7] Y.G. Zhang, A.L. Chang, J. Cao, Q. Wang, W. Kim, Y.M. Li, N. Morris, E. Yenilmez, J. Kong, and H.J. Dai, *Appl. Phys. Lett.* **79**, 3155 (2001).
[8] O. Englander, D. Christensen, J. Kim, L.W. Lin and S. J. S. Morris, *Nano Lett.* **5**, 705 (2005).
[9] H. B. Peng, T. G. Ristroph, G. M. Schurmann, G. M. King, J. Yoon, V. Narayanamurti and J. A. Golovchenko, *Appl. Phys. Lett.* **83**, 4238 (2003).
[10] J. P. McVittie, IEEE 1st International Symposium on Plasma Process-Induced Damage (USA), 7, (1996).
[11] G. F. You, M.C. Chang and C.Y. Wu, *IEEE Trans. Electron Dev.* **45**, 239 (1998).
[12] G. A. Roche and J. P. McVittie, K. C. Saraswat, 1st International Symposium on Plasma Process-Induced Damage, 71 (1996).
[13] S.Y. Fang and J. P. McVittie, *J. Appl. Phys*. **72**, 4865 (1992).
[14] S. Ma and J. P. McVittie, *IEEE Electron. Dev. Lett.,* **18**, 468 (1997).