Synthesis and Characterisation of Vertically Aligned Carbon Nanotubes using PECVD Method

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ABSTRACT

This paper reports how the various growth parameters affect the synthesis of vertically aligned carbon nanotubes, grown on Si substrate with Fe as the catalyst, using the PECVD method. By varying the growth conditions such as temperature, process pressure, C2H2 flow rate and deposition time, different morphologies and alignment of carbon nanotubes can be achieved. The morphology of the Fe catalyst upon which the CNTs were grown on were studied under the atomic force microscope (AFM). The morphology and alignment of the CNTs were examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

INTRODUCTION

Carbon nanotubes are interesting nanostructures with impressive electronic and mechanical properties, initially due to their unique electronic structures, and later their potential use in nano-sized electronics amongst many other fields.

Multi-walled nanotubes (MWNT) were first observed by Iijima in 1991. These structures can be described by two models: Russian Doll model and the Parchment model. In the Russian Doll model, the sheets of graphite are concentric and arranged cylindrically; in the Parchment mode, the sheets are rolled up into itself. Carbon nanotubes have remarkable mechanical properties. CNTs get their mechanical properties from the sp2 bonds between the atoms. It has a Young’s Modulus of about 1 TPa and tensile strength of 150 GPa. With a low density of 1.3g/cm3, this gives carbon nanotubes a specific strength of 4800 kN.m/kg, compared to steel, which has only 154 kN.m/kg. It also has very good conductivity, surpassing that of copper, and has unique thermal properties being an insulator on the surface and conducts heat along its core. These properties make carbon nanotubes one with many promising applications. CNTs undergo plastic deformation when placed under excess tensile strain. They are also not very strong under compression, causing buckling to occur due to their hollow structures and high aspect ratios.
Another property of its hollow structure is the sliding of an inner CNT within a larger outer CNT, with very little friction between them.

CNT can be either a semiconductor or a metallic conductor depending on the n-m number of the nanotube. If n = m or if (n – m) is a multiple of 3, the nanotube is metallic, otherwise it is a semiconductor. CNTs are capable of much higher current densities compared to copper. As for its thermal properties, CNTs has ballistic conduction, exhibiting good thermal conduction long the tube, and good insulation properties lateral to the tube axis. CNTs are also very stable under high temperatures of up to 2800K.

There are various ways to synthesize carbon nanotubes, with plasma-enhanced chemical vapor deposition (PECVD) being one of the more common methods. The advantage of CVD is being able to grow the carbon nanotubes on the desired substrate, control growth sites by arranging the catalyst and being able to be produced on an industrial scale efficiently and economically.

EXPERIMENTAL

Deposition of Fe metal film using RF magnetron sputtering

The RF sputtering process was carried out using Fe catalyst target and deposited onto the Si substrate, which were cut into small pieces of about 2cm by 2cm. The working pressure used is 15 mTorr, base pressure in the order of $10^{-6}$ mTorr, with 100W of RF power and a deposition time of 45mins.

Synthesis of CNT using PECVD

Several samples were then placed onto the heating element in the PECVD chamber and pumped down to high vacuum and the CVD process started. After the entire process has completed, the heating element is switched off to allow the samples to cool down before retrieval. The RF power used is 90W, and working pressure set to 1000 mTorr.

RESULTS AND DISCUSSION

The process of synthesis of CNTs by PECVD involves catalyst preparation and growth of carbon nanotube. Transition metals are often applied as catalysts for CNTs growth. These metals can be deposited onto the substrate by various methods which include dispersing colloidal solution, or thin film deposition using physical techniques such as sputtering and vacuum evaporation. In our case, the thin film was deposited using magnetron sputtering system. The morphology of the catalyst Fe film used in the synthesis of carbon nanotubes is studied using AFM. Figure 1 shows a typical AFM image of the Fe film deposited on Si substrate. The deposited catalyst film shows
quasi-spherical nanoparticles of diameter ~ 20 nm. The nanoparticles are densely packed and of uniform in diameter. The root mean square roughness measurement of the catalyst film is 3.5 nm.

![AFM image of the Fe nanoparticles on Si substrate.](image)

It has been reported that a high degree of crystallinity of CNTs can be achieved at high temperature, and also the activity of the catalyst depends on the growth temperature. In our experiments, at 250 °C we observed that the nanotubes are generally more randomly aligned as compared to 450 °C. The low reactivity of catalyst particle with the hydrocarbon gas, leads to the formation of curled nanotubes as well as amorphous carbonaceous deposits.

The effect of time on the growth of carbon nanotubes was also studied. The increase in deposition time from 90 to 150 minutes causes the diameter of the nanotubes to increase noticeably, with the CNT grown for 90 minutes deposition time having a diameter of 20 nm while the ones grown for 150 minutes has larger diameter of 60 nm. The diameter of the CNT is also found to be dependent on the hydrocarbon flow rate. It is observed that the increase of C_2H_2 flow rate increases with the diameter. CNT grown under a C_2H_2 flow rate of 28 sccm have a diameter of 20 nm, and one which was grown under 50 sccm has a diameter of 110 nm.

After many attempts, vertically-aligned CNT were synthesized with growth parameters of 28 sccm flow rate, 2000 mTorr process pressure, 100W RF power, 450 °C chuck temperature and 90 minutes deposition time. The CNT grown has a diameter of 20 nm, and were vertical-aligned. The nanotubes have length ~39 µm, and a growth rate of 7.2 nm/sec. It is generally believed that CNTs grown in a high density will be aligned due to the steric interaction between adjacent nanotubes which enables them to grow only upward from the substrate. It is observed that the nanotubes buckle and bend easily under some pressure as shown in Figure 2.
TEM characterisation was carried out by dispersing carbon nanotubes on TEM grid (Figure 3a). The carbon structures can be observed to have hollow interior. In general, the carbon nanotubes are multi-walled as they consist of 4-10 walls (Figure 3b). The interlayer space is found to be 0.34 nm, corresponding to the (002) plane of the graphitic carbon.
CONCLUSION

From the study above, it has been shown that varying the synthesis parameters can affect the diameter of the CNT as well as its alignment. There is only a small range of growth parameters under which the CNT can be vertically aligned. A suitable set of growth parameters have been found, and can be further optimized to allow good controllability of its morphology and structural composition.

REFERENCES

