

3 Methodology

In the previous chapter some background on Carbon Nanotubes science has been laid. Some of the synthesis methods for producing both pristine and Boron doped Carbon Nanotubes have been briefly described. Then, the main physical properties of Carbon Nanotube and doped Carbon Nanotubes have been presented, together with the main characterization methods found in literature.

In the present chapter, the methodologies used in the present thesis will be introduced. It will be described in detail the experimental setup for producing the Carbon Nanotube material, as well the synthesis steps. The characterization methods and the objectives of each analysis technique will also be described.

In the next chapter, a discussion of the results from the characterization methods will be conducted to see if the objectives of the work were achieved, and to compare with existing empirical results from literature.

3.1. Experiment proposal

In this section, it will be summarized the general experiment schedule, and the seized objectives. First a retrospective of past works that inspired this thesis is to be given. Then, the thesis experimental proposal will be posed. And at last, the expected results will be stated.

As described, in section “ Substitutional Doped Carbon Nanotubes synthesis”, there exist some work in the literature on the synthesis of Boron doped Carbon Nanotubes by Chemical Vapor Deposition.

The works by Ayala et. al. [15,34], demonstrate the production of B-doped SWNTs using high vacuum CVD, with the peculiarity that the precursor substance, is at the same time the Boron source (Triisopropyl Borate, $B(OC_3H_7)_3$), for it contained both Carbon and Boron atoms in its structure. The authors investigate the structure and Boron incorporation by changing synthesis temperature.

In the work by Monteiro et. al., [35,36], using the same synthesis methods from Ayala et. al., it is studied a new precursor/Boron source molecule (Triethyl Borate, $B(OC_2H_5)_3$), and compared to the previous one, used by Ayala et.al. in [15,34]. In Monteiro et. al. works, the effects of the synthesis temperature is investigated as to its effects on structure and Boron incorporation profile of the aforementioned substances.

In reference [14], Boron doped multiwall Carbon Nanotubes are produced using as precursor Methane (CH_4), and as Boron source Trimethyl Borate ($B(OCH_3)_3$). The authors study the change in structure of the produced tubes, by changing the feed rate of the Boron source. That is, instead of studying temperature influence on the synthesis, this work studies the change in the doped Carbon material by actually changing the amount of Boron being fed into the reaction.

It should be believed that a way for tailoring controlled doping levels is to control the proportion of Carbon atoms to Boron atoms being introduced into the reactor. In the work done by Xu et. al. [64], for example, the authors managed to produce gradient doping profiles on Nitrogen doped Carbon Nanotubes, by continuously changing the N source concentration on the precursor solution. The same should be possible to be done on B doped Carbon Nanotubes, although no report exists in the literature, to the best of this thesis author's knowledge.

This thesis proposes to study the Boron incorporation profile on SWNTs by synthesizing Boron doped SWNT with different proportion of Carbon to Boron being fed into the CVD reactor, but keeping synthesis temperature constant throughout different synthesis. It will be used as precursors Ethyl Alcohol (as a standard undoped material, like was done in [36]), Triisopropyl Borate, Triethyl Borate, and Trimethyl Borate, and solutions of these.

It is expected that different doping levels will be produced. The different doping levels will be measured using XPS.

Also, since the idea is to study the feasibility of controlling the doping level, a quick characterization technique, would be beneficial. XPS technique, although useful to measure doping levels, takes hours to be accomplished, and fails to measure very low doping levels. As discussed in section “Physical properties of Boron doped Carbon Nanotubes”, Raman technique has a good sensibility to detect low Boron doping concentrations; thus, could be used as a quick measurement of Boron concentration of synthesized material.

It has been done in [36], a calibration between XPS doping measurements and G^+ peak position. In the present work, a similar calibration will be done and will be compared with literature results.

3.2. Experimental Description

This section describes how the experiments were performed, and what equipment was used. First, it will be described the catalyst synthesis, that is, how the catalyst used to synthesizing Carbon Nanotubes was prepared. Second, the synthesis equipment will be described; then, the synthesis steps; and, at last, the characterization equipment, and methodology will be described.

3.2.1. Powder Catalyst synthesis

Powder catalyst production has been reported in the literature, [5,15,28,35]. The general idea is to disperse a mesoporous material (MgO , Al_2O_3) and a metal containing substance (Nitrates, Acetates, etc.), in a liquid solution. The mixture is dried while dispersing, to produce a homogeneous material.

In this thesis work, it has been used the same recipe as [35], which is adapted from [65].

The powder catalyst is composed of a mixture of Iron Nitrate, and Magnesium Oxide (MgO) mesoporous powder. The mixture is prepared by the following recipe:

- Add in a Beaker, Magnesium Oxide (MgO , Sigma-Aldrich 325 mesh, $\geq 99\%$), 5 g, and Iron Nitrate Nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma-Aldrich, $\geq 98\%$), 2.5 g.
- Add Methanol until the mixture reaches 40 ml, and cover the Beaker so as to slow the evaporation rate of Methanol.
- Stir the mixture using a magnetic stirrer for 30 min, so as to make a homogeneous mixture.
- Sonicate the material for 24 hours so as to disperse the Iron Nitrate and the Magnesium Oxide in the Methanol. At the end of sonication, one will have a hard, but still impregnated with some residual Methanol, material.
- Calcinate at 60 °C for 24 h to evaporate the Methanol.
- Grind the resultant solid in a crucible, until a fine powder is formed.

3.2.2. Synthesis system

It was built a home-made high vacuum chemical vapor deposition system to synthesize our material, the same one as used in [35], which is similar from the setup used in [65]. The system is composed basically of a vacuum chamber, vacuum pumps, a furnace, gas suppliers, a needle valve, and a quartz crucible. In this section, a broad description of the physical components of the system will be given.

3.2.2.1. Vacuum chamber

The vacuum chamber is composed of all the parts that will be pumped to high vacuum conditions. The vacuum chamber's most important part is the quartz tube, which is the reactor where the synthesis will happen.

The quartz tube is 1 inch diameter per 1 meter long. The advantage in this chemical vapor deposition setup is that the reactor can be easily detached from the system, to be cleaned in between synthesis. The piece that allows it is a pair of moveable adaptors (Figure 22), that links the quartz tube to KF25 flange.

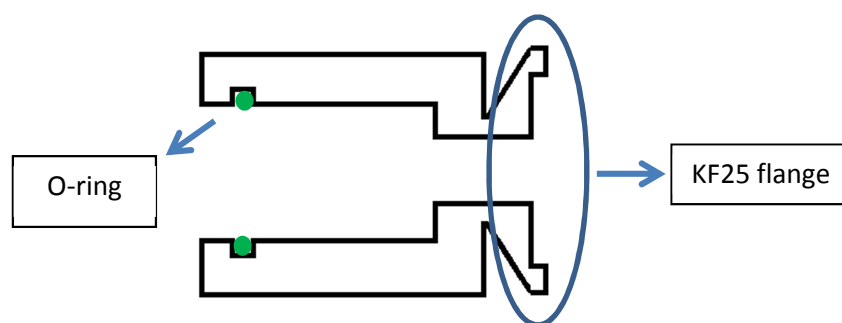


Figure 22: This figure is a schematic of the tube-KF25 adaptor. On the left side the quartz tube enters, sliding on the O-ring. On the right side, the KF25 flange allows the quartz tube to be linked to the rest of the vacuum system.

The connection of the quartz tube and the adaptor presents no leak problem, so that high vacuum conditions are achievable.

3.2.2.2. Vacuum pumps

There are two pump systems. The first one, which is composed of a single mechanical pump, is used for control of the synthesis ambient conditions. The second one is composed of a turbo molecular (Pfeiffer, model TC600) and a backing mechanical pump for the cleaning step.

The first pump system, hereafter referred to as pump A, will be mainly used during supply of gases to control the pressure of the chemicals in the vacuum chamber. The second pump system, hereafter referred to as pump B, will be used during raise of temperature to the synthesis temperature to keep a high vacuum condition.

3.2.2.3. Furnace

The furnace is an electrical furnace. It is 30cm wide, and capable of keeping uniform temperature inside, so that no temperature gradient is expected in the reaction zone. The quartz tube crosses the furnace, to be heated, in its central portion, only.

The furnace used is programmable, which allows the user to choose the objective temperature, and at what rate will the temperature rise.

3.2.2.4. Gas/vapor suppliers

The only gas/vapors to be supplied in the experiment are H_2 gas, and vapor from the precursor substances.

The H_2 , (99.99% pure, from White Martins) kept in a high pressure vessel, is supplied to the CVD system by a mass flow controller of 100sccm.

The precursors used in this work are all in liquid phase at ambient condition and are kept in small quartz tubes which are opened to the vacuum chamber through valves at the moment of the synthesis. The precursor supply system is another advantage of this CVD setup. The tube has a flange-like format in its open end, so that it can be connected to KF16 flange (Figure 23). This setup makes change of precursor an easy maneuver.

The precursor tube connection to KF16 presents no detectable vacuum leak. This way, by opening the precursor tube to the vacuum chamber for a few seconds before synthesis start, no contamination with atmospheric air is expected during synthesis.

By using liquid precursors, it was possible to exploit low rates of deposition in a simple way: the liquid being stored in the precursor tube, when opened to the vacuum chamber, will evaporate in a rate dictated by the vapor pressure of the liquid, which is in the 1 – 100 *torr* range, in our case.

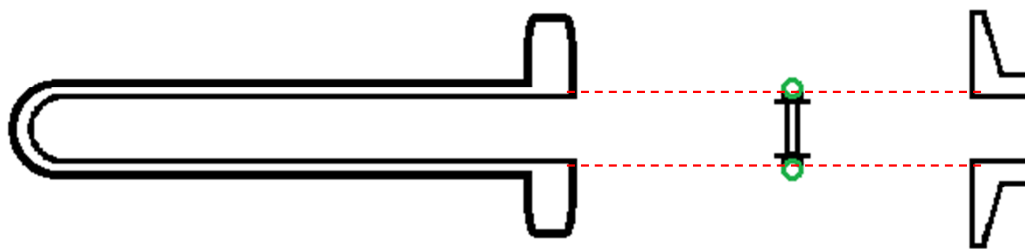


Figure 23: This figure shows how the quartz tube is designed so that it can easily be connected to a metallic KF16 flange.

3.2.2.5. Needle Valve

A needle valve (model EVN 116, from Pfeiffer) connecting the vacuum chamber to pump A is of utmost importance in the system's functionality. When feeding the reactor with chemical vapor or gases the system is pumped by pump A, with a speed determined by the needle valve. This way, the user controls the ambient pressure in the chamber during reaction.

3.2.2.6. Quartz Crucible

A quartz crucible is used to store the catalyst. After loading the crucible with catalyst material, it is pushed into the reactor with a clean metallic stick, so that the crucible sits in the middle of the furnace.

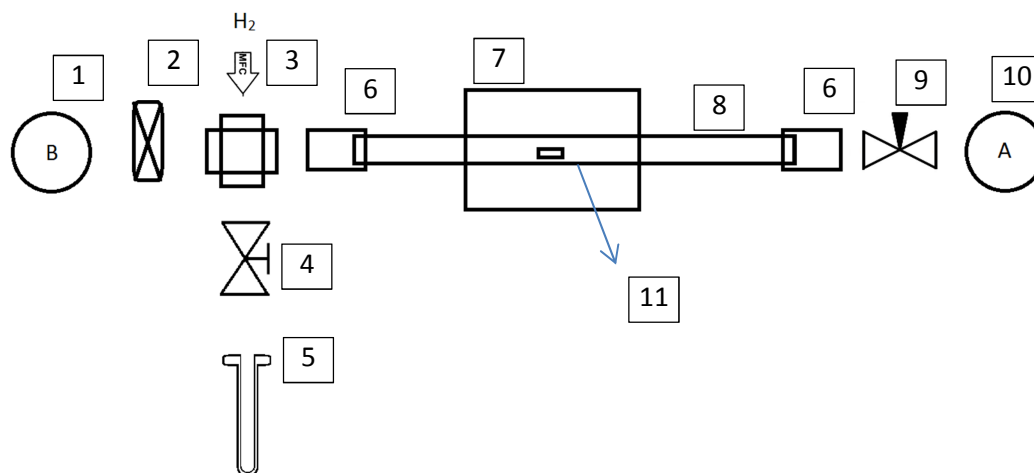


Figure 24: The complete assembly of the vacuum system. The numbers identify the components. (1) pump B, (2) gate valve, (3) mass flow controller, (4) valve, (5) precursor tube, (6) quartz tube adaptor, (7) furnace, (8) quartz tube, (9) needle valve, (10) pump A, (11) quartz crucible.

The complete CVD high vacuum system is sketched in Figure 24, above.

3.2.3. Synthesis Procedure

This section is devoted to the description of the steps used to synthesize the SWNTs of this thesis.

Synthesis steps are as follows:

- Purging the H_2 supply and the tubes with the precursor. First, the H_2 mass flow controller (MFC) is turned on at 10 *sccm*, until 0 *sccm* flow is reached. Then, the precursor tube's valve is opened for 10 seconds. Third, the system is evacuated to high vacuum, less than 4×10^{-5} *mbar*.
- The temperature is raised in steps of 50 °C, until 200 °C. At each step, the pressure will rise because of Nitrogen oxide (decomposition of Iron nitrate) and moisture degassing of the catalyst, so one should wait until the pressure reaches values lower than 4.0×10^{-5} *mbar*, before proceeding to the next 50 °C step.
- At 200 °C, the temperature is raised directly to 700 °C. In this stage, degassing still happens although in a slower rate, so pump A is to be used, which will keep ~ 0.1 *torr* vacuum conditions.
- At 700 °C, the reduction of the metal catalyst is performed by flowing H_2 in a 10.0 *sccm* rate, and keeping pressure in the chamber at 65 *torr* for 10 min, by adjusting the needle valve.
- Temperature is set to rise to 800 °C, while the chamber is evacuated to $\leq 1.0 \times 10^{-4}$ *mbar*.
- At 800 °C, synthesis takes place. The precursor tube is opened to the reactor, and the pressure in the chamber is controlled by the needle valve to be right lower than the ambient vapor pressure of the precursor, so that one prevents turbulent flow in the reaction zone. Synthesis proceeds for 10 *min*.
- The precursor tube is closed, and the chamber is evacuated by pump B, while furnace is shut off. The system is cooled down to ambient temperatures and under high vacuum conditions.

The only variable in the above steps is the precursor substance used, and the vapor pressure kept during synthesis.

To organize the different synthesis made, Table 2 is used. In it, each synthesis is referred to as an experiment run, and a description of the precursor substance, and vapor pressure used is given. The values for the precursor vapor pressures at laboratory ambient temperature (23 °C) were taken from [66].

For the final experiment runs, it was attempted to create a Nanotube junction *in situ*, by changing the precursor suddenly in the middle of the synthesis step (5 *min* for each precursor). It is expected to work since, as will be seen in the next chapter, the diameter distribution for different precursors are similar, giving a higher chance that Nanotube growth will keep going continuously when changing precursor.

3.3.Characterization Methods

This section will give a brief description of the methods used to analyze the material synthesized in the present work. Each characterization method will be

described in terms of the equipment used, and what is expected by using this method.

	substance	Ambient vapor pressure	Controlled pressure at reactor
1	Ethanol	52 torr	65 torr
2	TiB	7.7 torr	7 torr
3	TiB+TeB (5:2 volume)	9.7 torr	9 torr
4	TeB	14.8 torr	13 torr
5	TeB	14.8 torr	25 torr
6	TeB	14.8 torr	23 torr
7	TmB	125 torr	90 torr
8	TmB (@ 2 °C)	44.1 torr	36 torr
9	TmB (@ 2 °C)	44.1 torr	36 torr
10	TmB (@ 2 °C)	44.1 torr	15 torr
11	TeB/Ethanol	14.8 torr / 52 torr	13 torr / 65 torr
12	TiB/TeB	7.7 torr / 14.8 torr	90 torr / 40 torr
13	TiB/TeB	7.7 torr / 14.8 torr	7 torr / 13 torr

Table 2: This table presents the experiments done in this thesis. The first column identifies each experiment run number. In the second column, the abbreviations TiB, TeB, and TmB mean Triisopropyl, Triethyl, and Trimethyl Borate, respectively. The third column has the vapor pressures of the precursor liquids estimated at 23 °C, except for experiment run (6), where it is estimated at 2 °C (the liquid precursor is kept at this temperature in this run). The fourth column presents the pressure kept inside the vacuum chamber by the needle valve during synthesis step.

3.3.1. Raman Spectroscopy

This thesis used a Raman Spectrometer NTegra Spectra from the company NT-MDT. The spectrometer uses 453 nm solid state laser.

Raman Spectroscopy will be the main characterization method, in the sense that it will be the one to give insight into the physics of Boron doped SWNTs.

The RBM band will be analyzed to check qualitatively for changes in diameter distributions between different experiment runs.

The I_D/I_G ratio will be calculated as to understand the effect of Boron on the

structure of SWNTs; and the peak positions D , G^- , G^+ , and G' will be analyzed to characterize shifts owing to Boron doping. All these resonances will be fitted by Lorentzians to get the parameters peak position, area, and bandwidth (full width at half maximum, FWHM). In the analysis, linear background will be subtracted from the signal to remove influence from amorphous material produced.

Special attention will be given to G^- and G^+ peak shifts. They will be analyzed taking into account the RBM band, so that shifts are correctly assigned as a doping effect, and not as diameter dependent effect (see in section “Raman Spectra of Carbon Nanotubes”, the subsection “Tangential Mode (G)”).

To calibrate Raman with doping levels, the peak shifts will be plotted against doping concentration, as measured by XPS (next section). The calibration will be compared to other results in the literature.

3.3.2. X-Ray Photoelectric Spectroscopy

A surface analysis chamber equipped with a hemispherical analyzer Alpha 110 from Thermo has been used in this thesis. All experiment runs were analyzed with $Al K\alpha$ line 1486.6 eV.

For interpreting quantitatively XPS, each element peak observed in the spectra will be deconvolved in its components, after subtraction of a Shirley-type background. For the deconvolution step, it will be needed the positions of each component. This information can be found in literature, and is illustrated in the tables below.

B1s									
Peak components	Reference	Lyu, [37]	Ayala, [15,62]	Jacques [67]	Cermignani [68]	Monteiro [35,36]	Jacobsohn, [69]	Suzuki, [61]	Michal, [70]
Elemental B			187	187		188	188		187.5
B ₄ C		187.9	187.8	187.8	187.5	187.5			
B-C sp ² systems (in graphite or BC ₃)		189	189	188.8	188.5	188.5			
BC ₂ O		190		190	~190.5	189.8	190		
BCO ₂		192		192	~192.1		192		
Mg-B-O compounds						192.4			
B ₂ O ₃		193.2	> 192.8	193.2	193	193.1	193.2		
B in SWNT			191.5 to 192.1			191.4 to 191.8		191.8	
B in DWNT			191.4						
B in MWNT									191.5

Table 3: This table presents some published component positions in the B1s peak.

The importance of XPS to this thesis is to measure doping levels. The problem is that no standard exists for the quantification of Boron doping levels on SWNTs, mainly because it is not completely established the position of B – C bond component in B1s spectra, mainly because curvature effects have not been completely understood ([34,35,37,61,62]). In [35], it has been theoretically calculated that a ~3eV shift is to be expected for B – C component position in a (10,0) SWNT in relation to B – C component position in graphite owing to curvature effects of SWNTs. As a consequence, B – C component in (10,0) SWNT is to be found around ~191.5 eV, and this result agrees with experimental results shown in Table 3, even when considering DWNTs.

Another objective of XPS in this work is to check for by-products in the synthesis, for example Boron oxide, Boron carbide, etc.; because the formation of these by-

products is a competing process to substitutional incorporation of Boron on SWNT. This analysis will be important to understand the doping profile.

On the Results chapter, the component positions found in the present thesis will be compared to literature results shown in Table 3 and Table 4.

At last, XPS will be used to estimate production yield by the same method used in [35].

C1s						
Peak components	Reference	Lyu, [37]	Ayala, [15]	Jacques, [67]	Monteiro, [35,36]	Jacobsohn, [69]
C-C		284.5	284.5		284.5	284.5 – 285
C-O		286.5				~286
C=O		288.5				
B ₄ C				282.6		282.9
B-C in graphite			281.8	284.0		
Oxi Boron carbide						283.8
$\pi \rightarrow \pi^*$ shake up						

Table 4: This table gives some published results on the positions of C1s components positions as a function of chemical environment.

3.3.3. Scanning Electron Microscopy

It is used a JSM-6701F scanning electron microscope (SEM) by JEOL company, to characterize morphology of the produced samples at sub micrometer scale.

The SEM microscope is used to compare qualitatively different experiment runs with respect to Carbon Nanotube yield and morphology. As SEM has limited resolution capabilities, no individual SWNT is expected to be imaged with this method, but SWNT soots, and MWNTs. Nonetheless, sample's general morphology should give insight into the quality of the produced SWNT.

For example, the existence of big amounts of amorphous material, and scarce Carbon Nanotube material is an evidence for low SWNT yield. Also, length of the observable Carbon Nanotube and Carbon Nanotube soots is expected to be a good estimate of the produced SWNT length.

SEM is used in two operation modes: secondary electron microscopy (SEI), and SCANNING transmission microscopy (STEM).

SEI mode of operation is used to observe samples as produced, that is, with no preparation, other than laying the material on a sample holder. As a consequence SEI is mainly used to characterize yield.

STEM is used as an attempt to observe the inner structure of the produced MWNTs, and to observe smaller diameter tubes. Different from SEI, it needs some preparation step to disperse the produced material. It is used a similar dispersion recipe as can be found in [15], and [28]:

Sonicate approximately 2 mg of the synthesized Carbon Nanotube material in 10 ml isopropanol for 30 min.

After sonication, the resulting liquid is dropped on a STEM grid.