PRODUCTION OF VERTICAL-ALIGNED CARBON NANOTUBES (VACNTS) WITH DIRECT CURRENT PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION (DCPECVD)

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In this investigation we could synthesis Carbon Nanotubes (CNT) with DCPECVD method for Vertical-Aligned CNT (VACNT). We have utilized a silicon sheet with 60 nm nickel layer as catalyst, C_2H_2 gas and CNTs synthesized on it with about 2 μm height and 50 nm diameter. They are mix of single wall and multi wall CNTs. We changed some synthesis conditions for some problems and now we work to optimize new condition for CNT synthesis.

Introduction

Carbon nanotubes were discovered in 1991 by means of transmission electron microscopy in the multiwalled form that consists of concentric shells of seamless cylinders of graphene (a layer of graphite). The quasi one-dimensional structure, large mechanical strength, and the conjugated electronic structure are among the most commonly mentioned properties of carbon nanotubes. Current and potential applications of carbon nanotubes include the probing tip in scanning tunneling microscopy (STM), artificial "muscle", units of electronic memory storage, to name just a few. The fascinating properties and potential uses have attracted much research interest in the carbon nanotubes.

The geometries, electronic properties and actuation of single-walled carbon nanotubes (SWNTs) obtained from high-level quantum mechanical calculations are presented in this entry. The commonly used quantum mechanical methods are first reviewed, then the behaviors of small to medium SWNTs with different structures are discussed and comparison with experimental results is made when possible. The behaviors of different groups of SWNTs are attributed to their electronic band structures.

Shortly after the discovery of carbon nanotubes, the geometries and electronic band structures of these quasi one-dimensional extended systems were described in general terms. Idealized single-walled carbon nanotubes can be viewed as formed by rolling up a graphene sheet along the chiral vector (n,m), where n and m are numbers of the two lattice vectors (a1 and a2) of graphene needed to construct the chiral vector. The translational vector is perpendicular to the chiral vector, thus parallel to the tube axis.

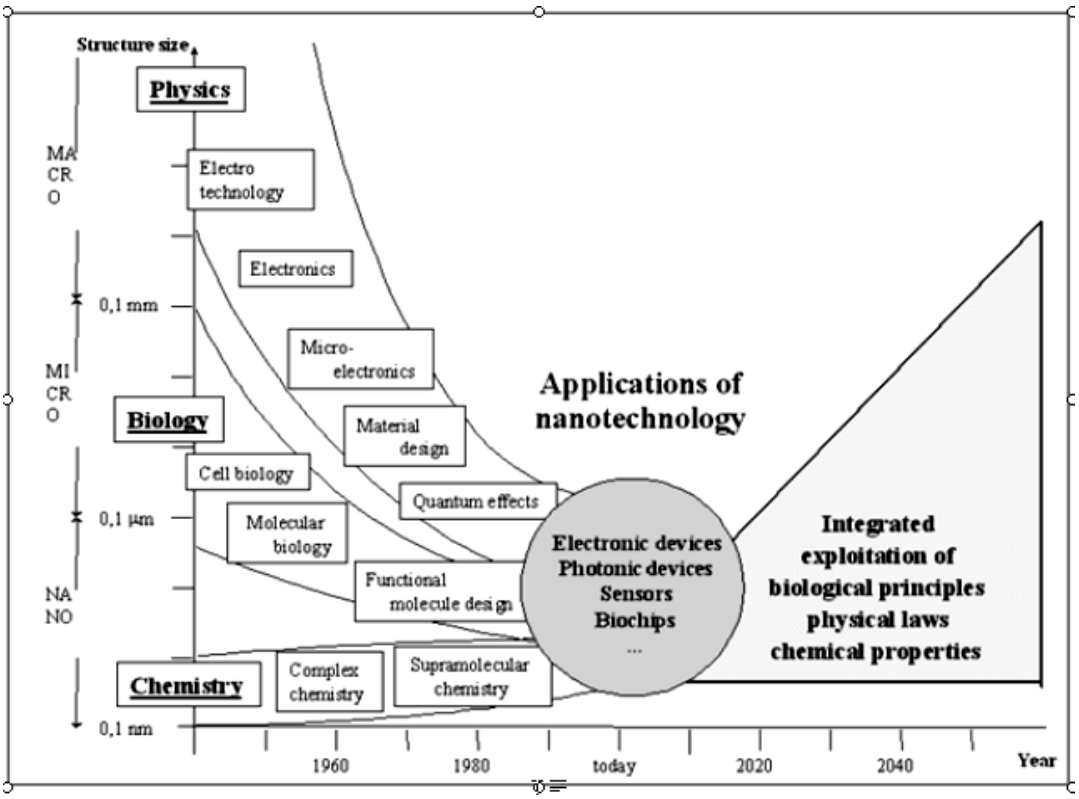

Fig.1. The convergence of the disciplines and multisector applications

Fig. 1 shows the chiral vector of a (5,3) chiral SWNT. Because of the two-dimensional symmetry of graphene, (n,m) is the same as (m,n), therefore by convention n is larger than or equal to m. Depending on the values of n and m, SWNTs can be achiral or chiral: (n,n) armchair and (n,0) zigzag nanotubes are achiral, whereas general (n>m>0) nanotubes are chiral. For a detailed discussion of the general aspects of the geometrical and electronic structures of SWNTs, see other related entries in this encyclopedia. The characteristic behavior of SWNTs shows significant deviations from the behavior of graphene, mostly because the finite dimension perpendicular to the tube axis introduces quantization of the energy levels leading to subgroups of ''metallic'' and "semiconducting" tubes. The importance of the remainder of the (n_m)/3 division has been discovered by applying a simple tight binding theory to the electronic structure of SWNTs. This simplification leads to results that we refer to as "ideal" in this entry. The remainder of (n_m)/3 is related to the mapping of the highest occupied and lowest unoccupied levels of SWNTs to the energy levels of graphene that are closest to the Fermi energy, and this leads to the broad categories of "metallic" (n_m=3i, i is an integer) and "semiconducting" (n_m=3i+1 and 3i+2) SWNTs.

The observed SWNTs have diameters from a half to a few nanometers and lengths up to several micrometers, hence the name. In both graphite and nanotubes, the carbon atoms are in a sp2 hybridized form with one p atomic orbital perpendicular to the surface of graphene or the tube left to form the p molecular orbitals. Each carbon atom in graphite is sp2 hybridized and has three bonds connecting with its neighbors. These three bonds are symmetrically related and have identical length of 1.42 A° [1].

Carbon Nanotube (CNT) Growth Methods

Some methods developed for growing of CNTs such as arc-discharge, laser ablation, and chemical vapor deposition (CVD) that have explained below [2].

Arc-discharge Method

The carbon arc discharge method is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and requires further purification - to separate the CNTs from the soot and the residual catalytic metals present in the crude product. This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure. Recent investigations have shown that it is also possible to create CNTs with the arc method in liquid nitrogen. A direct current of 50 to 100A, driven by a potential difference of approximately 20 V, creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode. [2]

Laser Ablation Methods

In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of >70wt% purity. Samples were prepared by laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon, followed by heat treatment in a vacuum at 1000°C to remove the C60 and other fullerenes. The initial laser vaporization pulse was followed by a second pulse, to vaporize the target more uniformly. The use of two successive laser pulses minimizes the amount of carbon deposited as soot. The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The material produced by this method appears as a mat of "ropes", 10-20 nm in diameter and up to 100 μm or more in length. Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis. By varying the growth temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied.

Arc-discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs. However, both methods suffer from drawbacks. The first is that both methods involve evaporating the carbon source, so it has been unclear how to scale up production to the industrial level using these approaches. The second issue relates to the fact that vaporization methods grow CNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The CNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications [2].

Chemical Vapor Deposition (CVD)

Chemical vapor deposition of hydrocarbons over a metal catalyst is a classical method that has been used to produce various carbon materials such as carbon fibres and filaments for over twenty years. Large amounts of CNTs can be formed by catalytic CVD of acetylene over nickel, cobalt and iron catalysts supported on silica or zeolite. The carbon deposition activity seems to relate to the cobalt content of the catalyst, whereas the CNTs' selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon/silica catalyst.

Some researchers are experimenting with the formation of CNTs from ethylene. Supported catalysts such as iron, cobalt, and nickel, containing either a single metal or a mixture of metals, seem to induce the growth of isolated single walled nanotubes or single walled nanotubes bundles in the ethylene atmosphere. CVD of carbon within the pores of a thin alumina template with or without a Nickel catalyst has been achieved. Ethylene was used with reaction temperatures of 545°C for Nickel-catalysed CVD, and 900°C for an uncatalysed process. The resultant carbon nanostructures have open ends, with no caps. Methane has also been used as a carbon source. In particular it has been used to obtain 'nanotube chips' containing isolated single walled nanotubes at controlled locations. High yields of single walled nanotubes have been obtained by catalytic decomposition of an H_2/CH_4 mixture over well-dispersed metal particles such as Cobalt, Nickel, and Iron on magnesium oxide at 1000°C. The reduction produces very small transition metal particles at a temperature of usually >600°C. The decomposition of CH_4 over the freshly formed nanoparticles prevents their

further growth, and thus results in a very high proportion of single walled nanotubes and fewer multi walled nanotubes [3].

Methods and material

In this project for Carbon Nanotube (CNT) synthesis we have used DCPECVD method for Vertical-Aligned CNT (VACNT). We have utilized a silicon sheet of 1×1 cm^2 dimension which is coated with 60 nm nickel layer as catalyst. The silicon sheet placed on a heater into the chamber. The chamber is evacuated to base pressure 1×10^{-5} torr (Fig 1). The substrates are heated to 700° C on the hydrogen ambient at a pressure of 10 torr. The silicon and heater are as cathode and a grid with 2 cm diameter is settled just over the silicon as anode (Fig. 2). A DC discharge between cathode (sample) and the anode is initiated using a 1 kW supply. The anode–cathode distance is 6 mm. The difference potential is increased to about 300 V.

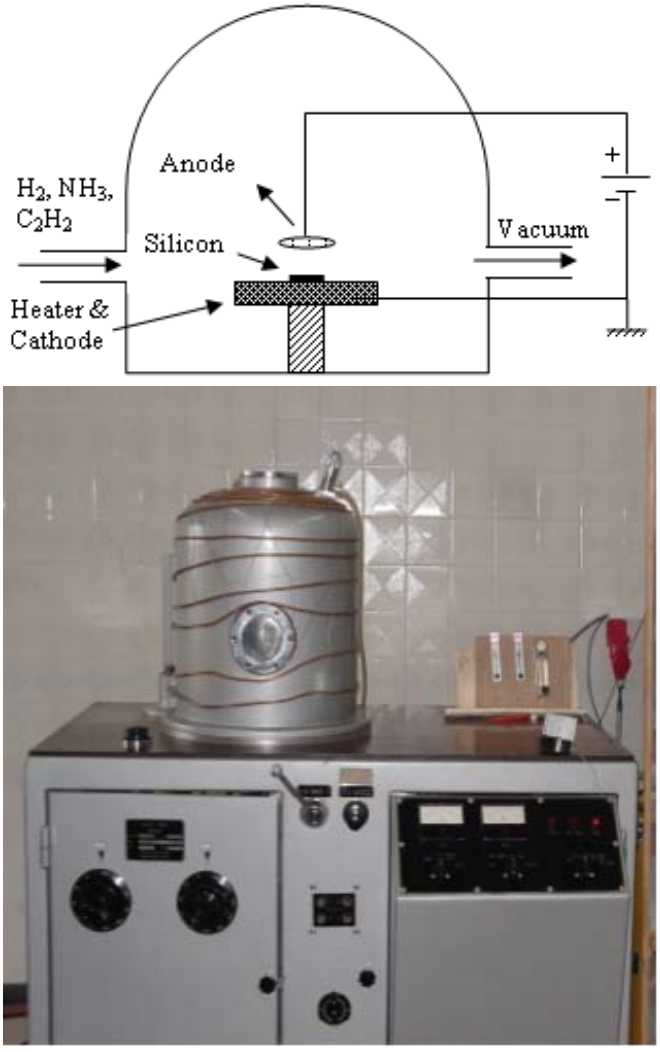

Fig .1. Schematic and picture of CNTs synthesis chamber

The growth of CNTs is performed in two steps. The first consist of formation of Ni islands by etching the surface by NH_3 ions (100 sccm) and H_2 ions (100 sccm) for 5 min (Fig 3). The second step is related to the growth of CNTs using C_2H_2 ions (100 sccm), H_2 (100 sccm) and NH_3 (20 sccm) at a pressure of 10 torr for 20 min.

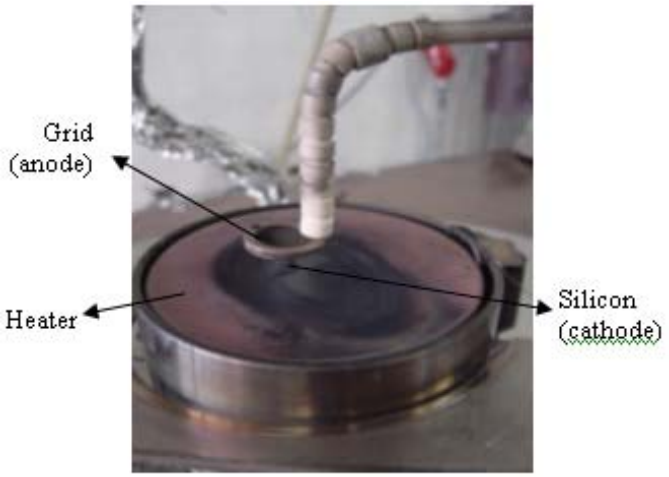

Fig. 2. Heater, silicon and grid

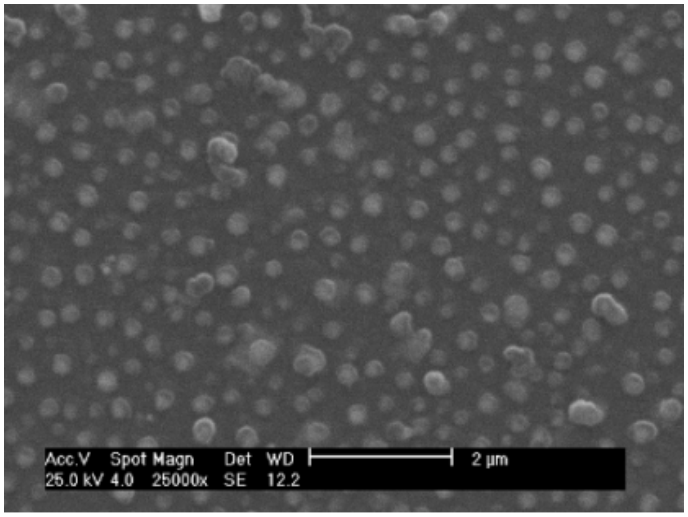

Fig. 3. Ni islands by etching the silicon surface

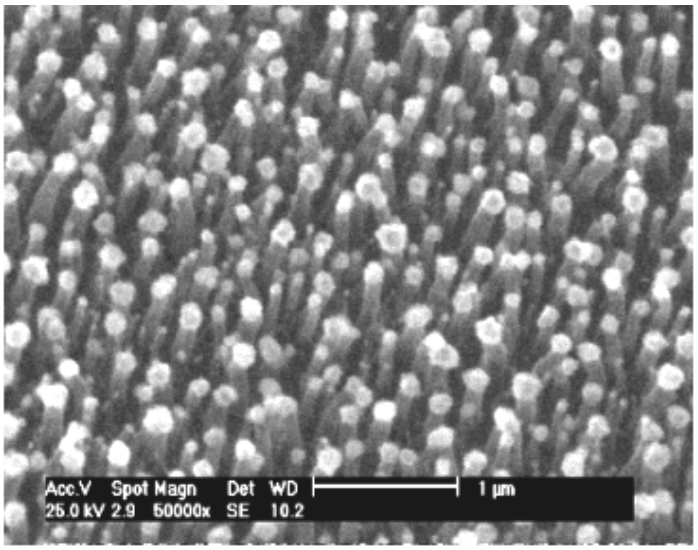

Fig. 4. Vertical and aligned CNTs that synthesized on silicon sheet

Results

At the beginning, the vertical and aligned CNTs were synthesized using our apparatus (Fig.4). They have about 2 µm height and 50 nm diameter. They are mix of single wall and multi wall CNTs. But a problem concerning the transfer

of heat to the chamber wall remains. Hence we were obligated to change heater insulator. To resolve this problem we have placed a cylindrical ceramic (alumina) around the heater. The heat transfer reduces but as a result of this change, we cannot synthesize the VACNTs. So for the moment we try to obtain the novels parameters to obtain the VACNTs. Therefore for producing the CNTs we tried more and achieved to some results but they aren't enough. At the moment we could produced the CNTs but they aren't aligned and vertical (Fig. 5). In this interaction, many parameters must be controlled until reach to desired results.

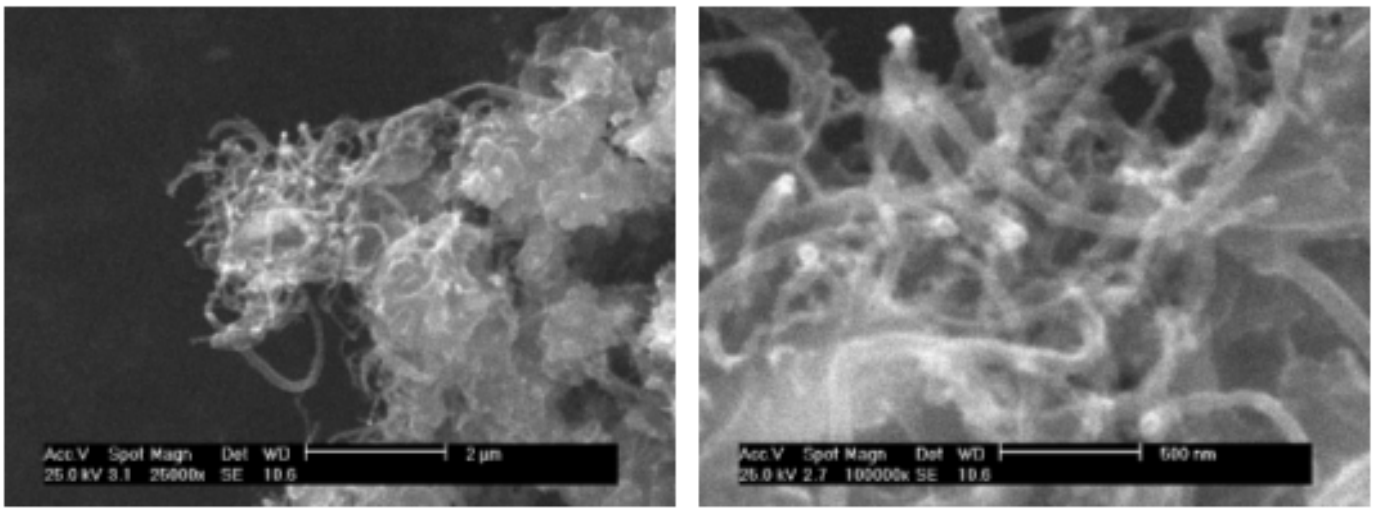

Fig. 5. CNTs that They aren't vertical and aligned

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SABİT CƏRƏYAN PLAZMASINDA BUXARLANMA ÜSULU İLƏ NİZAMLI DÜZÜLÜŞLÜ KARBON NANOBORULARIN ALINMASI TEXNOLOGİYASI

Məqalədə nizamlı şaquli düzülüşlü karbon nanoborularının alınma texnologiyasının nəticələri verilmişdir. Sintez zamanı silisium altlıq üzərində diametri Ø60nm olan aktiv xassəli Ni katalitik mərkəzlərdən istifadə olunmuşdur. Karbon nanoborularının alınması zamanı C_2H_2 qazından istifadə edilmişdir. Diametri Ø50nm və uzunluğu 2mm karbon nanoboruları sintez olunmuşdur. Karbon nanoborularının alınma texnologiyasının optimallaşdırılması ilə əlaqədar tədqiqat işləri aparılmışdır.

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ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ УГЛЕРОДНЫХ НАНОТРУБОК В УСЛОВИЯХ ИСПАРЕНИЯ ПЛАЗМОЙ ПОСТОЯННОГО ТОКА

В работе приведены результаты технологии получения вертикально упорядоченных углеродных нанотрубок. При синтезе использовали кремниевую подложку с активными каталитическими центрами из Ni с размером Ø60нм. Для получения нанотрубок использован газ C_2H_2. Синтезированы углеродные нанотрубки диаметром Ø50нм и длиной 2 мм. Проведены исследования по оптимизации технологии получения углеродных нанотрубок.

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