Chapter I Introduction

Richard Feynman suggested in his famous lecture, entitled "There's Plenty of Room at the Bottom", and predicted the rise of nanotechnology in 1959. Three decades later, Feynman's vision has become the greatest scientific frontier of the century. It opened a new field of "Nanostructures" having dimensions of about 10 to 1000Å, a size that is small for engineering standards, common for biological standards, and large to chemists. Countless researchers now are developing sorts of nano-technologies on earth hardly. In the days to come, something amazing will be realized such as：car needn't to be washed, TVs are going to become ultra thin and power-saving, all data of a library can save into one disk, etc. Let's wait and see the easy life to be carried out in the feature.

1.1 Introduction to Carbon nanotubes (CNTs)

Carbon, a very common element in nature, has many different kinds of structures depending on its bonding. Among all of them, the most familiar to the general public are graphite and diamond. So-called graphite structure means the carbon atoms of hexagonal arrays in an ABAB-planar stacking arrangement bonded to the three nearest neighbors by strong covalent trigonal sp^2 bonds [Fig. 1-1]. And the carbon atoms in diamond structure are bonded to their nearest neighbors by strong covalent tetrahedral sp^3-bonding hybridization [Fig. 1-2]. Though they are both composed of carbon, the costs of them are as far removed as heaven from earth. Until 1985, Kroto and Smalley found a new carbon structure, C_{60} [Fig. 1-3].[Kroto-1985-12] Another type of carbon structure was known by people.

At 1991, Dr. Sumio Iijima sitting at an electron microscope at the NEC Fundamental Research Laboratory in Tsukuba, Japan, first noticed odd nano scale threads lying in smear of soot.[Iijima-1991-56] It is made of pure carbon with exquisitely long and thin geometry. Soon, it has become known as CNTs, and been an intensely study scientific topic of ever since, because of its unique morphology with excellent mechanical and electrical properties.

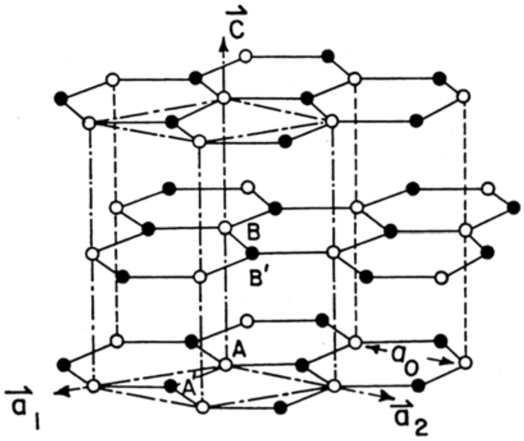


Fig. 1-1. Graphite structure

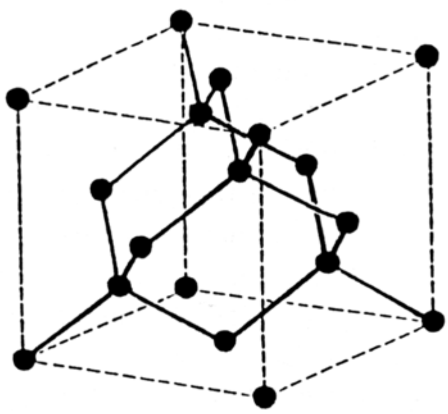


Fig. 1-2. Diamond structure

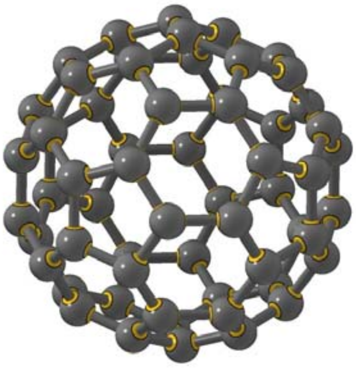
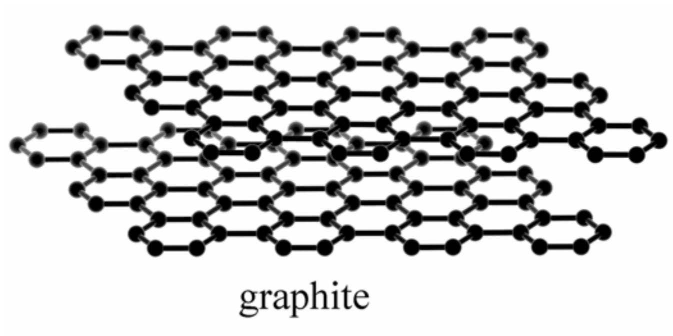
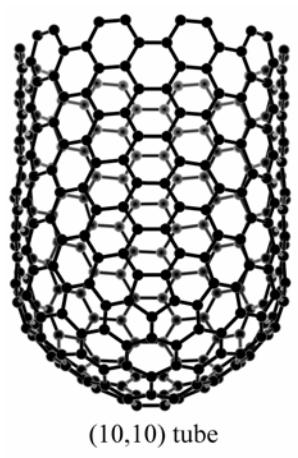


Fig. 1-3. C_{60}

CNTs are one dimension nanostructure of carbon bonded by sp^2 and sp^3 bonds with hollow and cylindrical construction. We can simply image that it is a graphene sheet [Fig. 1-4(a)] shaped like a roll in nano-scale [Fig. 1-4(b)]. The multi-walled CNTs (MWNTs) and single-walled CNTs (SWNTs) are defined whether the no. of rolled graphene layers is more than one or not. It is said that the CNTs have extremely high aspect ratio just because the diameters of CNTs only from 1-2 nm to 8-90nm, but the length of a tube could be from several nanometers to several micrometers. Although graphite and CNTs are both composed of graphite structure of carbon, the price of CNTs is still much higher even now.

CNTs have attracted considerable attention in recent years. Various methods have been used for synthesizing CNTs, e.g. arc discharge, laser ablation and chemical vapor deposition (CVD), where the CVD methods are the most effective way to synthesize MWNTs. In this method, the source gases of hydrocarbon





(a) (b)

Fig. 1-4. (a) Graphite sheet (b) formed CNT rolled by the graphite sheet.

or other carbon-containing compounds over the pre-deposited catalyst substrates are usually used. The well aligned CNTs with random distribution can be easily synthesized. Moreover, the possible growth mechanisms including the vertically, horizontally or helically oriented CNTs and bamboo-like CNTs have been reported to explain the morphologies under various synthesizing conditions. However, the actual growth mechanisms of CNTs are not well understood yet.

Due to many unique properties of CNTs, such as high aspect ratio, small radius of curvature at the tip, extraordinary mechanical strength and chemical stability, undoubtedly, CNTs can be drown on many applications like field emission display (FED), biology technology, fuel cell, etc. In addition to enhancing the performance of original products, these applications of CNTs are going to greatly change the lifestyle. Until now, more and more physical or commercial products based on CNTs have been developed and published. As time goes by, it is convinced that CNTs will become one part of life.

1.2 Introduction to Anodic Aluminum Oxide (AAO)

In recent years, a great deal of research teams have put into fabricating nano-scale periodic arrays, since such structurally and dimensionally well-defined nanostructure materials could be used for application in high-density magnetic memories, optoelectronic device, nanoelectrode, and quantum-dot device.

One of the most commonly employed techniques to create an array pattern is lithography. It is a very mature technique but always needs the photo equipments like steppers or scanners which have some optical limits about 80 nm[http://www.ave.nikon.co.jp/pec_e/products/ic.htm] with some problems to produce very high aspect ratio structures. Besides, it needs to design and manufacture a mask. So it costs a lot of money and takes lots of time to accomplish sub-90 nm scale size patterning especially for large area nano-structure.

Thus, a method termed “template synthesis” entails the preparation of a variety of micro- and nano-materials with a desired morphology. It provides a path for enhancing nanostructure order. In the broadest sense, a template is used on defining a central structure and the removal of the template creates a filled cavity with morphological features related to the template. Various porous “templates" are employed and the nanostructures are synthesized within the pores. If the templates have cylindrical pores of uniform diameter in nanoscale, mono-disperse of the desired material can be obtained within the voids of the template material. AAO membranes prepared by the electrochemical oxidation of Al with nanoporous structure just become a potential candidate as the role. In brief, one can produce an AAO membrane using an acid electrolyte with Al at anode and the other metal like Pt as cathode, then applying voltage to oxidize Al surface [Fig. 1-5].

The structure of AAO is characterized as a closely packed regular array of hexagonal columnar cells [Fig. 1-6], [Masuda-1998-L1340] each of which contains an elongated cylindrical nanopore geometrically normal to Al surface [Fig. 1-7] .[Li-2000-131] The pore diameter and interpore distance can be finely controlled by changing oxidation condition, e.g. voltage, electrolyte type and temperature, etc. Especially, AAO is a clean-room-free process. All we need is an electrobath, power supply, acid-electrolyte and some wires. Owing such charming merits, AAO has become a marvelous material for nanostructure fabrication.

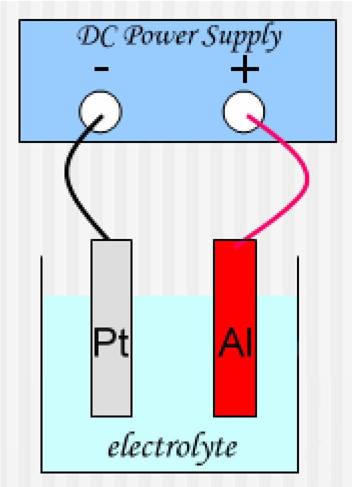
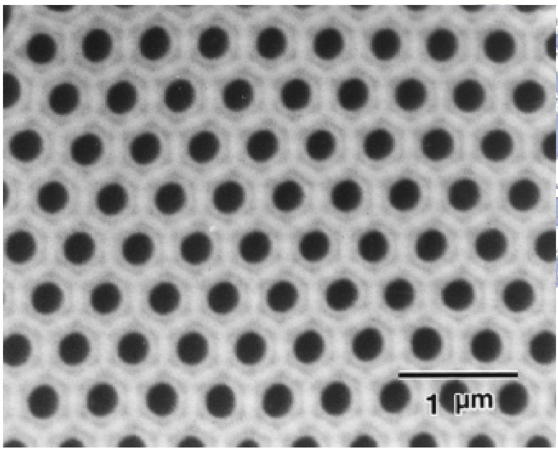


Fig. 1-5 Sketch for AAO fabrication



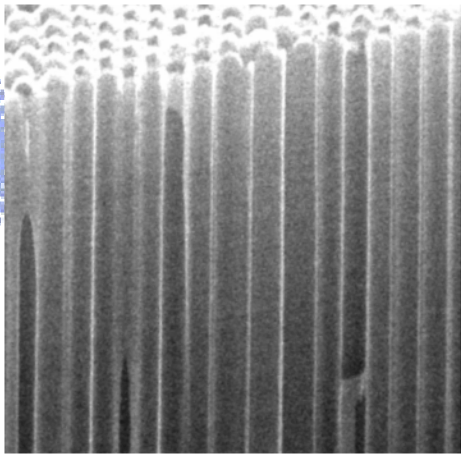


Fig. 1-6. Plane view of AAO[Masuda-1998-L1340] Fig. 1-7. Side view of AAO[Li-2000-131]

Using AAO as templates of synthesis nanomaterials is a very convenient and suitable way. Thus, with the AAO template approach, one is able to prepare mono-disperse nanowires[Sauer-2002-3243] and nanotubes of almost any desired geometry. The nanostructures can remain inside the pores of the AAO templates or they can be freed or fixed on substrate as an ensemble of nanoparticles.

[Chen-2004-3888] Alternatively, they can protrude from the surface like the bristles of a brush. The template method has been used for producing nanotubes, nanowires and nanoparticles composed of polymers, metals, semiconductors, carbon or other materials. Besides, AAO also can directly make use of some products like humidity hygrometers. [http://www.gepower.com/]

1.3 Motivation of This Research

For the practical application to field emission displays or high performance CNTs vacuum microelectronic devices, the growth of vertically aligned CNTs arrays on a large area with high packing density and ordered arrangement is necessary. As for this requirement, template methods are widely applied to produce well aligned and mono-dispersed CNT arrays. Ordered arrays of CNTs have been fabricated by using nanoporous AAO membranes as the template by several research groups.[Takashi-1996-2109, Li-1999-367, Tatsuya-1999-2044, Jung-1999-2047] The diameter of the self-ordered nanopores is tunable in the range of 10 to several hundred nanometers, making AAO an ideal template for fabricating ordered arrays of nano-structured materials.

Moreover, the field emission property of CNTs is critically affected by a field-screening effect caused by neighboring tubes. It is necessary to well control the length and the spacing of the tubes.[Nilsson-2000-2071] When AAO template is used alone (without transition metal catalyst) to grow CNTs, the diameter, the length, the arrangement, and the packing density of nanotubes can faithfully duplicate the nanopores of AAO. However, these tubes are very poor in graphitization.[Takashi-1996-2109, Eun-2002-277, Sui-2001-1523] In the case of the fabrication of CNTs assisted by AAO templates embedded with metal catalyst, the crystallinity of CNTs can be appreciably improved, but a relatively high tube growth rate will lead to the overgrowth and the entanglement of the dense tubes.[Tatsuya-1999-2044, Jeong-2002-1859] In order to obtain outstanding field emission properties, it needs a better crystallinity of CNTs. Therefore, selective growth of CNTs with catalyst way is preferable.

Growth carbon nanotubes generally use a high-temperature thermal chemical vapor deposition (CVD) process for catalyst pyrolysis of hydrocarbon precursors to grow CNTs. The plasma enhanced CVD is another potential alternative to dissociate the precursor gases with more efficiency. In this thesis, the preparation of CNT arrays in AAO templates by the microwave plasma electron cyclotron resonance CVD (ECR-CVD) was conducted.

And another key point of CNT applications is to realize the growth of vertically aligned CNT arrays on a large area with suitable tube number density and tube dimensions. The ECR-CVD owns so lower growth rate about 2 nm/minute [Lin-2002-922] as to get length control with ease. And we also propose the tube number density control of the Co-catalyzed CNTs on AAO template by simplified in situ regulating the flow rate ratio of methane (CH_4) and hydrogen (H_2) precursor gases during the CNT growth in a (ECR-CVD) system. It was found that the tube number density of the aligned CNT arrays decreases linearly following the increase of the CH_4 concentration.