1. Introduction

1.1. Background

It is well known that carbon nanotubes appear in a fascinating variety of forms, with one or several graphitic sheets, with closed or open tips, with well-ordered and disordered structure. Imagine take a sheet of graphite, a simple planar assembly of carbon atoms disposed in a honeycomb lattice, and roll it up to form a cylinder. You would obtain a very long, yet very thin cylindrical structure. It could have properties similar to graphite, be flexible but hard to stretch. Since 1991, the dream of fabricating, manipulating, characterizing and modifying such graphite structure has come true [1.1]. These objects were named carbon nanotube and became one of the most fascinating materials that have been discovered in recent years. Nanotubes shows excellent electronic [1.2-1.5] and mechanical properties [1.6-1.8] that have triggered strongest effect toward various potential applications. The possibilities range from composite materials, nanoelectronics, microscope probe, chemical and biological sensors, to electron sources.

In ideal case, a carbon nanotube consists of either one cylindrical grapheme sheet (single wall carbon nanotube, SWNT), or several nested cylinders with an inter-layer spacing of 0.34-0.36nm that is close to the typical spacing of turbostratic graphite (multiwall nanotube, MWNT). There are many possible way to roll up the graphite sheet. One can roll up the sheet along one of the symmetry axis: this gives either zigzag tube, or armchair tube. It is also possible to roll up the sheet in a direction that differs from any symmetry axis and obtains a chiral tube (Fig.1.1). In most cases, the layers of MWNTs are chiral and of different helicities.

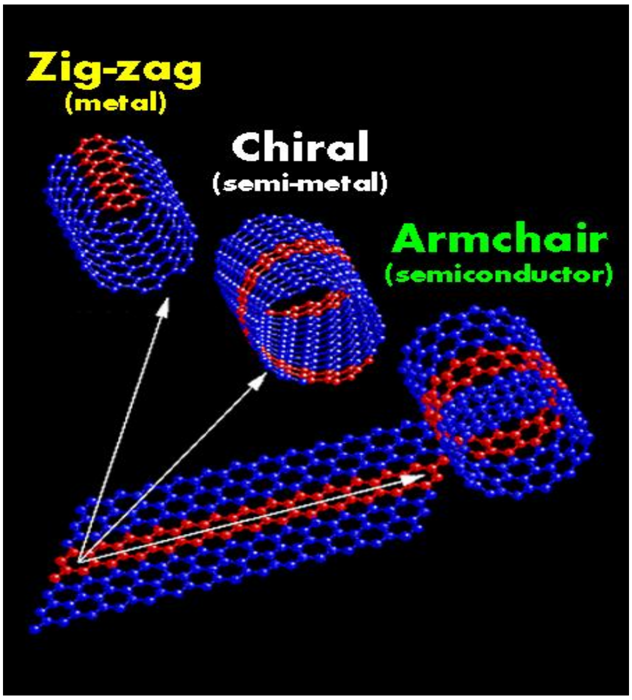

Figure 1.1: Schematic diagram of various types of carbon nanotubes. According to symmetry axis to the roll up the graphite sheet, CNTs are classified into three types: (a) zigzag tube, (b) armchair tube, and it is also possible to roll up the sheet in a direction that differs from any symmetry axis and obtains a (c) chiral tube [17].

Defects in the hexagonal lattices are usually present in the form of pentagons and heptagons. Pentagons always produce a positive curvature of the grapheme layer (Fig1.2). Heptagons give rise to a negative curvature of the tube wall [1.9]. Defects consisting of several pentagons and heptagons have also been observed (Fig 1.3).Such an arrangement forms a link between two different tubes and is called a “juction” (Fig1.4). The electronic properties of carbon nanotubes have been studied in a large number of research works [1.10-1.12].All models show that the electronic properties vary in a predictable way from metallic to semi conducting with diameter and chirality. This is due to the band structure of grapheme and is absent in systems that can be described with usual free electron theory. Graphene is a zero-gap semiconductor with the energy bands of the Pi-electrons crossing the Fermi level at the edge of the Brillion zone, leading to Fermi surface of six points [1.13]. Grapheme should show a metallic behavior at room temperature since electrons can easily cross from the valence band to conduction band. However, it behaves as a semi-metal because electronic density at the Fermi surface is very low. Rolling up the grapheme sheet into a cylinder imposes periodic boundary conditions along the circumference and only a few limited number of wave vector are allowed in the direction perpendicular to the tube axis. When such vetors cross the edge of Brillion zone, and thus the Fermi surface, the tube is metallic. This is the case for all armchair tubes (Fig 1.5(a)) and one out of three zigzag and chiral tubes (Fig 1.5(b)). Otherwise, the band structure of the tubes shows a gap leading to semiconducting behavior, with a band gap that scales approximately with the inverse of the tube radius [1.13-1.14].

Figure 1.2 : A scheme of pentagon in a grapheme layer. Pentagons always produce a positive curvature (30^o) of the grapheme layer [19].

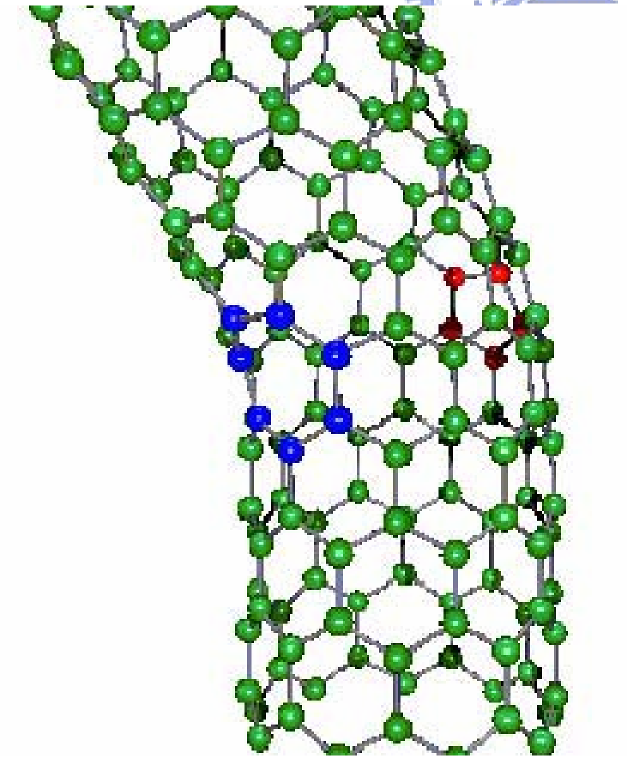

Figure 1.3: Defects of several on carbon nanotube. Red solid circles: pentagons always produce a positive curvature of the grapheme layer. Blue solid circles: heptagons give rise to a negative curvature of the tube wall [19].

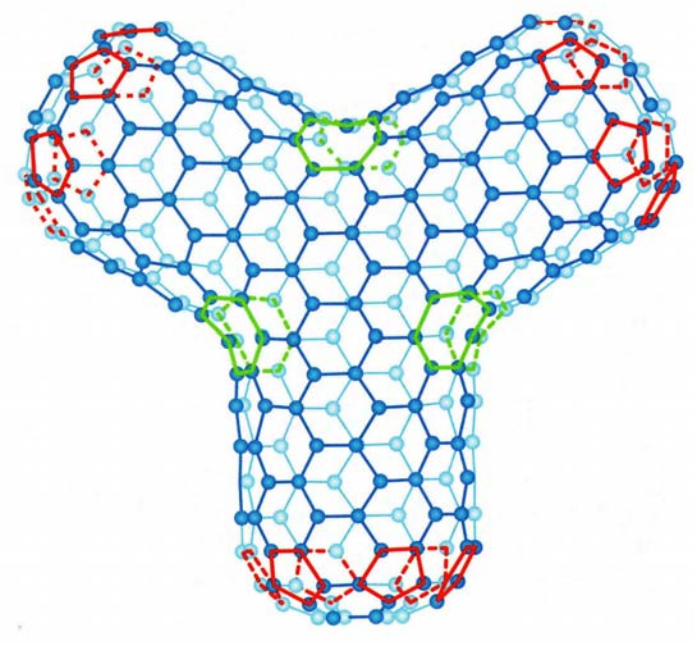

Figure 1.4: A so called “Y” junction of carbon nanotube [18].Red solids circles and green solids are pentagons and heptagons, respectively.

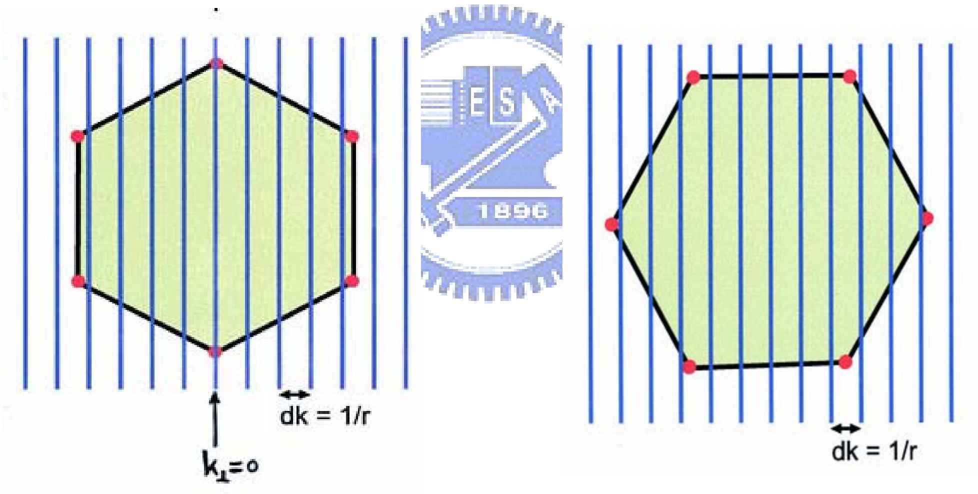

Figure 1.5:Brillouin zone folded model of armchair and zigzag nanotubes [20].

1.2. Motivation

Carbon nanotubes are excellent field emitters for application in the cold cathode flat panel display, electron guns, and many nanodevices, due to their high field emission current density, low turn-on field and stable currents. To enhance the field emission properties of nanotubes, some effective methods are used to treat the surface of carbon nanotube (Detail listed in Table2.7 (a) (b)).

The purpose of post-treatment was to remove amorphous carbon on the nanotube. It may also change the structure of carbon nanotube on the surface, such as removing the metal particle on the tip of tube (opening the tip) and reducing the wall of carbon nanotubes. Finally, it can also create the defect on the surface of the walls and modify carbon nanotube surface for uniform and homogenous emission- site distribution. The use of laser is very attractive, since it can be easily integrated to a manufacture line, and processing time is expected to be very short. Colbert and Smalley [1.15] had observed the enhancement of field emission of CNTs by using laser irradiation and they interpreted this phenomenon as being due to the presence of localized plasma, which is induced by instant vaporization on CNTs and ionization of the species. In this study the microwave plasma chemical vapor deposition (MPCVD) system is employed to synthesize carbon nanotubes and KrF excimer laser is employed for the post-treatment of CNTs. The effects of the post-treatment parameters such as laser power, pulse number, laser power density, and precursor atmosphere, on the field emission characteristics of the CNTs are discussed. It is our motivation that, by performing such comprehensive studies, including modifying growth and post-treatment processes, the I_D/I_G dependence on field emission properties can be obtained and manipulated.

Reference

[1.1] S. Iijima, Nature 354, 56 (1991):.

[1.2] N. Hamada , S.I Sawada, and A. Oshiyama ,Phys. Rev. Lett. 68 ,1579(1992).

[1.3] R. Saito, M. Fuijta , G. Dressalhaus, and M.S Dressalhaus, Appl. Phys. Lett. 60, 2204(1992).

[1.4] J.W.G. Wiloder, L.C Venema, A.G Rinzer, R.E Smalley, and C. Dekker, Nature 391, 59 (1998).

[1.5] T.W. Odem, H.J. Lin, P. Kin, and C.M. Lieber, Nature 391, 62(1998).

[1.6] M.M.J. Treacy, T.W. Ebbesce, and J.M. Gibson, Nature 381, 678(1996).

[1.7] M.R. Flvo, G.J. Clary, R.M. Tayler, V. Chi, J. F. Brooks, S. Washburn, and R. Superfine, Nature 389, 582(1997).

[1.8] E.W. Wong, P.E. Sheechan, C.M. Lieber, Science 277, 1971(1997).

[1.9] S. Iijmma, T. Ichihashi, and Y. Ando, Nature 356 , 777(1992).

[1.10] X. Blasé, L.X. Benedict, E.L. Shirley, and S.G. Louie, Phys. Rev. Lett. 72 , 1878(1994).

[1.11] J.W. Mintmire, C.T. White. Carbon 33, 893(1995).

[1.12] C.L. Kane, E.J Mele, Phys. Rev. Lett. 78, 1932(1977).

[1.13] P.R. Wallace, Phys. Rev.Lett. 71,622(1947)

[1.14] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, “Sicence of fullerence and carbon nanotube”, San Diego, Academic Press (1996).

[1.15] D.T. Colbert, R.E. Smalley, Carbon 33, 921(1995).

[1.16] N Hamada, S.I. Sawada, A. Oshiyama, Phys.Rev.Lett.68,1579 (1992).

[1.17] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, “Science of Fullerence and Carbon Nanotubes”. San Diego: Academic Press,1996.

[1.18] 美國 Rice 大學 R.E.Smally 研究小組照片,網址 Http://cnst.rice.edu/pics.html.

[1.19] 李峰.有機物催化熱解法制被單壁奈米碳管及其物理性質:[博士論文].瀋陽:中國科學院金屬研究所,2001.

[1.20] R.Saito,M.S. Dresslhaus, and G. Dresselhaus, “Physical Properties of Carbon Nanotubes”, Imperial College,1998.