

# Patterned growth of carbon nanotubes obtained by high density plasma chemical vapor deposition

**A P Mousinho, R D Mansano**

Laboratório de Sistemas Integráveis do Departamento de Engenharia de Sistemas Eletrônicos da Escola Politécnica da Universidade de São Paulo, Avenida Professor Luciano Gualberto, 158, trav. 3, São Paulo, SP, Brasil

E-mail: mousinho@lsi.usp.br

**Abstract.** Patterned growth of carbon nanotubes by chemical vapor deposition represents an assembly approach to place and orient nanotubes at a stage as early as when they are synthesized. In this work, the carbon nanotubes were obtained at room temperature by High Density Plasmas Chemical Vapor Deposition (HDPCVD) system. This CVD system uses a new concept of plasma generation, where a planar coil coupled to an RF system for plasma generation was used with an electrostatic shield for plasma densification. In this mode, high density plasmas are obtained. We also report the patterned growth of carbon nanotubes on full 4-in Si wafers, using pure methane plasmas and iron as precursor material (seed). Photolithography processes were used to pattern the regions on the silicon wafers. The carbon nanotubes were characterized by micro-Raman spectroscopy, the spectra showed very single-walled carbon nanotubes axial vibration modes around  $1590\text{ cm}^{-1}$  and radial breathing modes (RBM) around  $120\text{--}400\text{ cm}^{-1}$ , confirming that high quality of the carbon nanotubes obtained in this work. The carbon nanotubes were analyzed by atomic force microscopy and scanning electron microscopy too. The results showed that is possible obtain high-aligned carbon nanotubes with patterned growth on a silicon wafer with high reproducibility and control.

## 1. Introduction

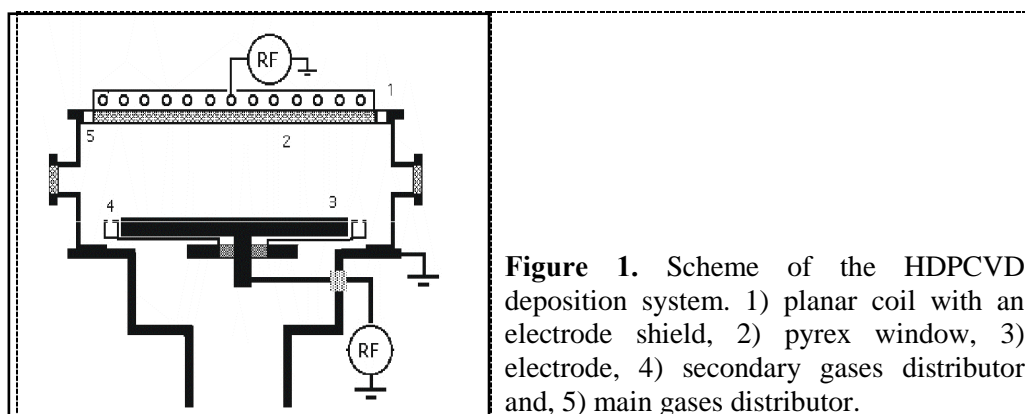
Carbon nanotubes (CNTs), with their exceptional anisotropic electrical, thermal and mechanical properties combined with their dimensions – nanometers in diameter and micrometers in length – are ideal candidates for several applications and components in nanotechnology such as nano-wires, transistors, field emitters, reinforced nano-composites and conducting filler in insulating materials[1]. CNTs were discovered in 1991. Remarkable progress has been made in the ensuing years, including the discovery of the two basic types of CNTs (single-wall and multiwall). Great strides have been taken in their synthesis; purification and elucidation of the fundamental physical properties, with important steps are being taken toward realistic practical applications [2]. CNTs are a new form of carbon that shows an equivalent form a bi-dimensional grapheme sheet wrapped as a tube. Single-walled carbon nanotubes (SWCNTs), made of cylindrically rolled grapheme sheets, have attracted a lot of attention due to their interesting and potentially useful electrical and mechanical properties. In particular, regarding their mechanical properties, they have been hailed as the flexible springs of nature. SWCNTs can be conductive and semiconducting. The electrical properties of the CNTs depend on the diameter of the tubes and the chiral angle [3-8]. The CNTs exhibit excellent properties for many applications, including: electrical, electro-optical, optical, optoelectronic, mechanical, electromechanical, magnetic, electromagnetic, chemical, electrochemical, thermal and thermoelectric



properties [9]. Additionally, their incredible strength (a consequence of the famously strong carbon bond in the tubular structure) poses further advantages in nano-mechanic applications. CNTs forest is a new class of established materials that can be used for many applications [10]. Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapor deposition [8]. Patterned growth of CNTs by chemical vapor deposition represents an assembly approach to place and orient CNTs at a stage as early as when they are synthesized [1]. In this work, we report a method for obtaining patterned growth of CNTs forest at room temperature by High Density Plasmas Chemical Vapor Deposition (HDPCVD) system. We report the patterned growth of CNTs on full 4-in Si wafers, using high-density pure methane plasmas and iron as precursor material (seed). The method for obtaining patterned growth of CNTs included the iron deposition using Magnetron sputtering [11-12], the pattern of regions on the silicon wafers by photolithography processes [12-13] and the patterned growth of CNTs by HDPCVD. The parameters of plasma processes were varied. The CNTs were characterized by Scanning Electron Microscopy, Atomic Force Microscopy, and micro-Raman Spectroscopy [14-17]. The results showed that is possible obtain high-aligned CNTs with patterned growth on a silicon wafer with high reproducibility and control.

## 2. Materials and Methods

The CNTs were obtained by a HDPCVD system that uses a new concept of plasma generation. In this case, a planar coil coupled to an RF system for plasma generation, and an electrostatic shield for plasma densification are used. In this mode, high-density plasmas are obtained. For the ion acceleration another RF system in planar configuration is used (as seen in Figure 1).



**Figure 1.** Scheme of the HDPCVD deposition system. 1) planar coil with an electrode shield, 2) pyrex window, 3) electrode, 4) secondary gases distributor and, 5) main gases distributor.

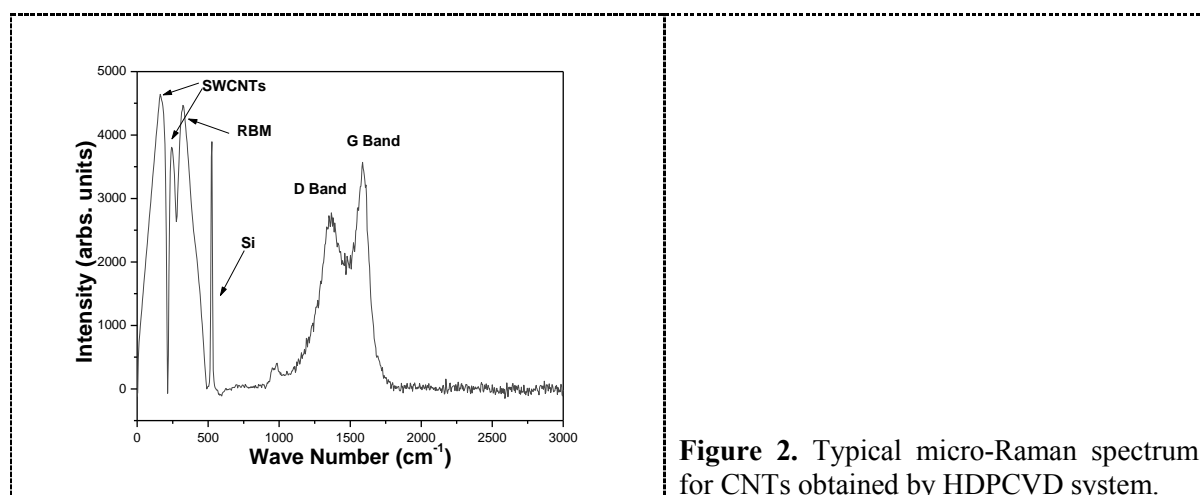
The substrate temperature was not controlled, but measured by a type K thermocouple, which indicated that the temperature never exceed 90 °C. For the CNTs growth, pure methane plasmas processes were used. The HDPCVD system has a main chamber (with diameter of 35 cm), where the electrostatic shield (with diameter of 30 cm) is localized. The electrostatic shield can be heated until 600 °C by an infrared heater. The planar coil has been put in the upper part of the chamber, above a borosilicate window and is covered with an electrode shield. RF power (13.56 MHz) is applied to the planar coil centre and also at the lower electrode (the RF systems are independent). The vacuum system is formed by a turbo-molecular pump (with nominal outflow of 400 l/s) and an auxiliary mechanical pump. The minimum basis pressure that the system can reach is  $2 \cdot 10^{-7}$  Torr. In the HDPCVD system, there are two gas distributors. The main distributor was constructed in the cover of the chamber, where a small homogenization chamber (secondary distributor of gases) exists. The distribution of the gases in the process chamber has been made by a holed ring. The HDPCVD system has been created to work with gases (six different types) and liquids (two different types) at the same time, thus it is possible to obtain the DLC films with additives (nitrogen, fluorine, oxygen, etc). The substrates used to obtain the CNTs were three-inch diameter silicon wafers, 380  $\mu\text{m}$  thick and with orientation (100). They were submitted to a Piranha clean, followed by a diluted HF dip. Iron

(precursor material) was deposited on the substrates by Magnetron Sputtering (200 W, 5 mTorr, 20-sccm argon and 30 min). The iron layer was defined using optical photolithography and O<sub>2</sub> plasma treatment. These steps were used to pattern the silicon wafers surface before the CNTs growth.

The CNTs were grown after the samples preparation, with the parameters: 15 mTorr, 250 W (coil power, RF, 13.56 MHz, remote plasma), 40-sccm methane and the deposition time were 3 hours. The structural properties and the diameter distribution of the CNTs were analyzed by Raman spectroscopy. The spectra were collected using a Renishaw micro-Raman 2000 spectrometer on a 40x objective with a photo multiplier. Unpolarized Raman spectra were acquired at  $\lambda = 514.5$  nm, the spectral resolution was about  $4 - 6$  cm<sup>-1</sup> and the power on the sample was kept well below 1 mW. For the characterization of the SWCNTs structure we used an atomic force microscope (AFM) model SPM 9500J3 (Shimadzu) in tapping mode (10 analyses per sample in different areas of  $15 \mu\text{m} \times 15 \mu\text{m}$  and  $5 \mu\text{m} \times 5 \mu\text{m}$ ). The scanning electron microscope (SEM) used it was a FEI NOVA nano500. The results obtained are shown in this work.

### 3. Results and Discussion

A typical micro-Raman spectrum obtained for CNTs grown by HDPCVD system is showed in Figure 2.

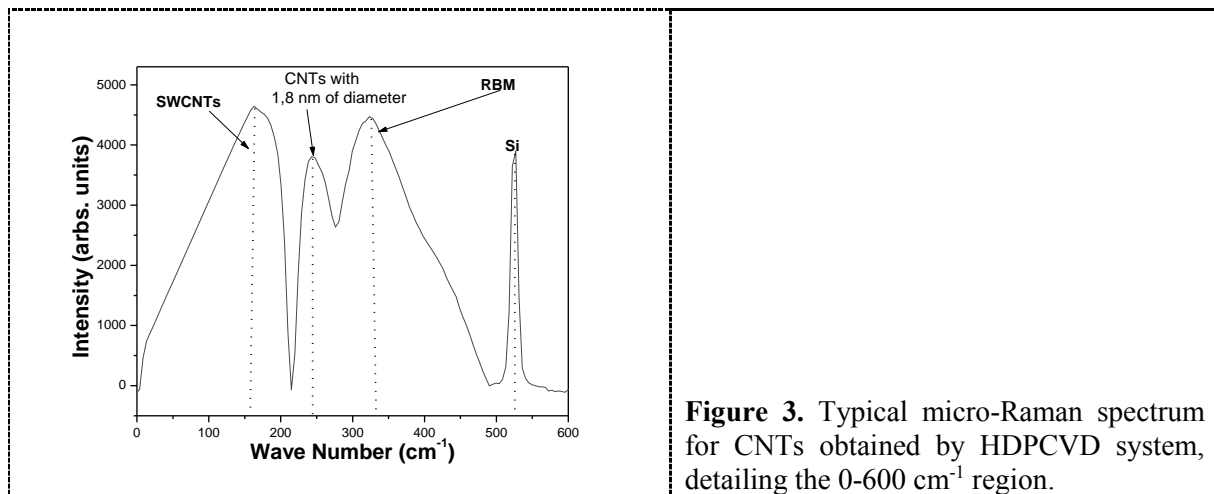


**Figure 2.** Typical micro-Raman spectrum for CNTs obtained by HDPCVD system.

Using chemical vapor deposition with methane gas for growing the CNTs, complex dissociations occur that could create a large variety of structural characteristics. In this way, observing the Figure 2, we can noticed the presence of four characteristics vibrational modes for a Raman spectrum of a unique CNT (RBM, G band, D band and G' band) and also some new vibrational modes related to CNTs with different diameters. The region between 0 and 600 cm<sup>-1</sup> is subdivided with some important peaks related to RBM, SWCNTs and CNTs with diameter of 1,8 nm and CNTs with bigger diameters. The micro-Raman spectrum showing details of this region is presented in Figure 3.

The main vibrational modes in CNTs obtained in this work, are centered in  $\sim 150$  cm<sup>-1</sup>,  $\sim 240$  cm<sup>-1</sup> and  $\sim 340$  cm<sup>-1</sup>. These peaks are related to the Radial Breathing Mode (RBM). Radial breathing mode (RBM) of CNTs is a low frequency mode, but accounts for the strongest feature observed in the CNT Raman spectrum. For the RBM, all of the carbon atoms in a CNT move in the radial direction synchronously, which generates an effect similar to “breathing” [18]. This mode is unique to CNTs, and is not observed on other carbon systems. Raman measurement of the RBM in CNTs is a standard, straightforward method for precisely determining the diameter of a CNT, distinguishing the CNT chiral-index assignments, or characterizing CNT clusters [18].

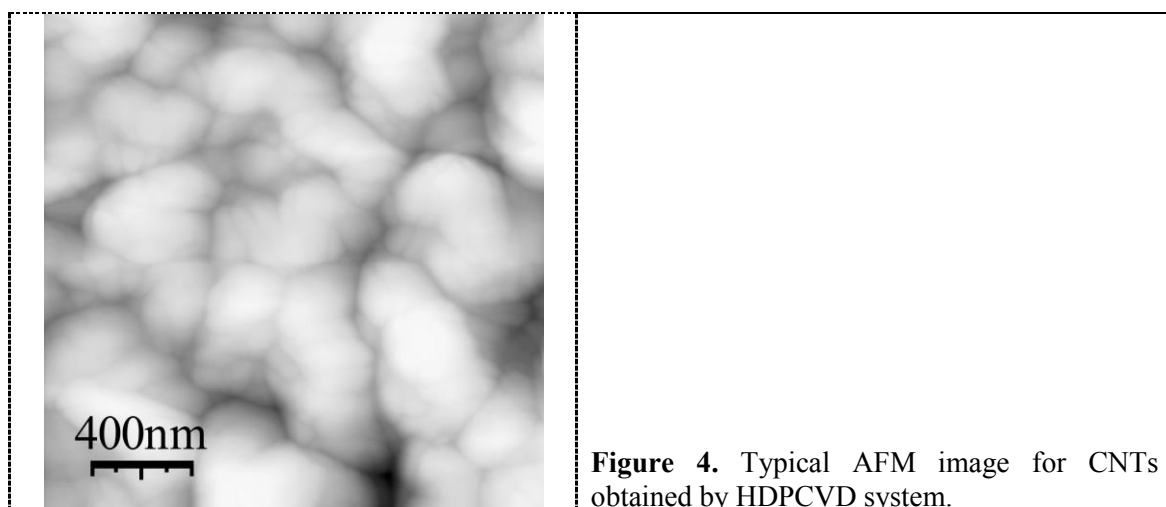
In this work, the three peaks that compose the RBM region for Raman spectra obtained for CNTs are related with CNTs with diameter of 1,8 nm and CNTs with larger diameters. The difference in the diameters of the CNTs obtained in this work is related with the segregation of carbon atoms in the iron crystal structure.



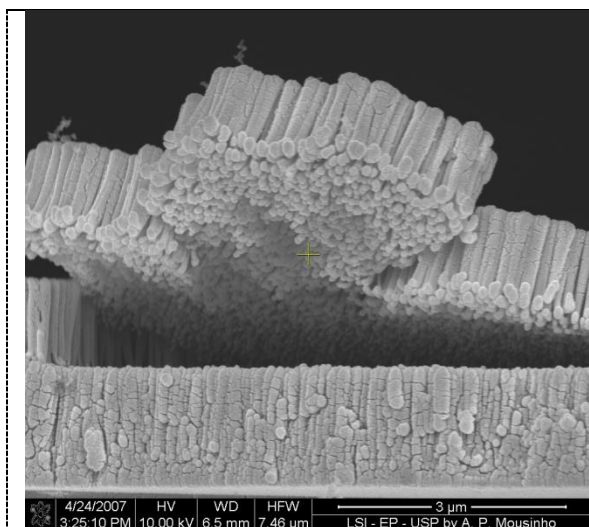
**Figure 3.** Typical micro-Raman spectrum for CNTs obtained by HDPCVD system, detailing the 0-600  $\text{cm}^{-1}$  region.

The presence of iron promotes the high-alignment of CNTs and contributes to the definition of CNTs diameters. Using HDPCVD system is possible control the CNTs diameters. The peak centered at  $\sim 150 \text{ cm}^{-1}$ , indicates the presence of SWCNTs in the samples. The combination of the peak centered in  $\sim 150 \text{ cm}^{-1}$  and the G band centered in  $1560\text{-}1600 \text{ cm}^{-1}$  are related with the strong presence of armchair SWCNTs. The presence of many vibrational modes indicates that we have obtained SWCNTs with a large range of the diameters due the presence of the iron in the samples. Besides, there is a presence of other peaks that are related with vibrational modes of the second order. They are related with CNTs with different diameters and other kinds of carbon nanostructure formation in the samples.

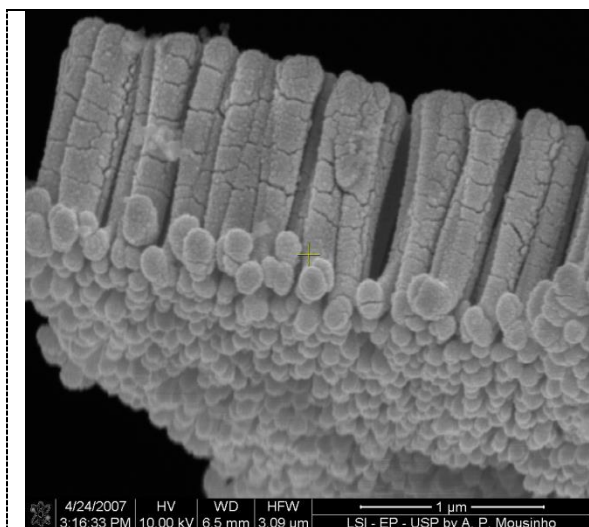
Using conventional photolithograph and oxygen plasma treatment we could promote the high-aligned CNTs growth. The iron layer was patterned and the high-aligned CNTs are grown in the regions with iron precursor and in the other regions (without iron), it occur the diamond-like carbon (DLC) formation. Using the photolithography processes we could define the regions where the CNTs would be grown. Thus, we could obtain the patterned growth of CNTs with high-aligned degree. The results could be proved by Scanning Electron Microscopy and Atomic Force Microscopy and they are showed in the next figures.



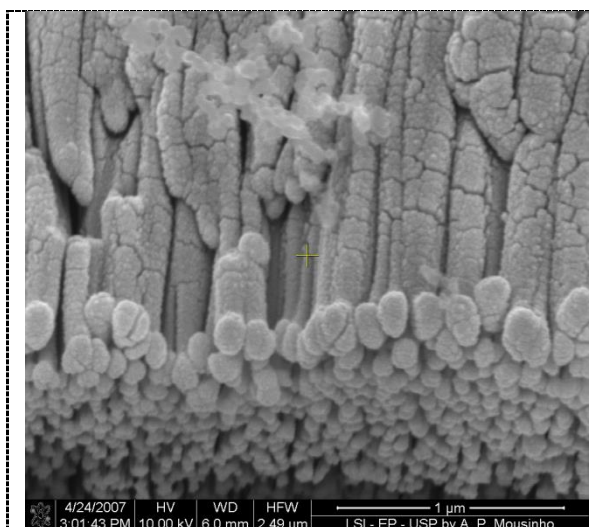
**Figure 4.** Typical AFM image for CNTs obtained by HDPCVD system.



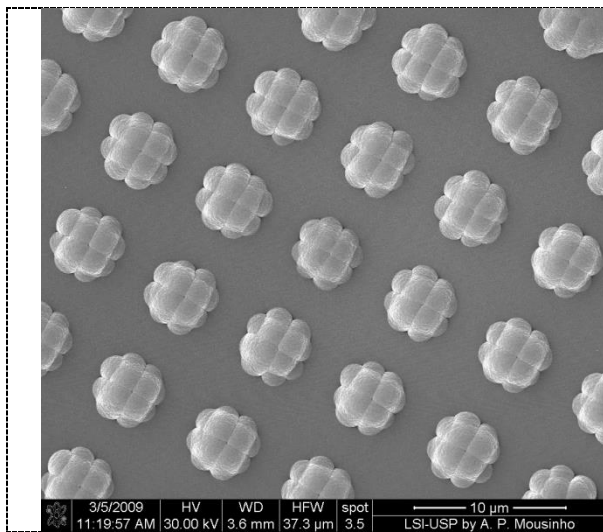
**Figure 5.** SEM micrograph of high-aligned SWCNTs obtained by HDPCVD system.



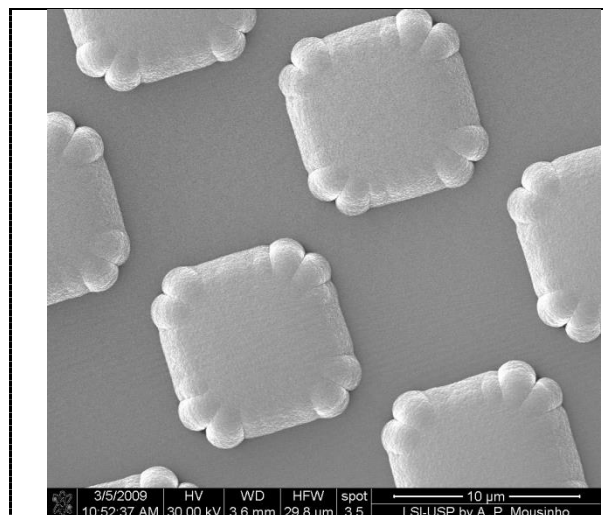
**Figure 6.** SEM micrograph of high-aligned SWCNTs obtained by HDPCVD system.



**Figure 7.** SEM micrograph of high-aligned SWCNTs obtained by HDPCVD system.



**Figure 8.** SEM micrograph of patterned growth of high-aligned SWCNTs obtained by HDPCVD system (The “flowers” are islands of CNTs).



**Figure 9.** SEM micrograph of patterned growth of high-aligned SWCNTs obtained by HDPCVD system (The “squares” are islands of CNTs).

Observing the AFM image and the SEM micrographs we can observe that the CNTs grow up in “clusters” (like a bouquet of flowers). These clusters have high-density of CNTs due the presence of iron in the samples. The presence of iron generates a roughness surfaces in the silicon wafers and promotes locally an increase of carbon-carbon bonds nucleation. With the photolithography processes, we could pattern the CNTs growth.

#### 4. Conclusions

In this work, we have obtained patterned growth of high-aligned carbon nanotubes using pure methane plasmas, iron as precursor material and, photolithography processes and high density plasma chemical vapor deposition techniques at room temperature. The CNTs were analyzed by micro-Raman spectroscopy, SEM and AFM Microscopy. The CNTs obtained in this work showed unique structural properties. With these results is possible obtaining patterned growth of CNTs forest for applications in SWCNT forest-based electronic and optoelectronic devices.

## 5. Acknowledgements

We gratefully acknowledge the Mr. Nelson Ordonez, PhD Adir José Moreira and Mr. Alexandre Camponucci, for providing technical support and FAPESP and CNPq for financial support.

## 6. References

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