

Overview of Bottom-up Nano Electronics Materials and Its Application

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Nanoelectronics materials have great attracted the fancy of many scientists and researchers world-wide. The small dimensions, strength and the remarkable physical properties of these structures made them unique materials with a whole range of promising application. In this review, the bottom-up nano electronics material's properties, advantage, disadvantage, various type of fabrication techniques and the present status application, have been disused.

Keywords: CNTs, SWNTs, MWNTs, Nanowires, Nanomaterials, Carbon Nanotubes, Armchair, Chiral, Zigzag, Bottom-Up Process.

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1. INTRODUCTION

Nanoelectronics represent "the extension of the engineering fields into the nanoscale ($1 \text{ nm} = 10^{-9} \text{ m}$) realm and concerns itself with the fabrication of objects which are anywhere from hundreds to tens of nanometers in size"

Nanoelectronics are divided into two techniques which are following:

- Top-down;
- Bottom-up.

Top-down methods start with large area blocks of materials (MOSFETS, transistor, CMOS etc) and carve out structures by selectively patterning and processing well-define areas on the block surface[1, 2].

Miniaturization of electronics devices over the last 40 year has resulted reduced in size, increased in logical speed, clock speed and production and decreasing in cost. Bottom up is a process use chemically or biologically inspired for developed and assembled of nanoscale building blocks into complex nanoarchitecturs for nanoelectronics devices [1, 3].

Materials for Nanoelectronics by bottom up process can be metallic, semiconductor, or isolator materials that have at least a nanosize dimension and produce quantum confinement of electron motion and render size dependence of physical properties and which are utilized to implement various functionalities of nanoelectronics devices. Industry's adoption of new materials for nanoelectronics such as spintronics (magnetic material), plastic electronics, nanotubes and nanowire [4].

This paper presents an overview on Materials for Nanoelectronics by bottom up process. These nanomaterials are nanowires and carbon nanotube. Further it provides a brief description of nanowires and carbon nanotubes (CNT) and its applications.

2. NANOWIRES

2.1 Selection of Nanowires

Nanowires are also known as quantum wires. The structure of nanowire is ultra thin; the diameter is also

in nanometer (10^{-9} m). Nanowires have "quantum effect" which affect transports properties. Their transverse energy is quantized into a series of discrete value E_0 "ground state" energy with E_1 "lower value" [5].

Different types of nanowires can be metallic (for example, Ni, Pt, Au, Ag), (Fig. 2), semiconducting (for example, Si, InP, GaN), (Fig. 3), insulating (for example, SiO_2 , TiO_2), (Fig. 1) Molecular nanowire (for example, DNA), (Fig. 4), and inorganic (for example, $\text{Mo}_6\text{Sg.xlx}$) [3].

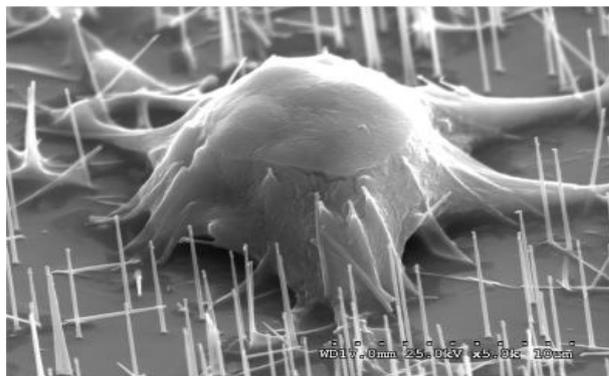


Fig. 1 – Insulating SiO_2 nanowires

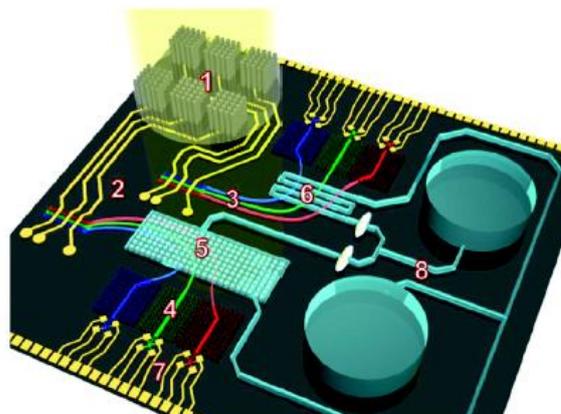


Fig. 2 – Metallic nanowires

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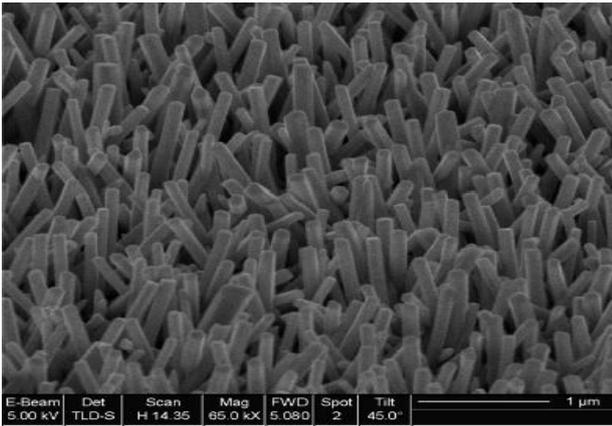


Fig. 3 – Semiconducting InGaN nanowires

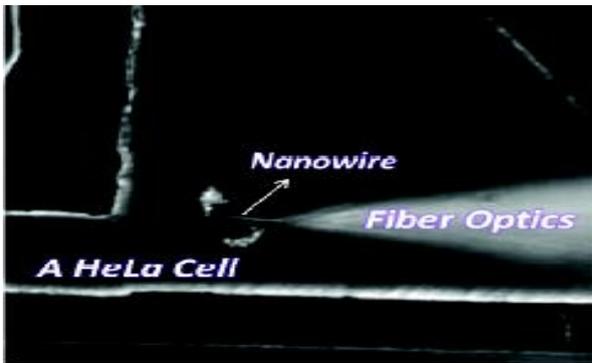


Fig. 4 –Molecular nanowires

In metallic nanowires conduction band of bulk metals is replaced by discrete energy states. Nanowires are metallic if they follow Kubo gap law. The discreteness of electronic states in a metal nanowire is characterized by the Kubo gap.

$$K_B T > \delta \tag{1}$$

And

$$\delta = 4E_f / 3n \tag{2}$$

where $K_B T$ is Kubo gap, T is temperature, E_f is Fermi energy gap, n is the number of electrons in a nanowire and δ is the average spacing between successive quantum levels [5, 6].

For example, using Equation 1 and 2 silver particles with a diameter of 3 nm, for which $\delta = 10$ meV and at room temperature.

Then $K_B T \approx 25$ meV for $T = 300$ K.

Result, silver follows the Kubo Gap Rule; it means this metal became a nanowire.

2.2 Resistance of Nanowire

The nanowire does not follow Ohm's law because it follows "quantum effect".

$$\frac{2e^2}{h} \approx 12.9 k\Omega^{-1}, \tag{3}$$

where e is electron charge and h is Planck constant 6.55×10^{-34} J.s.

They are inverse of the well-known resistance unit

h/e^2 which is roughly equal to 25812.8Ω which is referred to as, Using Equation Von Klitzing constant [1, 4].

2.3 Fabrication Method for Nanowire

2.3.1 Template method

In this method, the template consists of nanosized pores or voids that are arranged in a prescribed and ordered manner in a host material to be grown as a nanowire. The pores of the template are then filled with the material to be grown as a nanowire, called source material. The most commonly used template for nanowire growth is anodic alumina. The alumina template is obtained by anodizing Al films in certain acids. During the anodization process an electrical current flows between the cathode and an Al thin film; this plays the role of the anode [1, 5, 6]. This etching process results in an alumina film (membrane) that contains a regular hexagonal array of parallel and almost identical cylindrical channels, as shown in Fig. 4. The alumina pores have a diameter in the range of 20-200 nm, are separated by 50-400 nm, and have a density of 10^9 - 10^{11} cm^{-3} depending on the etching conditions [8, 9]. Anodization process is used to obtain very regular pore arrangements, highly ordered imprints of alumina are produced, which are retained and filled with the source material [13]. The Fig. 5 clearly shows the working of anodic alumina.

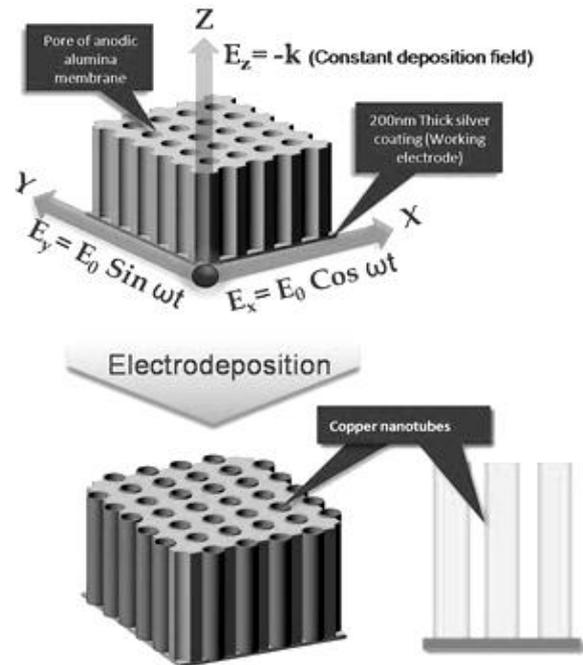


Fig. 5 – Anodic Alumina

2.3.2 CVD or MOCVD method

In this method, the nanowire precursor material is heated to produce vapors that penetrate the nanopores of the template, which are then cooled to get solidified nanowires. Single crystal nanowires are grown through this process with a diameter of 10 nm while other processes grow polycrystalline nanowires.

2.3.3 Vapor-liquid-solid (VLS) method

The vapor-liquid-solid (VSL) nanowire fabrication method is based on the fact that the vapors (V) of the source material can be absorbed into a liquid (L) droplet of a catalyst. The nanowire is obtained due to the solidification (S) of the source material.

2.4 Fusion of Nanowires

The nanowire is placed adjacent to the ends of the pieces to be joined, then a high voltage electric current is applied which fuses the wire end [1, 10]. This technique fuses wires as small as 10 nm. The (Fig. 6) clearly shows the fusion of nanowires.

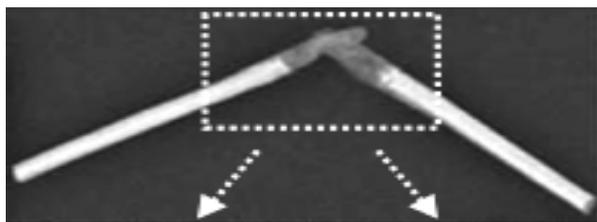


Fig. 6 – Soldering of nanowires

2.5 Advantage of Nanowire

1. The nanowires are used to build next generation of computer devices.
2. They are used to build logical circuits: AND, OR and NOT gates, this is one of the steps to future of digital computing.
3. Nanowires act as photon waveguides which help to build photon logic arrays [25].
4. Nanowire offers the studies at molecular-scale for molecular circuits or computer [11].

2.6 Disadvantage of Nanowire

Yet there is no idea of disadvantage of nanowires but the thing which has advantage on one hand it also has disadvantage on other face.

3. CARBON NANOTUBE

Carbon Nanotubes (CNTs) have received much attention as new class of nanomaterials since their discovery. These show unique mechanical, chemical, electrical and physical properties which led to a variety of applications such as scanning probes, Nanoelectronics and memory devices. Carbon Nanotubes also know as buckytubes allotropes of carbon with a honey comb lattice formed.

There are two types of carbon nanotubes single-wall carbon nanotubes and multi-wall carbon nanotubes.

3.1.1 Single-Wall Carbon Nanotubes

The SWCNTs can be imagined as a perfect graphene sheet (graphene being the same ploy-aromatic mono-atomic layer made of an hexagonal display of sp² hybridized carbon atoms that genuine graphite is built up with) rolled up into a cylinder, with the hexagonal rings put in contact to join seamlessly[18, 19]. Considering the simple procedure, there are countless different ways to roll up a graphene sheet in order to form a

nanotube. The (Fig. 7) clearly shows the single wall carbon nanotubes with its computer model.

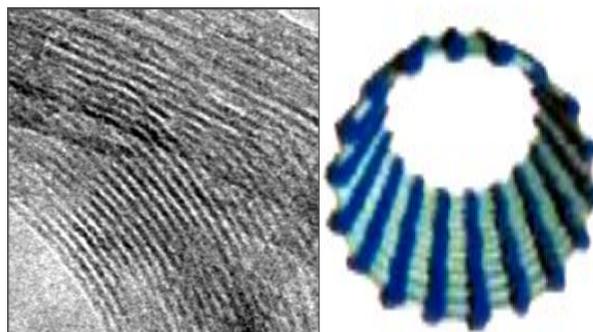


Fig. 7 – Single-wall carbon nanotubes and computer model of single wall nano tube

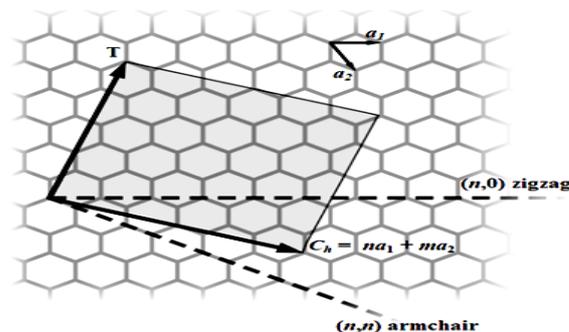


Fig. 8 – The (n, m) nano tube naming scheme can be thought of as a vector (C_h) in an infinite graphene sheet that describes how to "roll up" the graphene sheet to make the nanotube. T denotes the tube axis, and a_1 and a_2 are the unit vectors of graphene in real space

The way the graphene sheet is wrapped is represent by a pair of indices (n, m) called "Chiral vector". If $m = 0$, the nanotube are called "Zigzag". If $n = m$, the nanotube are called "Armchair" otherwise they are called "Chiral"[18, 20, 21, 23]. The (Fig. 9) clearly shows the armchair, zigzag and chiral single wall carbon nanotubes structure.

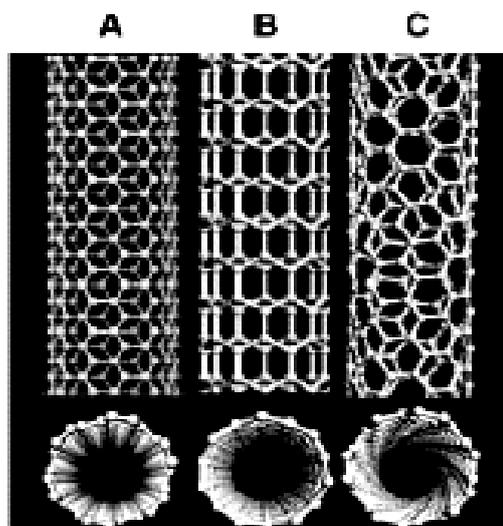


Fig. 9 – A. Armchair single-wall carbon nanotubes B. Zigzag single-wall carbon nanotubes C. Chiral single-wall carbon nanotubes

3.2 Multi-Wall Carbon Nanotubes

The MWCNTs, as implied by their name, consist of multiple graphene sheets rolled up in concentric CNTs, filling each other's inner cavities to end up with nanotube-filled nanotubes. The intertube distance in a MWCNTs is approximately that of the intergraphene distance in turbostratic, polyaromatic solids, i.e. 0.34 nm. As result of this, many layer that MWCNTs are built from, are much more rigid than that of SWCNTs. The (Fig. 10) clearly shows the multi wall carbon nanotubes with its computer model [28].

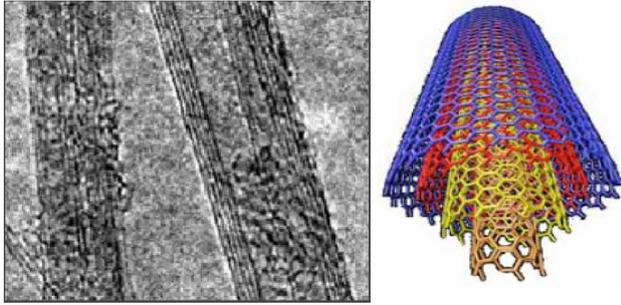


Fig. 10 – Multi-wall carbon nanotubes and computer model of multi wall nanotubes

3.3 Properties of Carbon Nanotubes

The chiral vector of a CNT, which links two equivalent crystallographic sites, is given by

$$C = na_1 + ma_2, \quad (4)$$

$$d = a_{c-c} \left[3m^2 + mn + n^2 \right]^{1/2} / \Pi = |C| / \Pi, \quad (5)$$

$$\Theta = \tan^{-1} \left[\sqrt{3}n / 2m + n \right], \quad (6)$$

where a_1 and a_2 are unit vectors of the graphene lattice, the numbers n and m are integers, $a_{c-c} = 1.42 \text{ \AA}$ is the carbon bond length, $|C|$ is the length of the chiral vector [28, 30, 31].

The set of integer number (n, m) describes uniquely the metallic or the semiconducting character of any CNT. In general, using Equation 4, 5 and 6, the CNT is metallic if $n = m$, it show a small bandgap (has allegedly a semi-metallic character) if $n - m = 3i$, with $i = 1, 2, 3, 4, \dots$ and is semiconducting when $n - m \neq 3i$, metallic CNT are also know as armchair CNTs and semiconducting CNT termed Zigzag CNT [30, 31].

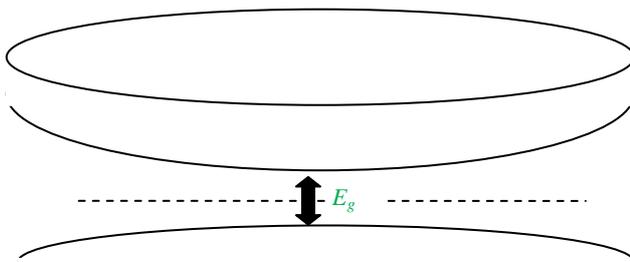


Fig. 11 – Semiconductor CNT band structure

The band gap of the semi conducting CNT is given by

$$E_g = 4h v_f / 3d \quad (7)$$

where Fermi velocity $v_f = 8 \times 10^7 \text{ m/s}$, h is plank constant and d is diameter of CNT.

$$E_g(\text{eV}) \approx 0.9/3d \text{ (nm)} \quad (8)$$

WCNTs have diameter ranging from a fraction of a nanometer to several nanometers, the semiconducting. using Equation 7 and 8, CNTs have a bandgap in the range 20 meV-2eV [17, 15].

3.4 Fabrication of CNTs

Various techniques have been developed to produce carbon nanotubes and well know techniques are arc discharge, laser ablation and chemical vapor deposition (CVD).

Most of these processes take place in vacuum or with inner gases mixed with pressure flow. Large quantities of nanotubes can be synthesized by these methods however; advances in catalysis and the continuous growth process are making CNTs more commercially viable.

3.4.1 Arc discharge method

Iijima observed CNTs under the microscope in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps intended to produce fullerenes. During this process the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Nanotubes were initially discovered using this technique [16, 29, 27]. The yield by this processes is up to 30 per cent by weight and it produces both single and multi walled nanotubes, however these are quite short (50μ). The (Fig. 12) clearly shows the arc discharge method.

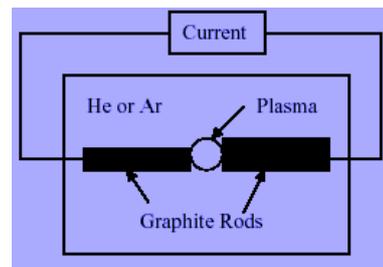


Fig. 12 – Arc Discharge

3.4.2 Laser ablation method

Laser ablation method was developed by Smalley and Rice in 1995. In the laser ablation process, a pulsed laser

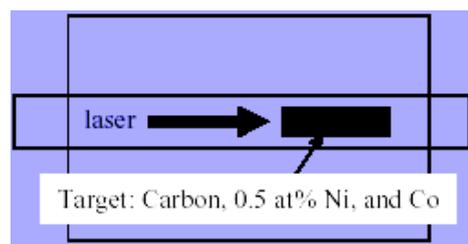


Fig. 13 – Laser ablation

Table 1 – All values of single walled carbon Nanotubes

| General Properties | |
|---|-----------------------------------|
| Average dia. of SWNT's : | 1.2 – 1.4 nm |
| Interlayer spacing | |
| (<i>n, n</i>) Armchair | 3.38 Å |
| (<i>n,0</i>) Zig-zag | 3.41 Å |
| (<i>n, m</i>) Chiral | 3.39 Å |
| Optical properties | |
| Fundamental gap | |
| For (<i>n, m</i>); <i>n-m</i> is divisible by 3 [metallic] | 0 eV |
| For (<i>n, m</i>); <i>n-m</i> is not divisible by 3[semiconducting] | ~ 0.5 eV |
| Electrical properties | |
| Resistivity | 10 ⁴ Ω/cm |
| Maximum current density | 10 ¹³ A/m ² |
| Thermal properties | |
| Thermal conductivity | ~ 2000 W/m/k |
| Phonon mean free path | ~ 100 nm |
| Relaxation time | ~ 10 ⁻¹¹ s |
| Elastic behavior | |
| Young's modulus(SWNT) | ~ 1 TPa |
| Young's modulus(MWNT) | 1.28 TPa |
| Maximum tensile strength | ~ 30 GPa |

Table 2 – Main Properties of carbon Nanotubes

| Mechanical | |
|---|--|
| 100 time stronger then steel (stress) and 6 time lighter | |
| High flexibility of CNTs, unlike carbon fiber | |
| Expansion by charge injection | |
| | |
| Electrical | |
| Metallic or semiconductor behavior according to chirality(way to graphene sheet is rolled on itself) | |
| As conductive as copper | |
| Easy turn able field emission | |
| | |
| Physico-chemical | |
| High specific area(several hundreds of m ² /g) | |
| Cavities enabling molecules storage inside the carbon nanotubes | |
| Chemical treatment on CNTs, enabling to fix other molecules to CNTs | |
| High thermal resistance(up to 1500 °C under vacuum) | |

vaporizes a graphite target in a high temperature reactor while an inter gas is bled into the chamber. The nanotubes developed on the cooler surfaces of the reactor as the vaporized carbon condenses. A water- cooled surface may be included in the system to collect the nanotubes. This method yields around 70 percent and produces primarily CWCNTs, with a controllable diameter determined by the reaction temperature. However it is more expensive [27, 29]. The (Fig. 13) clearly shows the laser ablation method.

3.4.3 Chemical vapor deposition method

In CVD method, a substrate is prepared with a layer of metals catalyst particles or in metals combination. Place substrate in oven, heat to 600-800 °C and slowly add a carbon bearing gas such as methane/ethylene/acetylene. As gas decomposes, it free up carbon atoms, which recombine in the form of Nanotubes. These method yields 100 percent of long nanotubes, easiest to scale up to industrial production of

long length, simple and pure nanotubes [27, 29]. There are two type of Chemical vapor deposition method are following:

- Thermal CVD,
- Plasma CVD.

The (Fig. 14 and Fig. 15) clearly show the thermal CVD and plasma CVD method respectively.

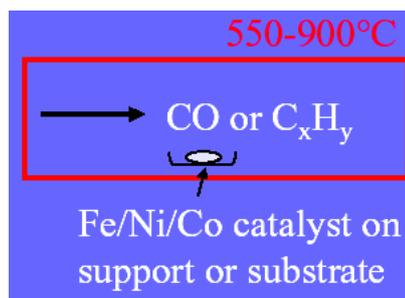


Fig. 14 – Thermal CVD

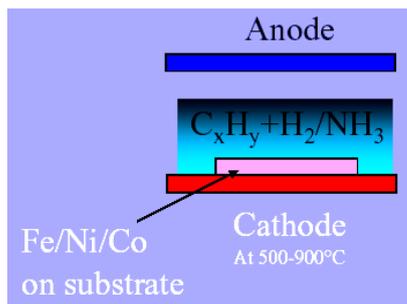


Fig. 15 – Plasma CVD

3.5 Application of Carbon Nanotubes

- The nanotubes are use to fabricated electronically nanocomponents (diodes, transistors etc) [7, 12, 13].
- The nanotubes are use as Electron gun, field emission, field emission display, Atomic force microscope (AFM) tips.
- These are also use to storage Hydrogen for fuel cell cars [7].
- CNTs are use to improved lifetime of batteries.
- CNTs are also use as biosensors for harmful gases, chemical analysis.

- CNTs are also use as multifunctional fillers in polymer composite [14].

CNTs are also having stronger mechanical properties. The (Fig. 16) clearly shows the mechanical properties of carbon nanotubes [7, 13, 24].

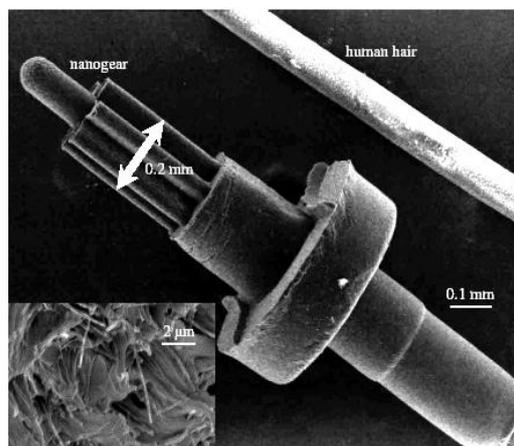


Fig. 16 – SEM image of the smallest working gear (carbon nanotube/nylon composite)

Table 3 – Summary of techniques: (a) Arc Discharge, (b) Chemical Vapor and (c) Laser Ablation

| Method | Arc discharge | Chemical vapor deposition | Laser ablation |
|---------------|---|---|---|
| Who | Ebbesen and Ajayan, NEC, Japan, 1992 | J.B Nagy, Univ. of Namur, Belgium and Endo, Shinshu University, Nagano, Japan | Smalley, Rice, 1995 |
| How | Connect two graphite rods to a power supply, place them a few mm apart and throw the switch. At 100 Amp, Carbon vaporizes and forms hot plasma. | Place substrate in oven, heat to 600°C -800°C, and slowly add a carbon bearing gas such as methane/ ethylene/ acetylene. As gas decomposes, it free up carbon atoms, which recombine in the form of NTs | Blast graphite with intense laser pulse; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs |
| Typical yield | 30 to 90 per cent | 20 to 100 per cent | Up to 70 per cent |
| SWNTs | Short tubes with inner dia. of 1 – 3 nm and outer dia. of approx. 10 nm | Long tubes with dia. ranging from 0.6 – 4 nm | Long Bundles of tubes (5-20 nm), with individual diameter from 1-2nm |
| MWNTs | Short tubes with inner dia. of 1 – 3 nm and outer dia. of approx. 10 nm | Long tubes with dia ranging from 10 – 240 nm | Not very much interest in this technique, as it is too expensive but MWNTs synthesis is possible. |
| Process | Can easily produce SWNT, MWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis | Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure possible | Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure. |
| Conclu-sion | Tubes tend to be Short with random sizes and direction; often needs a lots of purification | NTs are usually MWNTs and often riddled with defect | Costly technique, because it requires expensive laser and high power requirement, but is improving. |

Table 4 – Analytical method for quantitative/qualitative analysis of CNT samples

| Parameter | Technique | Analysis |
|---------------------|------------------|--|
| Purity | TGA | Quantitative-residual mass after TGA in air at 5 °C/min to 800 °C |
| | SEM/TEM | Qualitative-amorphous carbon impurities |
| | EDS | Qualitative-metal content |
| | Raman | Qualitative-relative amount of carbon impurities and damage/disorder |
| Thermal stability | TGA | Quantitative-burning temp. in TGA in air at 5 °C/min to 800 °C, $dM = dT$ peak max. |
| Homogeneity | TGA | Quantitative-standard deviation of burning temp. and residual mass taken on 3-5 samples |
| | SEM/TEM | Qualitative- image comparison |
| Dispensability | Ultra-sonication | Qualitative- time required to fully disperse (to the eye) low cone. CNT in DMF using standard settings |
| | UV/VIS/NIR | Quantitative- relative change in absorption spectra of sonicated low concentration CNT/DMF solution |
| Electronic property | AFM/UVSTM | Quantitative-band gap, conductivity of a single CNT could be measured through DOS plot |

3.5 Disadvantage of CNTs

As impressive as Nanoelectronics might be, there are also potential disadvantages of CNTs. Some of the problems with CNTs are practical while others fall under the ethical realm.

The Potential disadvantage of CNTs is that CNTs is poison and harmful for human body and CNTs are also use as Chemicals weapons. With all the good any science can do, there is always the capability of engineering evil potential [22].

4. APPLICATION OF NANO ELECTRONIC IN ROAD

4.1 Piezo Sensor

A piezoelectric sensor is a device that uses the piezoelectric effect to measure pressure, acceleration, strain or force by converting them to an electrical charge. Fig. 17 show that piezo sensor working.

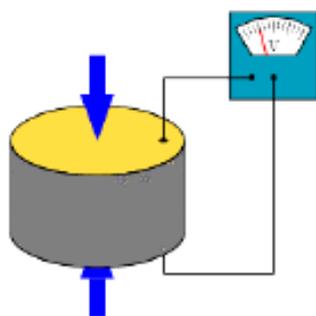


Fig. 17 – A piezo sensor disk generates a voltage when change in shape

4.2 Principle of Operation of Piezo Sensor

Depending on how a piezoelectric material is cut, three main modes of operation can be distinguished: transverse, longitudinal, and shear.

Transverse effect

A force is applied along a neutral axis (y) and the charges are generated along the (x) direction, perpendicular to the line of force. The amount of charge depends on the geometrical dimensions of the respective piezoelectric element. When dimensions *a*, *b*, *c* apply,

$$C_x = d_{xy}f_y b/a,$$

where *a* the dimension in line with the neutral axis is, *b* is in line with the charge generating axis and d_{xy} is the corresponding piezoelectric coefficient.

Longitudinal effect

The amount of charge produced is strictly proportional to the applied force and is independent of size and shape of the piezoelectric element. Using several elements that are mechanically in series and electricaly in parallel is the only way to increase the charge output. The resulting charge is

$$C_x = d_{xx}F_x n,$$

where d_{xx} is the piezoelectric coefficient for a charge in x-direction released by forces applied along x-direction (in pC / N). F_x is the applied Force in x-direction [N] and corresponds to the number of stacked elements.

4.3 Nanosensor Improve Road Sector

Sensors have been developed and used in construction to monitor and control the environment condition and the materials/structure performance. One advantage of these sensors is their dimension (10^{-9} m to 10^{-5} m). These sensors could be embedded into the structure during the construction process. A low cost piezo ceramic-based multi-functional device has been applied to monitor early age concrete properties such as moisture, temperature, relative humidity and early age strength development. The sensors can also be used to monitor concrete and bitumen road corrosion and cracking. The smart aggregate can also be used for structure health monitoring. The disclosed

system can monitor internal stresses, cracks and other physical forces in the structures during the structures life. It is capable of providing an early indication of the health of the structure before a failure of the structure can occur. Some of the sensors can also help to reduce sound and air pollution from road.

5. FUTURE OF NANOELECTRONICS

Nanoelectronics have witnessed a shift towards molecular system in recent years. Though the term molecular electronics is a pretty old one, its is only since very recent that single molecules have become focus of interest. To a great extent this was triggered by research on carbon nanotubes and nanowires. Before these nanomaterials the scene, molecular electronics was the

science of organic polymers, their synthesis, processing and doping. With these nanomaterials, we finally have a model system at hand that is equally of interest for chemists, material scientists and physicist. While these nanomaterials are supra molecular object for a chemist, they are one-dimensional soils for physicist. In the future, more of these supramolecular structures will be studied on a single molecule Level. Companies like, for example Motorola, IBM and Hewlett Packard, are starting to take an active part in this development. The ability to manipulate and characterize single molecules is an important first step for the exploration of suitable molecular functions. A fully functional chip, however, requires the ability to assemble the molecules with high precisions into a functional network.

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