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SYNTHESIS OF CARBON NANOTUBES BY MICROWAVE ASSISTED PLASMA DEPOSITION (MAPCVD) TECHNIQUE

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ABSTRACT

Microwave Plasma has been used to synthesise carbon nanotubes (CNT) in the hydrogen and methane environment on the Si substrate. RF sputtering is used for applying nickel catalyst surface of the substrate. Scanning Electron Microscope (SEM) analysis revealed the formation of tubular structure of the deposits, while High Resolution Transmission Electron Microscope (HRTEM) analysis revealed the structure of multiwalled CNT.

INTRODUCTION

Since its discovery by Ijima in 1991[1], carbon nanotubes have greatly garnered research interest around the world. This is due to the outstanding properties of CNT, especially their outstanding physical, chemical and electronic properties. Several methods, including arc discharge [2], laser ablation [3], microwave plasma chemical vapour deposition [4], thermal CVD, an many more have been used to synthesise the CNTs.

EXPERIMENTAL DETAILS

The CNTs were catalytically grown on the Si (size 1" x 1") substrate in the 2.45 GHz, 6kW MAPCVD system with CH_4/H_2 as source gases. Firstly, the SiO_2 barrier layer was grown on the Si substrate by thermal oxidation method. The Si substrate were put into the furnace and heated at 1100^o C for 20 hours. The SiO_2 barrier layer was essential in preventing the reaction of catalyst and the Si substrate to form metal-silicides, which would inhibit the growth of nanotubes. After the application of SiO_2 barrier layer, the substrate was put into the RF sputtering system for the application of Ni catalyst layer. The chamber was pumped-down to the base pressure of 10^{-6} mTorr to ensure clean environment. Argon gas was then introduced into the deposition chamber and at pressure of 10^{-3} mTorr, an RF power of 200 W was applied to the Ni target for 10 minutes to yield approximately 10 nm nickel layer on the substrate. The substrate was then transferred into a MAPCVD chamber for nanotubes growing process. The configuration of the MPACVD is shown in Figure. 1. Firstly, the chamber was evacuated to reach a base pressure of 10^{-3} mTorr. Then, hydrogen gas with flow rate of 100 sccm was fed into the deposition chamber and the pressure was maintained at 20 mTorr. The microwave power of 1 kW was applied to create plasma. This particular process is important because during this stage the Ni layer was transformed into a well-

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distributed nano-sized catalyst on Si substrate surface. Apart from that, since the system was not equipped with internal heating, the plasma was used to heat the substrate to reach the temperature suitable for nanotubes growth. After 10 minute, methane gas, with the flow rate of 100 sccm was introduced into the chamber, and the chamber pressure was raised and maintained at 50 mTorr. 2 kW of microwave power was applied to the plasma, and the duration of this particular process was 10 minutes. After the substrate had cooled down to room temperature, it was taken out from the deposition chamber for SEM and TEM analysis. For SEM analysis, a carbon conductive tape was pressed on the CNTs layer, so that the CNTs would adhere to the tape. It was then put into LEO FESEM for observation. For TEM analysis, the CNT deposits were scraped off from the Si substrate and ultrasonicated in ethanol. A drop of suspension was placed on TEM grid for further analysis.

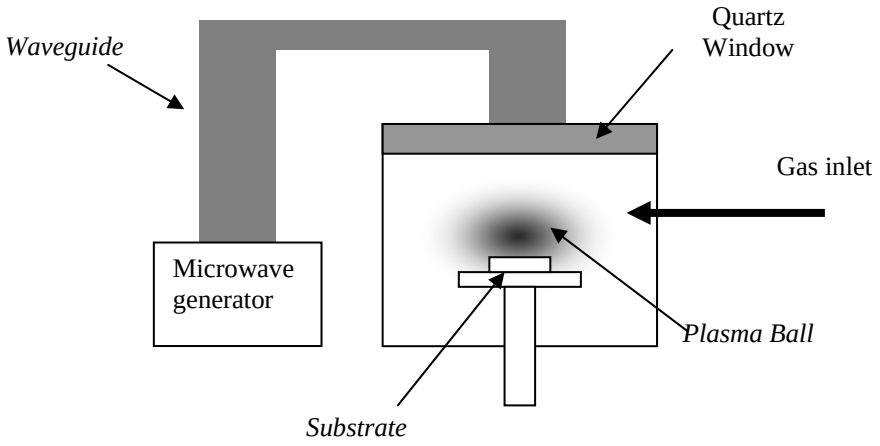

Figure 1: Schematic of the MPACVD reactor used for the growth of CNT films

RESULTS AND DISCUSSION

A proposed growth mechanism of CNTs is shown in Figure 2. The first stage is the formation of catalyst “nanoisland”or individual nanoparticles on the substrate surface was achieved by H_2 plasma pretreatment at 1kW for ten minute. This provides the seeds for subsequent growth of CNTs. With the introduction of CH_4, the carbon atoms will react with the nanoparticles and through some complex reactions, growth of CNTs is initiated.

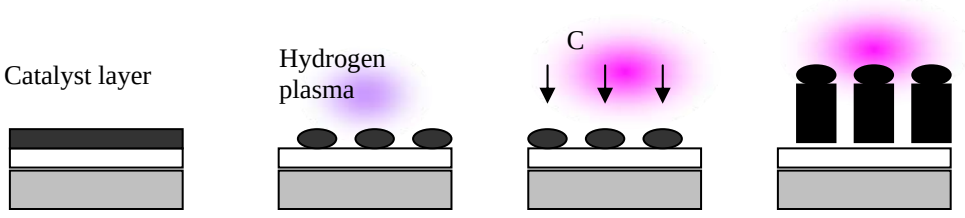

Figure 2: Schematic of growth mechanisms of CNTs

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Figure. 3 depicts the image of the deposited CNTs at 100X magnifications captured by FESEM. It can be observed that the CNTs grow randomly on the surface the substrate. This is related to catalyst density of Ni nanoparticles on the substrate. A high-density nanoparticles would result in more aligned CNTs growth. A less dense Ni nanoparticles would allow the individual nanotubes to grow randomly since they would have more space to grow in many directions, while a high density nanoparticles would restrict the sideways growth of the CNTs and the only way to grow was vertically upwards.
It was also observed that some carbonaceous particles, or impurities, (shown in the circles in Figure 2,) also existed. This is quite common occurrence for CVD method. It was known that the average yield of CNTs by this method was approximately 50 %. By optimizing the process parameters of CNTs deposition, we hope this occurrence can be minimised.

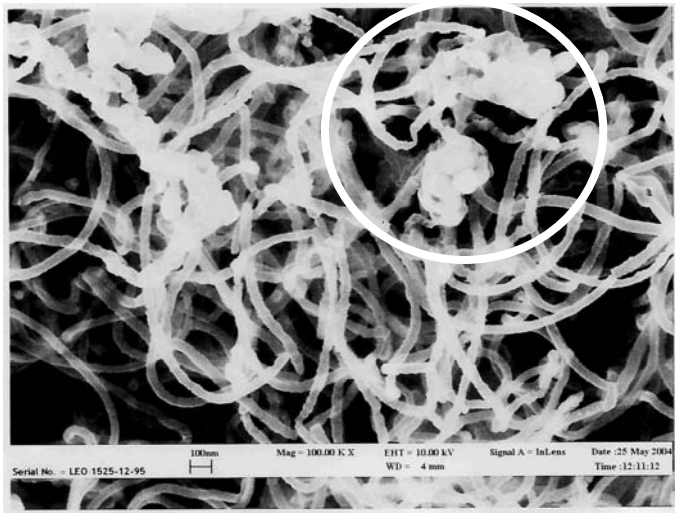

Figure. 3: SEM micrograph of CNTs with magnification of 100X

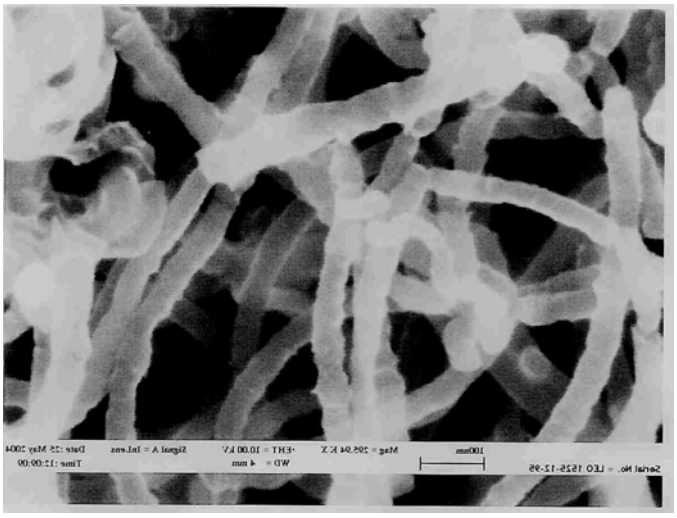

Figure. 4: SEM micrograph of CNTs with magnification of 295X

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Figure. 3, depicts the image of CNTs at higher magnification of 295X. From the picture it can be seen that the diameter of the CNTs obtained are in the range of 20 to 50 nanometers. The size diameter of the CNTs obtained depends on the type of catalyst used and also the amount of carbon species present. C.J Lee et al., comparing the three commonly used catalyst in their work, Fe, Co and Ni, found out that Fe would produced CNTs with average diameter of 130 nm, Co 110nm and Ni 100 nm while maintaining the other deposition parameters the same[6].

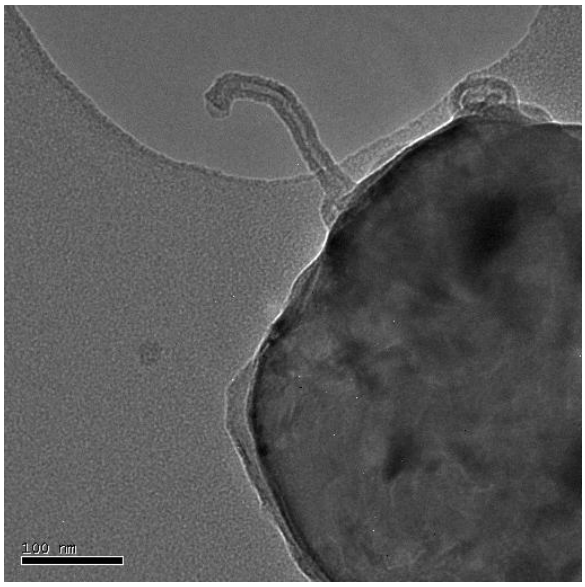

Figure 5: TEM micrograph of individual CNTs

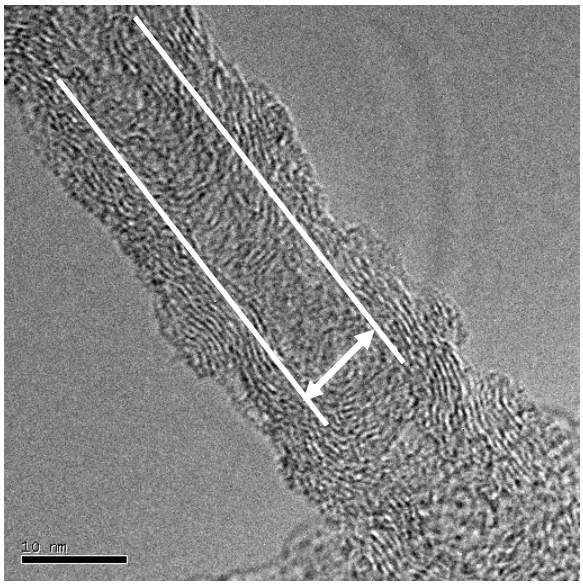

Figure 6: TEM micrograph of multiwalled CNTs

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Figure. 5 and 6 show the image of individual CNT obtained from TEM analysis. In Figure 6 it can be seen clearly the hollow tubular structure, confirming the nanotube structure. At higher magnification, depicted by image in Figure 7, it can be observed that the CNTs obtained were multiwalled CNT (MWNT) with outside diameter 20 nm and inside diameter of around 7 nm.

CONCLUSION

Multiwalled Carbon nanotubes (MWCNT) has been grown on Si substrate with SiO_2 interlayer by MAPCVD method by Ni catalyst applied by RF sputtering method. The diameter of the CNT was found to be ranging from 20 nm to 50nm. The CNTs grown was observed as having a multiwall structure with inner diameter of around 7nm. The results presented in this paper is preliminary, so further research needs to be conducted in the future to improvised and optimized the process of synthesizing CNTs through MAPCVD technique.

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