Materials Science in Semiconductor Processing 41 (2016) 67–82

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Review

# Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates

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ARTICLE INFO

*Article history:*
Received 4 August 2015
Accepted 4 August 2015

*Keywords:*
Carbon nanotubes
Catalytic chemical vapor deposition
CNT carbon sources
CNT catalysts
CNT substrates

ABSTRACT

Carbon nanotubes (CNTs) have been extensively studied during the past two decades and Catalytic Chemical Vapour Deposition (CCVD) technique has been untiredly employed by researchers to produce CNTs of various crystallographic configurations. In this paper the material aspects carbon sources, catalysts and substrates with regard to CCVD synthesis of carbon nanotubes are reviewed in light of latest developments and understandings in the field. The role of these materials in synthesis of CNTs is explained keeping the upto date literature in view. Latest research reports and their findings are presented with regard to effects of growth control aspects such as temperature, vapour pressure and catalyst concentration on CNT formation. Besides recent understandings with regard to preferential growth of CNTs are also discussed. From this literature review it is found that carbon diffusibility and carbon solubility of any catalyst are two important factors in determining CNT nucleation and growth. Moreover, addition of catalyst species to any transition metal catalyst can improve the catalyst performance and addition of water, air, alcohol etc. during CCVD process can increase the activity and lifetime of the catalyst besides enhances the production of CNTs.



**Contents**



## 1. Introduction

The market for carbon nanotubes (CNTs) is heating up due to their diverse commercial applications and the annual number of CNT related journal publications and issued patents continue to grow. Due to their extraordinary mechanical, electrical and optical properties, CNTs have stimulated extensive research since their discovery by Sumio Iijima in the early 1990s [1] as already reported in the year 1952 by Radushkevich and Lukyanovich [2]. Ideal CNTs may be described as nanoscale graphene cylinders (formed by rolled up one atom-thick sheets of graphite called graphene) that are closed at each end by half of a fullerene molecule and are of two types, structures comprising only one cylinder are termed Single Walled Carbon Nanotubes (SWCNTs) first observed by Iijima and Ichihashi in 1993 [3], whereas structures containing two or more concentric graphene cylinders are called as Multi-Walled Carbon Nanotubes (MWCNTs) [1]. Ideal SWCNTs are classified according to three possible crystallographic configurations, zigzag, armchair, and chiral, depending on how the graphene sheet is rolled up. In the zigzag conformation, two opposite

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http://dx.doi.org/10.1016/j.mssp.2015.08.013

C–C bonds of each hexagon are parallel to the tube axis, whereas in the armchair conformation the C–C bonds are perpendicular to the axis, in all other arrangements, the opposite C–C bonds lie at an angle to the tube axis, resulting in a so-called helical nanotube that is chiral.

SWCNTs may be metallic or semiconducting having bandgap in the range of 0.4 to about 2 eV while MWCNTs are zero bandgap metals (in case of MWCNTs where electrical conduction is through outer most shell and the large diameter of outer nanotube is responsible for 0 eV bandgap), so the electric properties of the two are different [4]. This difference is due to the reason that in case of SWCNTs graphene sheet can be rolled up with variable degrees of twist along its length and resulting SWCNTs may have various chiral structures [3–7]. Since the diameter range of SWCNTs is small (0.4–3 nm) than that of MWCNTs, hence SWCNTs are attracting materials for nano-electronics. The number of walls of MWCNT can vary from two to $>100$ and usually grow perpendicular to the substrate. Moreover, the length of vertically aligned MWCNT is relatively easy to measure.

In 2006 [8] a new kind of carbon nanostructure called few walled carbon nanotubes (FWCNTs) were reported consisting of 2–6 layers of side walls, length around tens of micrometres and diameter in the range of 2–8 nm. They have remarkable mechanical and electronic properties particularly when the outer most layer of the nanotube is functionalized and finds number of applications related to field emission [9] and next generation CNT based reinforced composite materials [10]. There is another class of carbon nanostructure called carbon nanofibers (CNFs) which have a unique morphology in that the grapheme planes are canted from the fibre axis resulting in exposed edge planes on the interior and exterior surfaces of the fibre. They are also called stacked-cup carbon nanotubes (SCCNTs). The diameters of CNFs ranges from 50 to 200 nm and are produced in a similar manner as CNTs are produced, however there are distinct differences which impact their performance and commercial applications.

CNTs may exhibit extraordinary aspect ratios and are found to grow up to several centimetres long [11,12]. The CNT properties are strongly dependent on their structure e.g, for typical diameters, all armchair SWCNTs and one-third of all zigzag nanotubes are metallic, the rest are semiconducting [13]. Furthermore both SWCNTs and MWCNTs possess a high surface area per unit weight, good mechanical properties, and high electrical conductivity at metallic state and high thermal conductivity/stability. Table 1 depicts some of the extraordinary properties of both SWCNTs and MWCNTs.

Due to these interesting properties CNTs are being investigated for a wide range of applications today. Reviews of CNTs applications, different methods of preparation and their mass production are reported in [3,4,28–45]. The various applications of CNTs include: electromagnetic and microwave absorbing coatings [46–52], thermal interface materials [53], ionic and electronic transport devices such as actuators [54,55], super capacitors [56], batteries [57,58], fibres [59–66], sensors [67,68], energy storage and energy conversion devices [69–75], radiation sources and nanometre-sized semiconductor devices [76,77], high aspect ratio nanotubes (electrically conductive wire with diameter in nanometre range) are highly desirable as field emission tips for applications such as field emission displays [78–84], X-ray tubes [85], electron sources for microscopy and lithography [86], gas discharge tubes [87], vacuum microwave amplifiers, scanning probe tips [88–90]. Besides doping of CNTs can be used in order to tune their electronic response [91], therefore CNTs can also act as a transistor or logic element [92–95]. Due their strong covalent bonding, high thermal conductivity and high aspect ratio CNTs are being used in interconnect applications [25,96–99]. They are also used as membranes for water purification and gas separation [100].

It is to be kept in mind that for above mentioned applications highly reliable synthesis techniques are required, that should be capable of obtaining large quantities of high purity materials. Furthermore, controlled growth at precise lithographically patterned areas is required for applications in nano-electronics and photonics for which understanding how to control the synthesis of CNTs is vital in order to deterministically integrate such nanostructures into various technologies. It is found that among various techniques developed for synthesis of CNTs, Catalyst Chemical Vapour Deposition (CCVD) is one of the best to satisfy the above mentioned requirements. Although there are other techniques which are being used for synthesis of CNT like arc discharge and laser ablation, however CVD is the most versatile and promising technique both in terms of bulk production and direct device integration as is evident from the analysis of comparative Table 2.

Fossil based hydrocarbons and plant based hydrocarbons are two mainly employed carbon sources for CVD synthesis of CNTs. Among fossil fuel hydrocarbon methane, natural gas, acetylene, benzene etc. are conventional carbon sources which are widely used for CNT research. There are also several reports on use of natural precursors for CNT synthesis such as camphor, turpentine oil, palm oil etc. On the other hand, transition metal nanoparticles (Fe, Ni and Co), are conventionally used to catalyze the growth of CNTs [104]. However, recently CNTs are also grown from noble metals [105–109], ceramic nanoparticle catalysts [110,111] and semiconducting nanoparticles [112–115]. These materials were regarded as unable to catalyze the dissociation of hydrocarbons, and in their bulk form they do not have a catalytic function to produce graphite. This leads to a new interpretation of the role of the catalyst in nanotube growth in which only a nanoscale curvature and carbon adsorption sites are necessary. This enhances the understanding of the structural requirements for the CVD of CNTs and suggests the theory that the essential role of the catalyst is partly determined by the nanoscale curvature of the particle.

**Table 1**
Some of the extraordinary properties of carbon nanotubes.

| | | (Refs.) |
|---|---|---|
| **Mechanical properties** | | |
| | 1. Young's modulus of SWCNTs ~ 1 TPa | [14] |
| | 2. Young's modulus of MWCNTs ~1–1.2 TPa | [15] |
| | 3. Tensile strength of SWCNT ropes ~60 GPa | [16] |
| | 4. Tensile strength of MWCNT ~0.15 TPa | [17] |
| **Thermal properties at room temperature** | 1. Thermal conductivity of SWCNT ~1750–5800 W/mk | [18] |
| | 2.Thermal conductivity of MWCNT >3000 W/mK | [19] |
| **Electronic properties** | 1. SWCNT bandgap | |
| | When n–m is divisible by 3 (0 eV, metallic) | [20] |
| | When n–m is not divisible by 3 (0.4–2 eV, semiconducting) | [21] |
| | 2. MWCNTs bandgap ~0 eV (non-semiconducting) | [21] |
| **Electrical properties** | 1.Typical resistivity of SWCNT and MWCNTs = $10^{-6}$ Ωm | [22,23] |
| | 2.Typical maximum current density = $10^{7}$-$10^{9}$ Acm$^{-2}$ | [24,25] |
| | 3. Typical quantized conductance (measured) = 12.9 kΩ$^{-1}$ | [26,27] |