3
Production techniques

There are several production schemes that are used to produce carbon nanotubes. I am going to briefly describe the most used ones and at the end I will give a complete description of the high vacuum chemical vapor deposition system that we have used.

3.1
Arc discharge

Arc discharge was the first reported technique to produce carbon nanotubes and it is very similar to the technique used on the mass production of C_{60} (2).

When first used for the production of carbon nanotubes, this technique consisted of passing a electrical current between two graphite electrodes separated by a few millimetres in a argon atmosphere around 100 torr. MWNTs were produced as a result of this growing scheme (2). Iijima, S et al., (26) first reported the formation of SWNTs by adding Fe to the graphite electrodes. Fig 3.1 shows an arc discharge scheme (5).

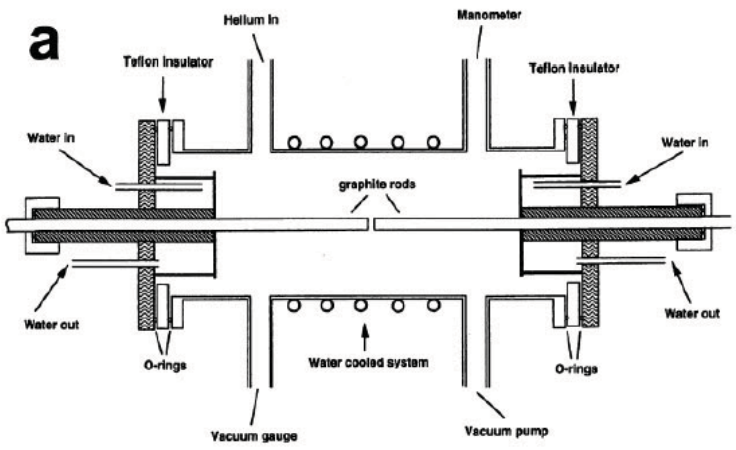

Figure 3.1: Diagram of a arc discharge scheme (5).

Despite of the high yields of SWNTs that can be obtained using a mixture of Ni and Y on the graphite electrodes (5) and the high quality of tubes, this process is extremely expensive and various other contaminant products such as amorphous carbon and encapsulated metal particles are produced (5).

3.2 Laser ablation

This technique consists of vaporizing a target in a Ar atmosphere inside a 1200^0C furnace using a high powered laser (5). Fig 3.2 shows a laser ablation scheme (27).

If the target is made of pure graphite, the result product is MWNTs (27) and as the arc discharge scheme, SWNTs are produced if metal particles are added to the graphite target (28).

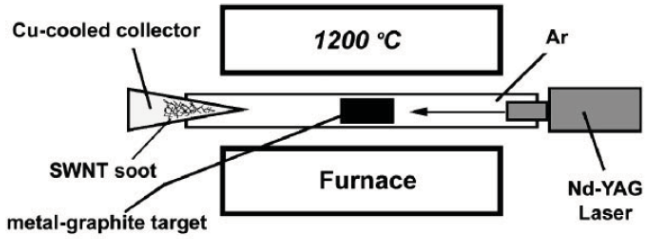

Figure 3.2: Diagram of a laser ablation scheme (5).

It is possible to have a higher amount of produced tubes by using a subpicosecond pulsed laser technique or using a porous graphite target with metal catalyst (5). But it is very difficult to reproduce the experiments with similar growing conditions and the production yield is not high enough to justify the elevated production cost (5).

3.3 Chemical vapour deposition

This method consists on the decomposition of a hydrocarbon on a controlled atmosphere at elevated temperatures and with the presence of a metallic catalyst (5).

It allows a several number of parameters combinations such as the hydrocarbon, the catalyst size, the temperature, the pressure of the precursor or the carrier gas and the deposition rate (5). Each change on the parameters will lead to the formation of a different structure and a different amount of the production sample (5). For instance, it is possible to achieve a high yield

of produced tubes, such as on the HipCo process where a gas phase of SWNTs are produced at a 10atm pressure of a CO gas, that is used as the carbon feedstock, and $Fe(CO)_5$ as catalyst. It is also possible to control the diameter of the produced tubes by changing the pressure and temperature of the CO (29).

Another example of this method configuration is the use of an inert gas carrier to leave a solution of the hydrocarbon and the catalyst inside the furnace. One example of this solution could be the use of Toluene or Benzene and Ferrocene as the carbon precursor and catalyst respectively (30). Fig 3.3 shows a scheme of this method and Fig 3.4 shows MWNTs prepared using the described solution.

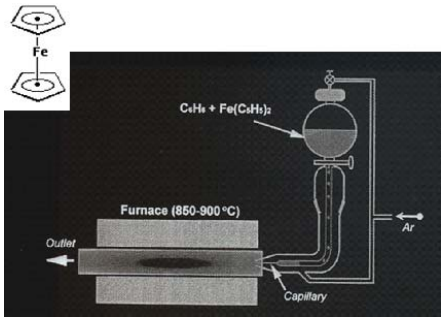

Figure 3.3: Scheme of chemical vapour deposition method (5).

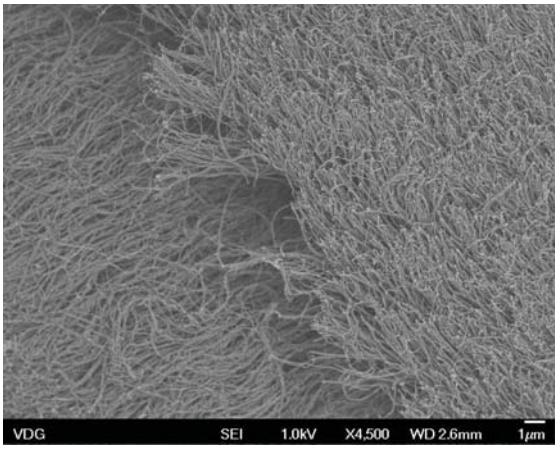

Figure 3.4: MWNTs prepared using a solution of Toluene and Ferrocene as the carbon precursor and catalyst respectively. Image provided by PUC-Rio

As advantages of this production method, is the easy scalability to produce large quantities of tubes (5) and the possibility to grow aligned forests of long tubes over a controlled area, as shown in Fig 3.5 (8).

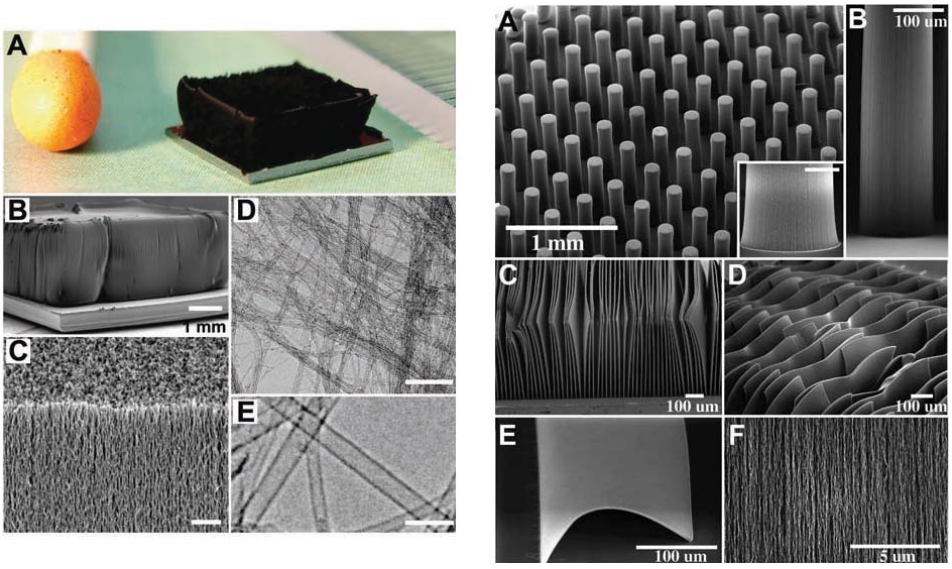

Figure 3.5: The figure on the left shows an aligned forests of long tubes and on the right the growth over a controlled area (8).

3.4 High vacuum CVD

The high vacuum chemical vapour deposition (HVCVD) system was the production method that we have built for the preparation of the boron doped SWNTs samples, having in mind, other works that reports this production method (31, 32, 33). For this reason, this method and the system construction will be explained in details.

HVCVD is a modified CVD scheme in which the atmosphere and catalyst are cleaned from any impurity and then, the vapour phase of the precursor is introduced into the reaction hot zone. This clean environment is capable to produce a high yield of high quality SWNT.

Table 3.1 lists all the basic materials for the construction of our deposition system. Materials which are not fully specified do not require further detailed description. O-rings and clamps are not listed.

Table 3.1: List of materials

Number	**Material**
1	Mechanical pump (any type)
1	Mechanical pump EDWARDS XDS 10
1	Turbo molecular pump
1	Long quartz tube with external diameter of 30mm and thickness of 2mm
1	KF 25 Mini gate valve VATLOCK
1	KF 16 EDWARDS speed valve
1	Glass test tube ended with a KF 16 shape
1	Furnace
1	MKS type 247, 4 channel readout
1	MKS type 1479A, N2 controller with 500sccm range
1	MKS type 1179A, N2 controller with 100sccm range
1	MKS type 660
1	MKS type 622 , Baratron with range of 100torr
1	EDWARDS TIC Instrument Controller
1	EDWARDS AIM-XL-NW25
1	Gas dosing and shut-off valve
1	Simple needle valve with KF 16 end
1	H_2 cylinder with all gauges, valves and a KF 16 outlet
1	KF 25 tee
1	KF 16 tee
1	Unequal tee with two aligned KF 25 and one KF 16
1	Reducing 4-way cross with two aligned KF 25 and two aligned KF 16
2	KF 25 90^0 Elbow
1	KF 16 90^0 Elbow
1	Small KF 25 Flexible hose
2	Long KF 16 Flexible hoses
2	Long KF 25 Flexible hoses
2	KF 16 to KF 25 tubulated reducing adapters
1	CF to KF 25 Adapters (Adapt the turbo pump to the system)
2	Adapters to link the quartz tube with the KF 25 system, Fig 3.6

And now the Lego begins. In order to simplify the description, the assembly processes will be divided in five sectors. At the end, I will show how these sectors forms the HVCVD system.

3.4.1
Sector 1 - The primary vacuum stage

The system is composed of two different vacuum stages. Sector 1 is related to one of these stages, which I will call primary vacuum stage. This is an important part of the system, since it will allow it to reach pressures on the order of 10^{-7}torr.

In this sector, the mechanical pump (any type) is linked to the turbo molecular pump by one of the long KF 25 Flexible hoses. The turbo pump is connected to the KF 25 90^0 Elbow, that is then connected to the KF 25 tee by the small KF 25 Flexible hose. The end of this tee which is aligned to the flexible rose is connected with the KF 25 Mini gate valve VATLOCK, while the other end is connected to the EDWARDS AIM-XL-NW25 which is linked to the EDWARDS TIC Instrument Controller.

The small flexible rose is not necessary, but we used it in order to minimize possible vibrations or accidental movements that could damage the quartz tube.

3.4.2
Sector 2 - Secondary vacuum stage

The secondary vacuum stage will work in conjunction with the primary stage and will play different roles on the system. It will allow the opening of the mini gate valve without damaging the turbo molecular pump and will clean the environment of the quartz tube during the growth process, thus maintaining a constant pressure of the H_2 and growth precursor.

This stage is composed of the mechanical pump EDWARDS XDS 10. The importance of this model is to prevent the oil contamination on the environment, in case of misuse of the system, since this model does not use oil as sealant or lubricant. This mechanical pump is connected with one of the long KF 25 flexible hoses, which is linked to the gas dosing and shut-off valve by the KF 16 to KF 25 tubulated reducing adapter. The other end of this gas dosing valve is connected to the KF 25 90^0 elbow by the other KF 16 to KF 25 tubulated reducing adapter. It is important to notice that both of the arms of this elbow must be parallel to the ground. The reason for this geometry is to prevent small particles coming from the quartz tube to enter the gas dosing valve.

3.4.3
Sector 3 - Heart of the system

This part is where the precursor takes place. It is connected with other important sectors such as the primary vacuum stage, to the quartz tube and to the sector responsible for the passage of the H_2 to the system.

The assembly of this sector begins with the reducing 4-way cross with two aligned KF 25 and two aligned KF 16. One of the KF 25 end is connected with the unequal tee. This tee is linked to the MKS baratron by the KF 16. The MKS 660 is to be linked to the MKS baratron and one of the KF 16 of the 4-way cross is to be connected with the KF 16 EDWARDS speed valve.

To finish this sector, the test tube ended with a KF 16 shape is connected vertically to one end of the simple needle valve while the other end is connected to the KF 16 90^0 elbow. This elbow is then connected to the remaining KF 16 end of the 4-way cross.

3.4.4
Sector 4 - Where the growth takes place

This is the simplest part of the system, but, since the quartz tube can be easily broken, I decided to create a sector just for it.

The two adapters are placed at the end of the quartz tube. Fig 3.6 shows a photography of one of the adapters and the o-ring inside of it. This dynamic o-ring is the responsible of sealing the inner part between the quartz tube and the adapter.

Figure 3.6: Adapter and the o-ring that seals the quartz tube.

The use of Apiezon to seal is highly recommended in all the o-rings, but it's use is mandatory on those two o-rings in order to prevent any damage to the quartz tube at the same time that is a good sealing agent.

3.4.5
Sector 5 - H_2 gas and air entrance

The importance of this sector is to allow the passage of H_2 into the system to reduce the catalyst and to allow the air entrance in order to open the system after the growth.

The assembly of this section begins with the long KF 16 flexible hose. One end of this hose is connected to the MKS type 1479A and the MKS type 1179A by the KF 16 tee. The 100sccm MKS is connected to the H_2 cylinder by the remaining KF 16 flexible hose, while the other MKS end is in contact with the atmosphere. Both MKS are linked to the MKS type 247. Just in case of a MKS failure, an optional valve can be connected with the open end of the MKS that is in contact with the atmosphere.

3.4.6
Final set up

Now, all sectors will be united to form the final HVCVD set up. First of all, the furnace will be placed around the quartz tube. Care must be taken and all the sectors must be placed on appropriate position to avoid breaking. No section can be sustained by another one.

After positioning the furnace around the quartz tube, connect the elbow of sector 2 and the tee of the sector 3 on each tube's adapters. After that, connect the remaining end of the 4-way cross of sector 3 on the mini gate valve of sector 1. At last, connect the long KF 16 flexible hose of sector 5 on the KF 16 EDWARDS speed valve of sector 3. Fig 3.7 shows a scheme of the system.

Assure that the exit of each mechanical pumps are not opened to the ambient air. Any carelessness could lead to a risk situation, allowing H_2 and other residues to scape into the laboratory.

3.4.7
Turning the system on

Turning the system on for the fist time is an important step, since it will allow any leakage to be discovered. For that, close the mini gate valve, fully open the gas dosing valve and the EDWARDS speed valve, turn on and open the MKS connected to the H_2 cylinder and close the MKS that is in

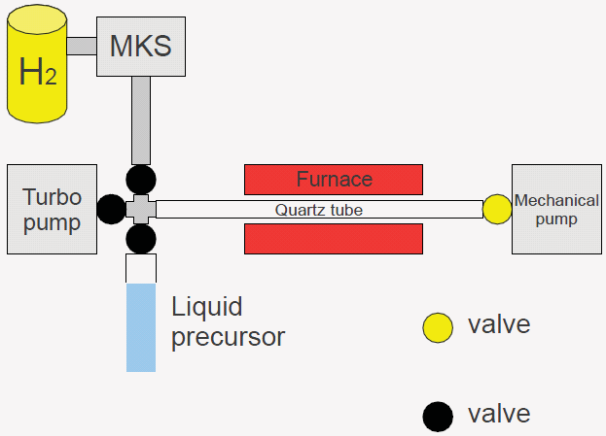

Figure 3.7: Scheme of the high vacuum CVD system that we used.

contact with the atmosphere. In case of using the optional valve, is highly recommended to open this last MKS and close this valve.

After the above procedure, the two mechanical pumps can be turned on, followed by the turbo molecular pump. Wait until the vacuum reach it's lower pressure on the tube's zone, fully close the gas dosing valve and then open the mini gate valve. Now it is possible to find leaking on the system by opening and closing the valves and MKSs. One possible mistake is to open the mini gate valve before closing the gas dosing one, what could lead to the passage of oil through this last valve into the system. That is the reason why we use the EDWARDS XDS 10 mechanical pump.

3.4.8 How to use the system

This system can be used following different procedures, and each one will basically depend on which catalyst is being used.

I will describe how to operate the system using a powder as catalyst, and because of that, we used a quartz crucible to support the powder.

To put the crucible inside the quartz tube, supposing that it is in high vacuum conditions, close the mini gate valve and open the MKS that is in contact with the atmosphere. Since the gas dosing valve is closed, the pressure inside the tube will begin to increase and then the sector 3, 4, 5 and part of the sector 2 will be able to be opened. I suggest to disconnect the junction between sectors 2 and 3 in order to put the crucible inside the tube, in the middle of the furnace. Also disconnect the test tube of sector 3, fill it with the liquid precursor, for example ethanol, and reconnect it to the system.

To return to vacuum conditions, reconnect the sectors 2 and 3, close the MKS that is in contact with the atmosphere and slowly open the gas dosing

valve until the pressure get stable. This procedure must be slow in order to prevent the powder from flying inside the tube. Another important step is to slowly open the valve at the test tube for a few seconds in order to clear the test tube environment from atmospheric air. It is impossible to make vacuum in this tube since there is always the vapour of the precursor. But at least no significant amount of atmospheric air will be present on the system and only during the initial moments of the growth. Close this valve and wait until the pressure get stable.

After that, the gas dosing valve is closed and the mini gate valve can be opened. The pressure will reach values on the order of 10^{-5}torr or less. The reason for this value to be higher than the system with no catalyst, is because the powder has many impurities that are evaporating into the system. In our case, the catalyst is a porous powder and was prepared in a Isopropyl alcohol solution.

In order to clean the catalyst, the temperature is slowly increased in a 50^0C step, maintaining a pressure around 10^{-5}torr. If the temperature increases to fast, the pressure will be too high for the turbo molecular pump and the powder will start to jump off the crucible.

This process can continue until the catalyst's reduction temperature is reached. Other possibility to accelerate the process is to close the mini gate valve and fully open the gas dosing valve when the temperature is around 300^0C. At this temperature, the powder is almost clean. After that, no step will be needed to increase the temperature until the reduction one.

When the reduction temperature is reached, close the mini gate valve if it is not closed and open the gas dosing valve if it is not opened. This will depend on which process above was followed. Open the H_2 cylinder and the corresponding MKS and control the gas pressure by the gas dosing valve. After the reduction, close the H_2 cylinder and MKS, wait for the pressure to become stable and then close the gas dosing valve, the EDWARDS speed valve and open the mini gate valve. Increase the temperature until the desired growing temperature while the pressure become around 10^{-5}torr. After reaching that temperature, close the mini gate valve, open test tube's valve and control the precursor's pressure with the gas dosing valve.

After this procedure, close the precursor's valve, fully open the gas dosing one and wait for the pressure to become stable. Then close this last valve, open the mini gate one, turn off the furnace and wait until the system be cool enough to take the sample from inside the tube.

When the temperature is around the ambient conditions, close the mini gate valve, slowly open the EDWARDS speed valve and open the gas dosing

valve to clean the system from possible H_2 remaining on sector 5. After that, close the gas dosing valve and open the MKS related to the air entrance on the system.