4
Boron doped carbon nanotubes

The substitutional boron doping of a carbon nanotube is when a carbon atom is substituted by a boron one. Doping can lead to several changes on the SWNT properties and allows the use of this structure for new applications.

This chapter is divided in three sections. The first section describes the production methods of boron doped carbon nanotubes and the techniques used to characterize the tubes. The second section regards the structural properties and the last one describes the electronic properties and some applications of this material.

4.1
Synthesis of boron doped carbon nanotubes

The production methods of boron doped carbon nanotubes are quite similar to the production methods of pure tubes. The main difference is the introduction of the boron atom at some stage of the growth, or after it.

B.C. Satishkumar et al., (34) produced boron doped multi wall carbon nanotubes by the pyrolysis of a mixture of C_2H_2 and B_2H_6. The produced tubes had a diameter in the range of 30 to 60nm. XPS and EELS revealed a doping concentration around 3%. It was also found that the doping level does not vary with the depth, and by using thermogravimetrics measurements, they found that the doped tubes have a increased resistance to oxidation, that can be an indication of a improved graphitization in comparison to the pure carbon nanotubes (34).

The arc discharge technique can be modified in order to obtain doped tubes (35). In the case described by Hsu, WK et al., (35), the graphite anode was filled with a BN powder and the cathode was made of pure graphite. The cathode and the anode where placed in a Helium atmosphere with a pressure of 500torr. EELS measurement found substitutional boron on the MWNTs, but could not determine the doping concentration due to the large dimensions of the tubes. It is important to mention that no trace of nitrogen was found on the sample (35).

Similar to the arc discharge, the laser vaporization technique can also be modified in order to synthesize boron doped tubes. On the study conducted by McGuire, K et al., (36), a mixture of a carbon paste, elemental boron, cobalt and nickel as catalysts were used as a target for the pulsed laser in a Argon atmosphere at 1100^0C (36). In that work, several targets with different boron to carbon concentrations were prepared. Despite the EELS measurements failing to detect the boron atoms on the nanotubes, thermopower measurements showed a permanent p-type behaviour for the produced tubes, in contrast to the undoped sample. Except by the 1.5% of boron to carbon concentration on the targets, all higher concentrations showed a more intense D band on the Raman scattering measurements in comparison to the sample prepared by the pure carbon target (36). XPS measurement was performed on tubes prepared by a similar condition and showed an upshifted boron 1s peak in relation to boron in graphite. The authors relate this energy upshift with the cylindrical structure of the SWNTs (37).

High vacuum CVD is also used to produce boron doped SWNTs by the decomposition of Triisopropyl Borate as a carbon and boron precursor (33, 32). The reported evidence for doping is a XPS measurement. As in the case described above, this measurement also revealed an upshifted boron 1s peak that was related to the boron presence on the cylindrical SWNT structure (33, 32). It is important to say that until now, such upshift had no theoretical background, and the reported peak alone provides almost no evidence for doping, since this peak could correspond to another boron environment. It is important to note, as will be explained on the next chapter, that based on discussions about our results, professors Rodrigo B. Capaz and L.A. Terrazos, showed a theoretical evidence for the upshift of the boron 1s peak on the XPS measurement, and that the calculated shift is in agreement with our experimental data (38). We found an upshifted G band peak on the Raman spectra of the doped samples produced by this method (38) while Suzuki, S et al.,(39) only found this shift under the presence of H_2 or Argon during the synthesis (39). Such shift on the Raman spectra is an evidence of doping (40) and we will try to explain the discrepancies between our work and the work made by Suzuki, S et al., (39) on the next chapters.

Unlike the previous methods where the boron atom is introduced on the SWNT structure during the growth of tubes, an additional method introduces this foreign atom after the growing process, in what is called substitutional reaction.

One of the approaches for this method is placing a B_2O_3 powder in a graphite crucible, and then covering the powder with MWNTs produced by CVD technique (41). After this procedure, the crucible with the powder and tubes, were placed in a Argon atmosphere at 1100^{0}C for 4 hours. EELS measurements revealed a boron to carbon concentration up to 10% doping the tubes. The oxygen of the B_2O_3 reacted with the carbon atoms that were substituted by the boron, and leaved the sample in the form of CO (41). As revealed by TEM and XRD measurements, it was also found that the presence of boron improved the graphitization of the MWNTs (41).

4.2
Structural and mechanical properties of boron doped carbon nanotubes

An interesting characteristic of the B-MWNT prepared by arc discharge, observed in X-ray and electron diffraction measurements, is an enhanced 3D ordering, that is a hexagonal unit cell stacking similar to the HOPG and graphite single crystal, and also observed the preferential formation of zigzag tubes over other chiralities (35). Such 3D ordering is not present in pure MWNTs due the presence of different chiralities on the different walls, then this feature can be explained by the presence of the prevailing zigzag structure among the tubes. Another important finding is that EELS shows the prevailing presence of boron on the tips of the tubes, rather than on the remaining structure of them.

One explanation for the higher prevalence of zigzag pattern among the samples is that the closure time for zigzag tubes with boron at the tips is larger in comparison to the armchair case. At the same time, the presence of boron at the tips of the tube is more favorable than the presence of this element on the rest of the structure (42).

4.3
Electronic properties of boron doped carbon nanotubes

Boron is a atom with five electrons and have the [He]$2s^2 2p^1$ electron configuration. Thus, for a low doping content on a carbon sp^2 configuration, we can consider that there will be one missing electron on the valence band of the structure per boron atom, when this element is making a substitutional doping.

For this reason, when the boron content in the SWNT is low, the rigid band model can be used with a negligible error (16). This model assumes that density of states of the low doped material is the same as the undoped material, but with a shifted Fermi level to inside the conduction or valence band of the undoped structure. Since boron atoms have one missing electron in comparison to carbon, the Fermi level is lowered in comparison to the undoped sample (16).

For a better understanding of the electronic properties of the B-SWNT, Wirtz, L et al., (9) made ab initial and self-consistent tight binding calculations on a semi conducting SWNTs structure doped with boron. They found that the B-doping of the tubes lowers the Fermi level while creates an acceptor state on what would be above the valence band of the undoped tube. They also found that different doping arrangement for the same doping level would lead to different results. For instance, if the boron atoms are randomly disposed in a high doping concentration, the Van Hove singularities would disappear and the density of states would resemble a zero dimensional structure. Fig 4.1 shows a plot for the calculated energy dispersion relations and the density of states of the B-SWNTs. All of those calculations shows a metallic behaviour for those tubes (9). Therefore, doping SWNTs with boron can be a good alternative in comparison to control the chirality to obtain metallic SWNTs.

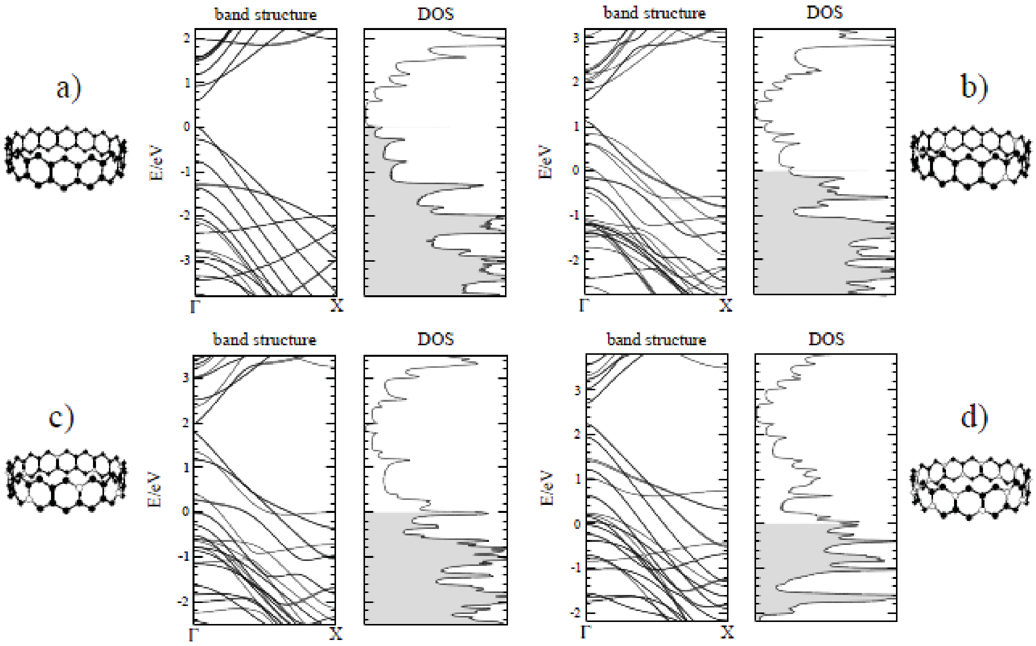

Figure 4.1: Plot of the calculated energy dispersion relations and the density of states of a a) 0at%, b) 6.25at%, c) 12.5at% and d) 25at% for a (16,0) boron doped SWNT (9).

STS experiments found an acceptor like peak on the local density of states of B-doped MWNTs, with a boron concentration around 1% to 5%, prepared by the arc discharge of a BN-rich anode (10). This peak could not be explained by the acceptor peak described above and the authors realized that one possible explanation is the presence of BC_3 nanodomains on the structure, as shown in Fig 4.2. In that case, the Fermi level is not so shifted as in the case of single boron atoms on the structure, and that acceptor state suggest a metallic behaviour for those tubes (10). Microwave conductivity measurements also shows a metallic profile for those tubes, in contrast to pure MWNTs (35).

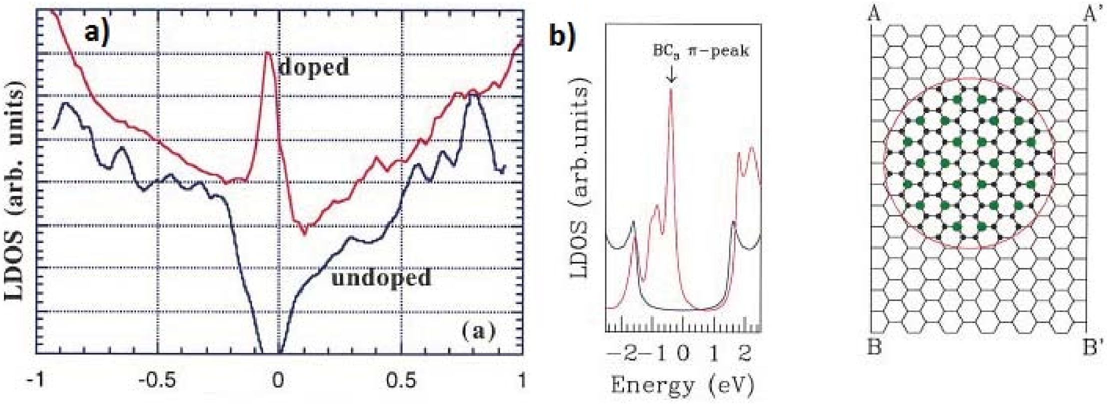

Figure 4.2: a) Shows the STS data for the doped and undoped sample and b) shows the theoretical local density of states associated with a BC_3 nanodomain (10).

Local density of states over the edges of the tubes revealed that substitutional boron at the tips leads to localized states near the Fermi level that allows a good field emission properties (43). Ab initial calculations shows that the work function is 1.7eV smaller for boron doped tubes when compared to undoped tubes, that has a work function around 5eV. Experiments with boron doped samples prepared by arc discharge shows a turn on voltage of 1.4V/μm, that is less than the half of the turn on voltages for pure carbon nanotubes and comparable to the best carbon based materials for cold cathodes (43). Another work regarding this property revealed that boron doped samples are able to support a field emission current of 400μA for periods greater than 3 hours. It was concluded on this work that boron doped tubes are good candidates to be applied on large surface area emitters in comparison to nitrogen doped tubes, which had shown more suitable for high electron current applications (20).

Boron doped SWNTs can also behave as superconductors. Murata, N et at., (18) showed that uniform thin films of boron doped SWNTs with doping level up to 2% exhibits a Meissner effect with a transition temperature T_c of 12K. They also concluded that a lower boron concentration and a higher uniformity of the film would lead to a T_c around 30K to 40K (18). One year later, Nakamura, J et al., (19) reported a thin film of a narrow diameter SWNTs with a boron doping level bellow 1% that exhibit a T_c of 19K under the application of a small pressure (19).

Some applications has arisen due to the metallic character of the boron doped carbon nanotubes. As an example that explores this feature is the transparent conduction of a film made of those tubes (22, 21). Those films were prepared by spraying different amounts of a solution of boron doped SWNTs prepared by a substitution reaction of B_2O_3 on different quartz substrates in order to have different films thickness. The electrical resistivity of each sample was measured with the optical transmittance at 550nm and compared to a pure carbon nanotube sample. It was found that the dc conductivity of the boron doped tubes are enhanced by a factor of 3.4 when compared to a pure sample at the same optical transmittance. This results implies that boron doped tubes are quite suitable for electronic applications in a huge types of substrates (22)

The properties and applications described above are the state of art on the research of boron doped carbon nanotubes and the applications described justify the research on that structure.