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# GROWTH OF CARBON NANOTUBES BY HF-CVD METHOD USING SIMPLE ROUTE

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## ABSTRACT

In this study, fast growth of pure carbon nanotubes (CNTs) via hot filament chemical vapor deposition (HF-CVD) technique was investigated. The surface morphology of CNTs films grown on (100) single crystal silicon substrates using Hydrogen ($H_2$) and Methane ($CH_4$) gas mixture with flow rates of 100 and 3 sccm (standard cubic centimeter) respectively is reported. The CNTs films were characterized by Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) techniques. It is shown that, due to high amount of the released carbon atoms, there was a formation of micro-crystalline graphite having size ~ 0.1 – 0.2 micrometer, but after covering the substrate surface by stainless steel mask having an array of ~1mm size holes, sufficiently large population of CNTs could be observed on the surface of the substrate with average diameter of ~200 nm. The formation of pure CNTs is confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis which shows that the atomic percentage of carbon was about 87% and the remaining percentage was due to silicon substrate.
**Keywords:** HF-CVD, carbon nanotubes, stainless steel mask, SEM micrographs, EDX analysis

## I. INTRODUCTION

Carbon is an important element not only because it is the forth most abundant element in the universe after Hydrogen, Helium and Oxygen, but also for its unique properties as a non-metallic tetravalent element that presents several allotropic forms including diamond, graphite, fullerene and nanotubes. Nowadays, carbon nanotubes are one of the most interesting carbon based materials. Even that their first observation was before about 20 years by Ijima [1,2], they have generated a huge activity in most areas of science and engineering due to their exceptional physical and chemical properties. No other material has shown the combination of mechanical, thermal and electronic properties attributed to them so they have opened new research areas in physics, chemistry and material science including electronic nano devices [3], electrical wiring [4], biodevices [5], probes for scanning microscopy [6].

Synthesis techniques of carbon nanotubes (CNTs) can be divided into two categories, chemical and physical, depending upon the process used to extract atomic carbon from the carbon carrying processor. Among these techniques, the chemical vapor deposition (CVD) [7], in which a hydro carbon is thermally decomposed over metallic catalyst is particularly attractive as it allows to selectively controlling the growth of CNTs with defined morphologies by adjusting reaction parameters such as carbon source, catalyst type, reaction temperature and so on. More importantly, it is the most suitable method for industrial scale

production because it is scalable and low cost. In addition to the classical thermal CVD, various CVD methods have been developed over time, including the plasma enhanced CVD (PE-CVD) and the hot-filament assisted CVD (HF-CVD) [8, 9]. The PE-CVD method presents many advantages such as control of the vertical allayment of nanotubes due to the intrinsic electric field of the plasma sheath and low processing temperature [10, 11]. However carbon nanotubes grown by PE-CVD are overwhelmingly carbon nanofibers or multi-walled carbon nanotubes (MWCNTs) with measurable structural defects. The synthesis of SWCNTs seems to be difficult by this method due to the production of high order hydrocarbons and radicals in plasma environment [12]. Depending on the final application HF-CVD could be even more desirable than plasma CVD become HF-CVD processes are more economical and suitable for large area and irregular-shaped substrates [13]. The aim of the present study is to grow SWCNTs via HF-CVD through utilizing $CH_4$ as carbon source and $H_2$ as a diluent gas by using simple route.

## II. EXPERIMENTAL DETAILS

The schematic diagram of HF-CVD system used in this study is shown in figure (1). It comprises essentially the following sub-units: **i)** The HW-CVD reactor which consists of a stainless steel vacuum chamber connected to turbo molecular pump through a throttle valve to accurately control the process pressure backed by a mechanical rotary pump. The substrate holder with internally mounted heater is located inside the reactor at a convenient distance from the filament. The reactor was baked for 4-5 hours at 200 $^{o}$C at a pressure < $10^{-6}$ mbar prior to the deposition. This allows the system to get degassed to minimize the possibility of the contamination in the deposited films, **ii)** Filament assembly which consists of stainless steel mounting electrodes specially designed so that 6 tungsten filaments each 0.5 cm apart, 2 cm length and 0.5 mm diameter can be mounted in parallel at a time. The design also enables to vary the distance between the substrate and the filament, **iii)** Power supply unit which supplies electric power to the filament by employing a high current AC transformer through a dimmer. Using filament assembly and power supply unit, filaments can be heated in the range of 1400-2200 $^{o}$C, **iv)** Gas handling system which consists of the mass flow controllers, gas lines, manual control valves, gas mixing cylinder and gas inlet valve. It is an important part of the system because it introduces all the gasses into the chamber in a controlled fashion. For safety reasons, bypass valves are also added to the main gas pipes to remove the hazardous gasses in case of any breakdown in the mass flow controllers. The type of substrate used in this study was (100) single crystal silicon wafer which was well characterized earlier and expected not to add any complexity during carbon nanotube deposition as well as during characterization of the deposited films. The area of the substrate used was about 2 $cm^2$ while the filament area is adjusted to be 6 $cm^2$. The c-Si wafers were cleaned by a 1 minute dip in dilute HF (5 %) to remove the native oxide layer from the wafer surface [14]. This cleaning method provides good adhesion of the films to the substrates. The substrates were loaded and the deposition chamber was evacuated to a base pressure less than $10^{-6}$ mbar. The chamber was baked for 2 hours at a temperature of 200 $^{o}$C prior to each deposition to minimize the possibility of the contamination of the deposited films. Before any deposition, it was found useful to carborize the filament. The carborization leads to formation of carbide layer on the

filament surface. This pretreatment of the filament involves heating it over 500 $^{o}$C for about 30 minutes at 1 Torr pressure of 1 sccm of methane gas flow rate.

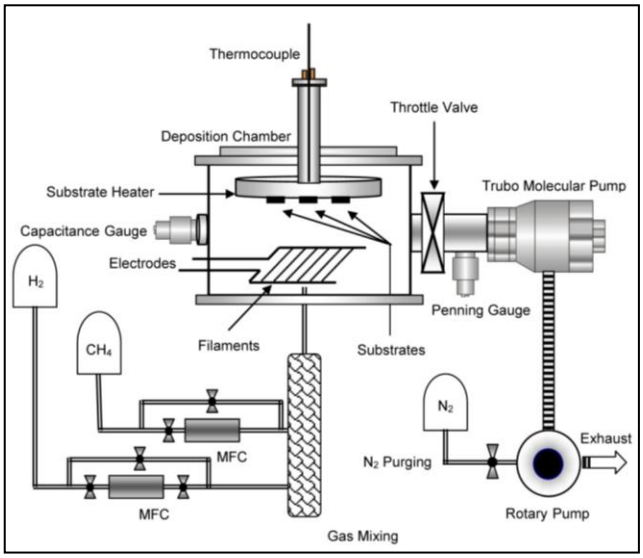


**Figure 1:** Schematic diagram of HF-CVD used in the present study

Then the substrate was loaded and heated to the desired temperature by setting the temperature controller. The chamber then was purged by hydrogen before introducing pure $CH_4$ and $H_2$ gases inside the chamber and starting the deposition process. The deposition was carried out for the desired amount of time and the films then were allowed to cool down to room temperature in vacuum. It is worthy to indicate that selecting the right conditions to grow carbon nanotubes has remained a trial and error approach and this has resulted in a lot of CNT growth papers, each having a specifically tuned recipe for growth, which is very difficult to reproduce in any other system or setup [15]. The deposition conditions used in this study is listed in Table (1). At least four specimens were synthesized under identical experimental conditions in order to check the reproducibility and repeatability of the results. The synthesized films were characterized by scanning electron microscope (SEM) (model JEOL, JSM-6360A) with operating voltage of 20 kV and the emission current of 60 mA. In this study, a simple experiment has been carried out to grow carbon nanotubes by HF-CVD method using $CH_4$ as a source gas and $H_2$ as a diluent gas.

**Table 1:** Deposition conditions for deposition of carbon nanotubes

| | |
|---|---|
| Filament temperature | 2000 ± 5 $^{o}$C |
| Deposition pressure | 30 - 35 Torr |
| Substrate temperature | 700 ± 5 $^{o}$C |
| $H_2$ flow rate | 100 sccm |
| Filament to substrate distance | 3 cm |
| Deposition time | 20 minutes |

## III. RESULTS and DISCUSION

The formation of CNTs needs a controlled supply of carbon atoms as well as a sufficient amount of nucleation; otherwise the experiment normally leads to graphitization of the substrate. Figure (2) shows SEM micrograph corresponding to 3 sccm flow rate of $CH_4$ gas. Other deposition conditions are listed in Table (1). It is clear that due to high amount of the released carbon atoms, there was a formation of micro-crystalline graphite having size ~ 0.1 – 0.2 micrometer. It is thus necessary to allow a precise control of the released carbon atoms on the substrate surface to increase the possibility of nucleation of the carbon nanotubes. In general it is very difficult to adjust methane flow for this purpose and one needs to perform a series of experiments with different amount of methane flow rates. Therefore, a new method was employed wherein the substrate surface was covered by stainless steel plate having an array of ~1mm size holes as shown in figure (3).

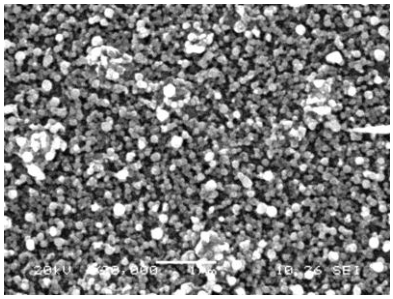

**Figure 2:** SEM micrograph showing the formation of micro-crystalline graphite having size ~ 0.1 – 0.2 micrometer.

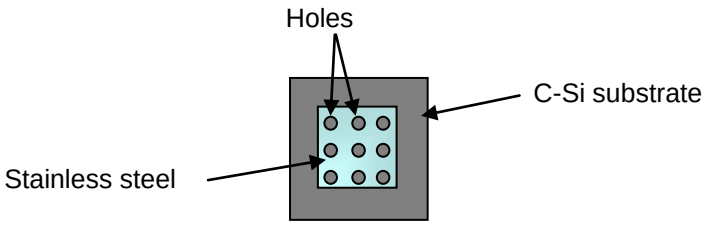


**Figure 3:** The crystal silicon substrate covered by stainless steel plate with holes

This setup allows a limited part of the substrate surface to be directly exposed to the gas phase while the surface below the metal plate receives a controlled amount of carbon which reduces systematically as one goes away from the hole in the metal plate. This idea shows successful results in getting CNTs in the first experimental run only.

The overview SEM image after deposition is shown in figure (4), wherein the variation in amount of deposition with respect to the hole is clear.

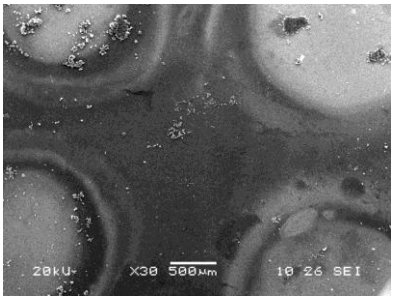


**Figure 4:** SEM micrograph showing the variation in amount of deposition with respect to the hole in the metal plate kept above the substrate

White rings of large population of CNTs can be observed; while only graphitization could be seen in regions correspond to the holes which were directly exposed to the gas phase. The black regions between the holes contained no carbon material. The SEM micrographs shown in figure (5) belong to different specimens deposited with metal plate on top. In all cases a large population of CNTs has been observed in the regions of white rings surrounding the central graphitic areas.

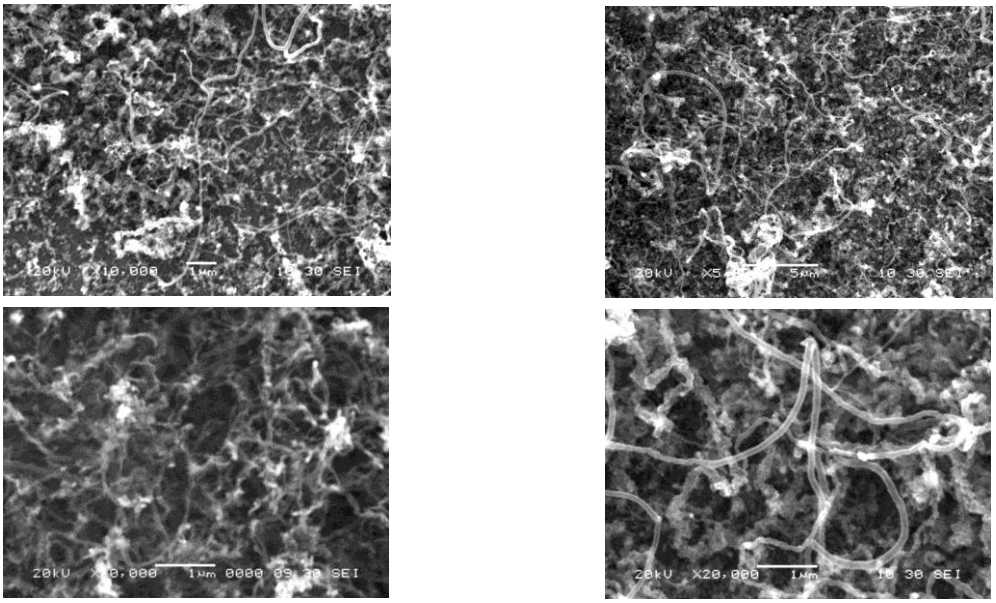

**Figure 5:** SEM micrographs belong to different specimens deposited with metal plate on top.

The magnified SEM images of a typical CNTs deposited in this study are shown in figure (6). It is clearly seen that sufficiently large population of CNTs exist on the surface of the substrate with average diameter of ~200 nm.

The formation of CNTs is confirmed by energy-dispersive X-ray spectroscopy (EDX). Figure (7) shows that the atomic percentage of carbon was about 87%. The remaining atomic percentage was due to silicon substrate.

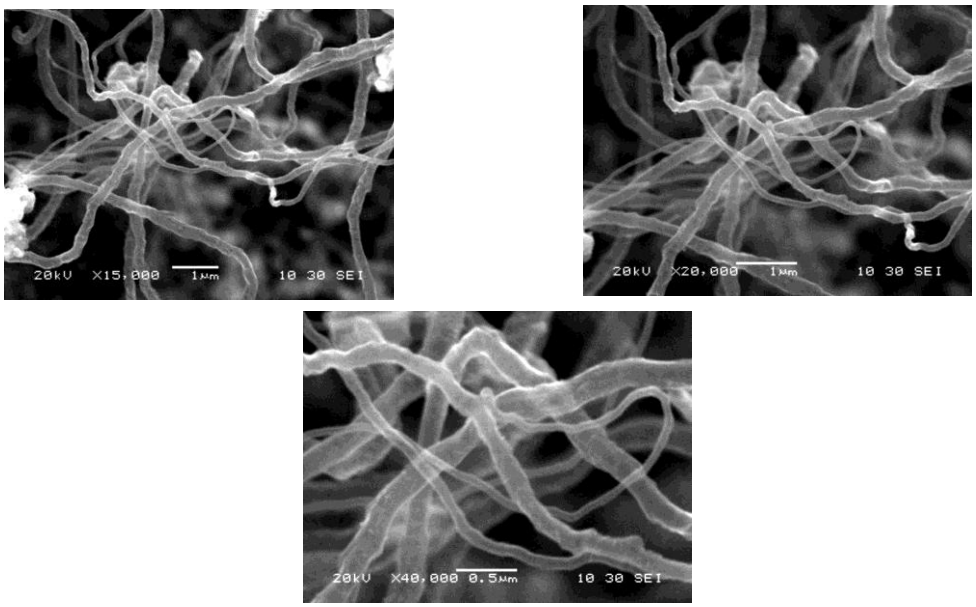


**Figure 6:** Typical CNTs deposited in this study with average diameter of ~200 nm.

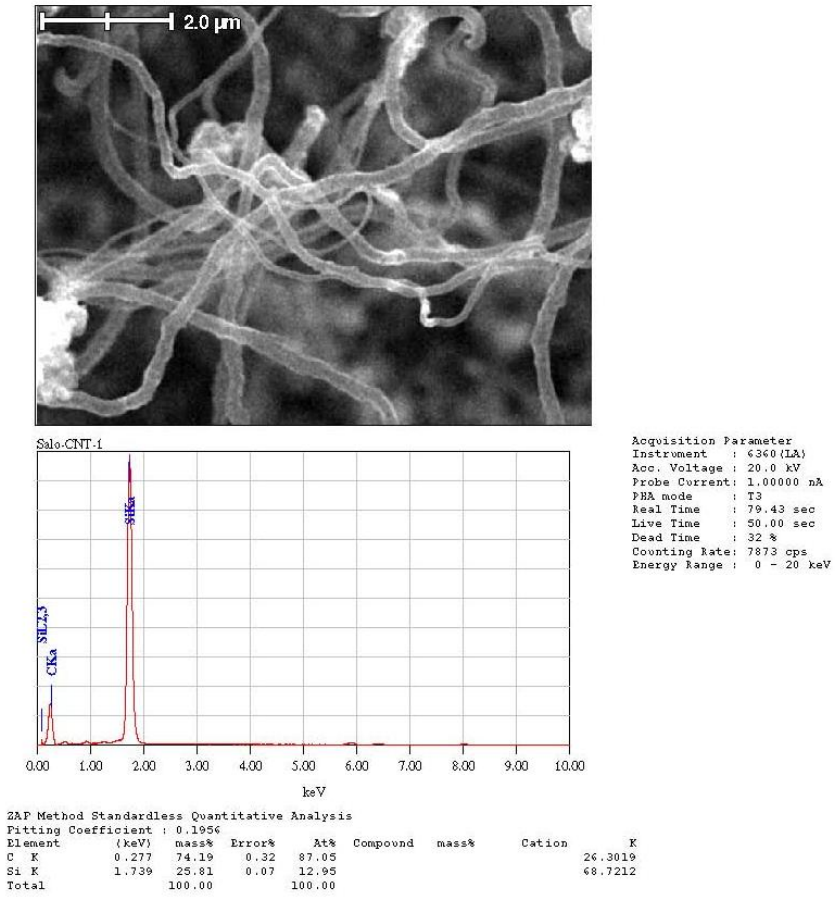


**Figure 7:** EDX spectra of CNTs grown in this study showing ~87% atomic percentage of carbon.

## IV. CONCLUSIONS

Pure CNTs have been successfully deposited by HF-CVD technique on (100) single crystal silicon substrates using $H_2$:$CH_4$ (100:3 sccm) gas mixture. The preliminary

experiments result in the formation of micro-crystalline graphite having size ~ 0.1 – 0.2 micrometer due to high amount of the released carbon atoms, while using the same deposition parameters the precise control of the released carbon atoms on the substrate surface could be achieved by covering the substrate surface with stainless steel mask having an array of ~1mm size holes, leading to a sufficiently large population of pure CNTs on the surface of the substrate with average diameter of ~200 nm.

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