1 MWCNTs manufactured by CCVD method

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Introduction

Carbon nanotubes, due to their unique properties, possess widespread potential applications, in particular in electronics, optoelectronics, medicine, textile and sports industry and are also frequently added as a reinforcement in composites for constructional parts.[1-4]. Such cylindrical rolled layers of graphene, ended with halves of fullerenes, may be modified differently to enhance their application options. For this reason, it is necessary to fabricate, in a controlled manner, high quality carbon nanotubes, which would significantly facilitate their application possibilities as modern engineering materials. Some common properties of different models of nanotubes fabrication have been known, including the influence of the presence of a catalyst on the type of nanotubes fabricated. A catalyst is a substance changing the speed of a chemical reaction, and, in case of the CVD method, it facilitates the decomposition of hydrocarbon gas. Noticeable research progress has been seen in the recent years as to the efficiency and effectiveness of carbon nanotube fabrication methods. This chapter presents recent results on the optimisation of a synthesis process of multi-walled carbon nanotubes by Catalytic-Chemical Vapour Deposition (CCVD) compared to other popular methods of CNTs synthesis. The authors' intention is to fabricate long carbon nanotubes growing perpendicular to a silicon substrate, parallel to each other, with minimum impurities. Three synthesis process optimisation parameters were chosen including temperature, time and a hydrogen flow rate, having impact on, respectively, the length of nanotubes, height of a CNTs "forest" layer and a contamination level. The materials obtained were subsequently analysed by transmission electron microscopy (S/TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy, X-ray diffractometery (XRD), and derivatography.

Review of CNTs fabrication methods

At current, the three most popular carbon nanotube fabrication methods include: Electric Arc Discharge, Pulsed Layer Deposition and Chemical Vapour Deposition (CVD) (Fig. 1.1). The first two methods include the condensation of carbon atoms produced by carbon source evaporation. The temperature in such processes is similar to a melting point of graphite of about 3000-4000°C [2,5-9]. This undisputed disadvantage may make it difficult to develop a suitable fabrication method that can be commuted at a large scale from a laboratory to industry, as high efficiency and low energy consumption for fabrication of pristine carbon nanotubes is a key criterion of method selection. Pulsed Arc and AC-Arc discharge [10,11,12] are the variants of the electric arc method popular in the recent years, and the following latest laser methods can be distinguished, which are differing in the laser type and work mode: pulsed Nd:YAG, CO₂ continuous wave, XeCl excimer, KrF excimer, pulsed double beam Nd:YAG [13,14,15,16].Process temperature for Chemical Vapour Deposition of around 250-1000°C is by far the lowest. The CVD method, due to its low cost and convenient application at an industrial scale, is currently the most attractive technology dedicated to a synthesis of nanostructural materials [6-7].

The multiple variants of the CVD method can be distinguished, which are dependent, among others, on the reaction chamber heating method or pressure in the working chamber, and the following can be differentiated [32-43]: Plasma Enhanced Chemical Vapor Deposition (PECVD), Hot–Filament Chemical Vapor Deposition (HFCVD), Laser Chemical Vapor Deposition (LCVD),

metallorganic Chemical Vapor Deposition (MOCVD), Radio Frequency Plasma Enhanced Chemical Vapor Deposition



FIGURE 1.1

The various available carbon nanotube fabrication methods [based on 3,7, 17, 18, 19-31]

(RF-PECVD), Microwave-Enhanced Chemical Vapor Deposition (MECVD), Aerosol-Assisted Chemical Vapor Deposition (AACVD), Photo Chemical Vapor Deposition (photo-CVD), Low Pressure Chemical Vapor Deposition (LPCVD), Atmospheric Pressure Chemical Vapor Deposition (APCVD), Ultrahigh Vacuum Chemical Vapor Deposition (UHVCVD). The methods mentioned have a substantial development potential and as such are undergoing constant improvements and modifications. In the O_2 -assisted plasma enhanced method (PECVD), the use of oxygen allows to effectively and repetitively control the growth of densely packed carbon nanotubes [44]. Oxygen is present when heating a metallic catalyst, and is also a component of the gas atmosphere in a nanotubes growth process. The vaporisation and pyrolysis of a carbon source is carried out at the same time in the ultrasonic spray pyrolysis method, hence this process enables the growth of carbon nanotubes without using a vacuum pump and hydrogen [45]. The activity and lifetime of a catalyst in the water assisted CVD process are enhanced by the use of water. It has been pointed out that water helps to maintain catalyst activity and enables the synthesis of a 99.98 % pure product [46]. A forest of single-walled carbon nanotubes with the height of 2.5 mm was produced in 10 min. with the water assisted CVD method. The injection CVD method consists of pumping and spraying of a metallocene-hydrocarbon solution into a furnace. Opposite to classical CVD, the injection CVD method does not require a catalyst synthesis stage, as catalytic particles are generated in situ continuously for the entire duration of growth of the carbon nanomaterial [17]. The alcohol CVD method applies catalysts in the form of a ferrocene and ethanol solution at different proportions [47, 48]. The rate of ferrocene and ethanol is an important process parameter because when the concentration of ferrocene is too low, the high content of amorphous carbon is observed in the final product, and when the concentration is too high, a large quantity of metal nanoparticles is created. It has been evidenced according to the references [47] that an optimum concentration of ferrocene should be within 1–1.5 % by mass (wt %). The alcohol CVD method was modified by using a high-performance laser for evaporation of a metal (Co, Rh) disc. Single-walled carbon nanotubes with the diameter of 0.96-1.68 nm are synthesised this way using ethanol as a source of carbon [49]. In the hot filament CVD method, a hot filament is placed near the substrate and assists the distribution of hydrocarbon gas. A stream of electrons emitted from a hot filament is increasing the density of homogenous nucleation of nanoparticles in the gas environment and of nucleation of nuclei on the substrate surface [50,51]. Metal and carbon filaments can be used in the process discussed, however, in case of the growth of carbon nanotubes, it is more advantageous to apply a carbon filament, because a metal filament may create impurities [52]. Multi-walled carbon nanotubes with the diameter of more than 20 nm were synthesised with the HFCVD method using a thin catalyst film without a silicon substrate. Randomly oriented carbon nanotubes with the diameter of 15-20 nm and the length of several microns and carbon nanotubes were also synthesised with the radio-frequency PECVD method. The radio frequency of 13.56 MHz and device capacity of 700 W were used in a growth process. The nickel deposited onto a silicon substrate was used as a catalyst in the process and the source of carbon was acetylene [53,54]. In the microwave plasma enhanced CVD method, microwave plasma enables hydrocarbon decomposition in a gas environment and on the substrate surface, as a uniform stream of active particles is created, such as ions or radicals [55]. Vertically oriented single- and double-walled carbon nanotubes with the diameter of approx. 2 nm and multi-walled nanotubes with the diameter of 4 nm were obtained with the microwave plasma enhanced CVD method. A Co-Ti catalyst deposited on a silicon substrate without a buffer layer was produced in the process [56,57]. A classical thermal CVD method is carried out under atmospheric pressure with the participation of reagents activated with thermal energy [58]. Catalytic Chemical Vapour Deposition (CCVD) with a catalyst deposited onto a substrate and with a floated catalyst or as a fluidised bed can be classified as a variant of this method according to the manner in which a catalyst is supplied. Table 1.1 presents the examples of representative results of investigations into carbon nanotubes synthesis conditions in CVD processes with a floated catalyst and a catalyst deposited onto a substrate.

TABLE 1.1

The results of carbon nanotubes synthesis investigations performed with CVD methods with catalyst deposited onto surface and floated catalyst [30,32,33,35,41,47,59-72]

Type of hydrocarbon gas or carbon oxide	Carrier gas	Catalyst type	Synthesis temperature [°C]	Variant of CVD process – form of catalyst	Diameter [nm] and type of synthesised nanotubes
Ethanol	Ar	Co/Al ₂ O ₃	550	Deposited	10-20
(C₂H₅OH)				substrate	Multi-walled
Benzene (C ₆ H ₆)	Ar/H₂	Ferrocene	600	Floated	10-30
					Multi-walled
			550		2-20
					Multi-walled

Type of hydrocarbon gas or carbon oxide	Carrier gas	Catalyst type	Synthesis temperature [°C]	Variant of CVD process – form of catalyst	Diameter [nm] and type of synthesised nanotubes
Methane (CH₄)	Ar	Fe-Mo/ Al ₂ O ₂	700.750	Floated	2-45
					Single-walled
			600		0,8-1,2
					Single-walled
Acetylene (C_2H_2)	N ₂	Fe-Co/Al ₂ O ₃	700	Deposited	31-41
· · - ·	-	·		substrate	Multi-walled
Carbon oxide	He	Co-Mo/SiO ₂	700	Deposited	1 Single-walled
(CO)		-		substrate	Ŭ I
Acetylene (C_2H_2)	Ar	Ferrocene	600-800	Deposited	10-20
-				substrate	Multi-walled
Ethanol	Ar	Fe-Co	700-800	Deposited	1 Single-walled
(C ₂ H ₅ OH)				substrate	
Toluene	Ar/H ₂	Ferrocene	800,900	Floated	20-25
(methylbenzene					Multi-walled
) C ₆ H ₅ -CH ₃					
Ethanol	He	Fe/ Al ₂ O ₃	800	-	0,78-1,05
(C ₂ H ₅ OH)					Single-walled
Methane (CH ₄)	H ₂	Fe-Mo/MgO	860	Deposited	- Double-walled
	L			substrate	
Acetylene (C ₂ H ₂)	N ₂	Fe-Co/ Al ₂ O ₃	700	Deposited	31-41
	L			substrate	Multi-walled
Methane (CH ₄)	Ar/H ₂	Fe-Mo/Al ₂ O ₃	900	Deposited substrate	0,9-2,7 Single-walled
			ļ		
Methane (CH ₄)	N ₂	Fe/ Al ₂ O ₃ -	900	Deposited	- Multi-walled
		SiO ₂		substrate	
Acetylene (C ₂ H ₂)	Ar	Ferrocene	900-1000	Floated	- Single-walled
Ethanol	Ar	Ferrocene	1100	Floated	20-40
(C₂H₅OH)			ļ		Multi-walled
Toluene	H ₂	Ferrocene	1200	Floated	20-70
(methylbenzene					Multi-walled
) C ₆ H ₅ -CH ₃	L				
Acetylene (C ₂ H ₂)	Ar	Ferrocene	950-1200	Floated	1,9
	L				Double-walled
Carbon oxide	He	Pd/La ₂ O ₃ /	673	Deposited	10-50
(CO)		Al ₂ O ₃		substrate	Multi-walled
Methane (CH ₄)	H ₂	LaNi ₅	600	Deposited	20 nm
	 			substrate	Multi-walled
Ethylene (C ₂ H ₄)	H ₂	Ni	650-850	Deposited	25-60 Wielościenne
				substrate	

Type of hydrocarbon gas or carbon oxide	Carrier gas	Catalyst type	Synthesis temperature [°C]	Variant of CVD process – form of catalyst	Diameter [nm] and type of synthesised nanotubes
Acetylene (C ₂ H ₂)	N ₂	Co/zeolite	700	Deposited substrate	- Multi-walled
Acetylene (C ₂ H ₂)	N ₂	Co/CaCo ₃	700	Deposited substrate	- Multi-walled
Toluene (methylbenzene) C ₆ H ₅ -CH ₃	Ar/H ₂	Ferrocene	590-850	Deposited substrate	16-45 Multi-walled
Acetylene (C ₂ H ₂)	NH ₃	Ni-Co/ SiO ₂	700	Deposited substrate	5-10 Single-walled &Multi-walled
Methane (CH ₄)	H ₂	Fe/sepiolite Fe/kaolinite	600 450-520	Deposited substrate	10-20 Multi-walled 10-25 Multi-walled
Acetylene (C ₂ H ₂)	Не	Fe/Ru	700	Floated	13-30 Multi-walled
Acetylene (C_2H_2)	N ₂ /NH ₃	Fe/ SiO ₂	600-1050	Deposited substrate	13-80 Multi-walled

CCVD method of CNTs manufacturing

Catalytic Chemical Vapour Deposition (CCVD), a CVD derivative, enables the mass synthesis of highquality nanotubes and is characterised by the presence of a catalyst during nanotube synthesis. The general mechanism of nanotube growth consists of the thermal dispersion of hydrocarbons catalysed by a transition metal (e.g. Fe, Ni, Mo, Co or combination thereof) [3,6,18,73-76], and also dissolution of carbon into a metal until the said metal reaches its solubility limit. Carbon solubility in Fe is 20.2%, in Ni - 10.7 %, in Mo - 60-70 %, in Co - 13.9 %, whereas in Cu - $2x 10^{-4}$ % and occurs at a melting point of respective metals [77]). Efficiency has also been demonstrated of non-metallic catalysts such as: kaolinite, montmorillonite, nontronite, sepiolite, zeolite [18,32,33,78] and metal organic compounds: ferrocene, nickelocene, cobaltocene [18,79,80]. The precipitation of carbon from the saturated metal particles, and the resulted carbon extrusion following super-saturation of the metal nano-particle, results in the formation of a cylindrical graphitic carbon allotrope with sp² hybridisation. Thermal and plasma assisted decomposition of the carbon precursor, typically the hydrocarbons, is an exothermic reaction, releasing heat to a metallic catalyst particle, whereas carbon crystallisation is an endothermic reaction and absorbs heat from the metal zone. A thermal gradient guarantees continuity in the growth process. A thermal gradient guarantees continuity in a growth process. Catalytic pyrolysis can be controlled by selecting a suitable catalyst, hydrocarbon or carbon-containing gas, temperature, and process time. It is hence possible to fabricate, with fine control, vertically oriented single-walled and multi-walled carbon nanotubes (MWCNT) on various substrates, including; glass, ceramics and silicon [3,6-7,73,74,81]. The key

issue for the practical or broad utilisation of nanostructural carbon materials is to engineer the carbon nanotube growth and morphology accurately and reproducibly. There are several essential parameters influencing the type and form of the final nanographitic products, including, principally, the type and flow rate of the following gases: hydrocarbon, inert carrier and hydrogen amorphous carbon etching agent; the type, size and form of catalyst particles which can be deposited on a substrate or suspended; the process time and temperature and orientation of a working chamber (vertical or horizontal) [81-84].

Multi-walled carbon nanotubes are synthesised by Catalytic-Chemical Vapour Deposition (CCVD) on a silicon substrate coated with a catalyst in the form of a thin Fe film and two nanometric ceramic buffer layers (Fig. 1.2). The process is carried out in a tube furnace in which a quartz process pipe is situated. Thermocouples are located in the 3 primary growth zones: at the tube entrance, centre, and end of the furnace. Fig. 1.3. shows a schematic of a system for carbon nanotubes synthesis by the CCVD method. A silicon wafer is placed on a feeder in the next stage, and then a specimen is introduced in the presence of H_2 and Ar into the heated furnace and is heated for 15 minutes. Following the preheating, a source of carbon in the form of C_2H_4 and process gases (H_2 and Ar) is introduced into a working chamber. To terminate nanotube growth, hydrocarbon supply is stopped, the feeder is removed together with the specimen from the furnace, the system is purged with Ar, the furnace is cooled gradually to 200 °C, the system is purged again to complete the process.



FIGURE 1.2

Substrate for synthesis of carbon nanotubes and proposed growth model of multi-walled carbon nanotubes manufactured by CCVD [18,83,85]

Multi-walled carbon nanotubes were synthesised by CCVD. Ethylene was supplied for 15, 30 or 45 minutes. A concentration of Ar in the multi-walled carbon nanotubes growth process was a constant parameter and was 1 SLPM (Standard Litre per Minute, where 1 SLPM = 1,68875 Pa^*m^3/s), while the concentration of H₂varied and was 200, 300 or 500 SCCM (Standard Cubic Centimetres per Minute, where 1 SCCM = 0,0016 Pa^*m^3/s) depending on the experiment carried out. An additional experiment was undertaken after performing the planned series of experiments and selecting the



FIGURE 1.3

Diagram of device for MWCNTs fabrication by CCVD

TABLE 1.2

VAMWCNTs synthesis parameters for all the experiments carried out

Sample	Temperature [°C]	Time [min]	H ₂ [SCCM*]	C ₂ H ₄ [SCCM*]	Ar [SLPM*]	Catalyst
1	700	45	200	300	1	2 nm Fe
2	750	45	200	300	1	2 nm Fe
3	800	45	200	300	1	2 nm Fe
4	750	15	200	300	1	2 nm Fe
5	750	30	200	300	1	2 nm Fe
6	750	45	300	300	1	2 nm Fe
7	750	45	500	300	1	2 nm Fe
						2 nm Fe
8	750	45	300	300	1	(in a quartz
						boat)

*The working units used in an American EasyTube[®] 2000 device; 1 SLPM = 1,68875 Pa*m³/s; 1 SCCM = 0,0016 Pa*m³/s optimum time of synthesis enabling to fabricate the highest layer of nanotubes, and the experiment differed from the previous ones in that a silicon wafer was placed on the feeder in a quartz boat as shown in Fig. 1.4. Table 1.2 presents MWCNTs synthesis process conditions for all the experiments carried out.



FIGURE 1.4

Silicon wafer placed in quartz boat in loading chamber of CCVD device directly before entering the specimen into the furnace

All the experiments were carried out by applying constant synthesis time and a constant concentration of process gases with respect to the first three specimens (1 to 3). The parameters were chosen experimentally with the aid of literature data to investigate the impact of the varying temperature on the length of the synthesised nanotubes. A temperature of 750°C was chosen for the next tests, which enabled to achieve the best results and had a constant value in the subsequent experiments. A variable parameter in tests 4 and 5 was carbon nanotubes synthesis time of, respectively: 15 and 30 min., as compared to the results of the experiment conducted earlier lasting 45 minutes. A hydrogen flow rate was changed in the next trials, i.e. in experiments 6 and 7 which were, respectively, 300 and 500 SCCM, in order to check the impact of this parameter on the amount of impurities in the final product. The temperature and time parameters remained at a constant level, optimised at the earlier stage of the experiments and were, respectively, 750 °C and 45 min. Experiment 8 was carried out in the conditions of experiment 6, however, a silicon substrate with a catalyst was additionally placed in a quartz boat. Figure 1.5 shows a concept presenting the optimisation method of parameters of multi-walled carbon nanotubes manufacturing at the particular stages of the experiment.

Variable	Temperature [°C]		Time [min]			H ₂ flow rate [SCCM]			Growth in a quartz boat	
parametero	700 750 800		15	30	45	200	300	500	Yes	No
Constant parameters	time, grow	ime, gas flow rate, growth without a quartz boat v			temperature, gas flow rate, growth without a quartz boat		temperature, time, growth without a quartz boat		temperature, time, gas flow rate, growth in a quartz boat	
Aim	Maximum length of MWCNTs			Maximum height of MWCNTs layer		The best quality of MWCNTs			Maxi heig MW(lay	mum ht of CNTs /er

Concept of optimisation of multi-walled carbon nanotubes synthesis conditions by CVD method

MWCNTs manufactured by CCVD method under microscopes

The multi-walled carbon nanotubes produced were subjected to microscope observations using: transmission electron microscope (S/TEM), scanning electron microscope (SEM) and atomic force microscope (AFM).

S/TEM images were made using an S/TEM TITAN 80-300 device fitted with an electron gun with XFEG field emission, a Cs condenser spherical aberration corrector, a STEM scanning system, Bright Field (BF) and Dark Field (DF) detectors and High Angle Annular Dark Field (HAADF), and also an EDS spectrometer. The preparations for examinations in the S/TEM were prepared by dispergation the carbon nanotubes obtained in ethanol in an ultrasonic bath, and then by drop cast onto copper mesh and dried in air at room temperature.

Observations were performed in the bright and dark field using an HAADF detector working in the STEM mode using a transmission electron microscope (TEM). When an HAADF detector is used, a dark-grey material is visible and a metallic catalyst nanoparticle is visible as a lightly illuminating shape due to a large difference between the value of atomic numbers of the elements forming part of the material directly after a synthesis process: carbon (Z=6), iron (Z=26) (Fig.1.6). Photographs made using the BF detector are presented in Fig. 1.7-1.11. A full range of carbon nanotubes' surface imaging was achieved under the investigations undertaken, with a transmission electron microscope (S/TEM). Figures 1.6-1.11 show the clusters of carbon nanotubes as well as single nanotubes with visible graphene layers forming the structure of MWCNTs. The outcomes obtained also confirm that the material analysed is pure, about 90 %, however, a few cases of metallic impurities (Fig.1.6a) and the presence of amorphous carbon deposits (Fig.1.6b) were also observed. The images of the carbon nanotubes manufactured by CCVD at the temperature of, respectively, 700, 750 and 800°C allow to conclude that the longest nanotubes were produced at 750°C, as shown in figures 1.7-1.8. The number of graphene planes creating the structure of multi-walled carbon nanotubes is approx. 8-10



a) HAADF image of MWCNTs growth on Si substrate with Fe catalyst; yellow arrow indicates the catalyst nanoparticle, b) HAADF image of MWCNTs with carbon deposit



FIGURE 1.7

a) TEM image of MWCNTs fabricated at the temperature of 700 $^{\circ}$ C [86], b) TEM image of long MWCNT fabricated at the temperature of 750 $^{\circ}$ C [87]



a) TEM image of MWCNTs fabricated at the temperature of 800 °C, b) HRTEM image of MWCNTs fabricated at the temperature of 750 °C [87]

and depends on the temperature. The nanotubes observed are homogenous, and their length is several hundreds of nm (Fig. 1.7b) with the diameter of approx. 15 nm (Fig. 1.8b).

A series of experiments in the process conditions other than given in Table 1.2 were also carried out serving to find the optimum conditions of a multi-walled nanotubes fabrication process by CCVD. Figures 1.9-1.10 show carbon nanotubes containing catalyst particles, while nanotubes with a bamboo-like structure are shown in figure 1.11.Elongated catalyst particles (Fig.1.9a), (Fig.1.10b), irregularly shaped particles (Fig.1.9b), as well as spherically shaped particles (Fig.1.10a) were observed, closed within the carbon nanotubes. We believe this to be attributed to the stress [62] induced by the carbon material surrounding the catalyst particle. These observations allow us to conclude that a catalyst particle is lifted from the substrate upwards in the growth process, which is consistent with the tip growth mechanism of the nanotubes described in the literature [3,18,62] and signifies the active participation of a catalyst in the growth process of MWCNTs. Moreover, the photos presented also show that the graphene planes are surrounding a catalyst particle, which may cause limitation of carbon precursor access to the catalyst, thus inhibiting the carbon nanotubes growth process and the formation of metallic impurities. Photo 1.11. shows the fragments of a bamboo-like structure of multi-walled carbon nanotubes.

A growth mechanism of a nanotube with a bamboo-like structure proposed by Zhu and Ding [88, 89] relies on the tip-growth mechanism which, together with the base-growth mechanism, is part of a generally adopted vapour-liquid-solid (VLS) growth model. In the VLS mechanism, gas individuals containing carbon are dissolved in a catalyst particle. After reaching supersaturation levels, the excess carbon is precipitated in the form of a growing nanotube. In the base-growth model, a nanotube is growing from a catalyst which is mounted to the substrate, while in the tip-growth model, a catalyst particle is carried by a growing nanotube and becomes its tip. The growth of bamboo-like structured nanowires occurs as follows: while the growing carbon nanotube is lifting a catalyst particle, a closed hollow end of the tube is being formed. This may be caused by strong stresses between the catalyst particle and graphene planes formed as a result of high

temperature for the catalytic decomposition of hydrocarbon. The compartment layer is growing by the slow accumulation of carbon atoms on the catalyst surface, and then the compartment layer is detached from the catalyst particles due to stresses [88]. While the nanotube walls are growing, another compartment layer is formed on a catalyst particle and it is then connected with a nanotube wall, as shown in figure 1.12.



FIGURE 1.9

a) HRTEM image showing elongated catalyst particle shape in the multi-walled carbon nanotube structure [90], b) HRTEM image of multi-walled carbon nanotubes together with single irregularly-shaped catalyst particle within the multi-walled carbon nanotube structure



FIGURE 1.10

a) HRTEM image of cluster of multi-walled carbon nanotubes with spherical catalyst particle within the multiwalled carbon nanotube structure, b) HRTEM image of multi-walled carbon nanotubes together with elongated catalyst particles within the multi-walled carbon nanotube structure



a) HRTEM image of MWCNTs with bamboo-like structure, b) HRTEM image of MWCNTs with bamboo-like structure

Nanotubes formation mechanisms are still being investigated and there is no unequivocal theory until today explaining the growth of particular morphological types of carbon nanotubes.

The carbon nanotubes fabrication models seen in the literature are hypothetical and until now the concepts presented have not been backed up by hard scientific evidence. At present, it is not possible to present a single generally valid growth scheme of CNTs mainly due to the multitude and



FIGURE 1.12 Diagram of growth of bamboo-like structure carbon nanotube [88,89]

diversity of nanotubes synthesization methods. It is assumed most often with regard to CNTs produced with CVD methods that they grow according to the VLS model [91, 92, 93]. A double-step mechanism, according to which a thickening step of CNTs takes place after initiating the first step of growth through deposition of amorphous carbon [91,94, 95], constitutes an alternative proposal.

SEM images were made using Carl Zeiss Supra 35 equipped with X-rayspectrometers: an energy dispersion spectrometer (EDS) and wavelength spectrometer (WDS) and a system for analysing diffraction of back scattered electrons EBSD by EDAX. The high resolution and the precision imaging of the preparations viewed was achieved by applying a high-performance In-lens SE detector working at low beam voltage and at very small distance of the preparation examined to the electron gun.

A full imaging range of a vertical layer of carbon nanotubes was achieved directly after the process with the CCVD method, starting with a top view (Fig. 1.13) and side view (Fig. 1.14-Fig. 1.15). Measurements were also made of the height of the layer produced (Fig.1.15a, Fig. 1.15a). The observations made allow to conclude that the highest layer of nanotubes was obtained in the case



FIGURE 1.13

a) SEM image of multi-walled carbon nanotubes manufactured by CVD method on the silicon substrate (top view); the synthesis time of 45 min. [98], b) SEM image of multi-walled carbon nanotubes manufactured by CCVD method on the silicon substrate (top view); the synthesis time of 45 min. [99]

where the synthesis time was longest and was 45 minutes. For comparison, V.K. Kayastha et al. [96] have reached the height of a layer of vertically aligned carbon nanotubes of 150 μ m over 30 min. at 650 °C with the CCVD method and by applying a 1.5 nm thick Fe catalyst and acetylene as a source of carbon. A vertically aligned layer of multi-walled carbon nanotubes with the height of 0.75 mm over 30 minutes at 730 °C was also achieved by D.B. Geohegan et al. [97] with the CCVD method. A layer of Al (10 nm), Fe (1 nm) and Mo (0.2 nm) deposited onto a silicon substrate acted as a catalyst in the experiment, and acetylene was a source of carbon [97]. A full, uniform coverage of the silicon substrate was obtained in this case with a layer of carbon nanotubes for an equivalent growth time. The nanotube layer had the maximum height of 190 μ m. Due to the shorter MWCNTs growth process time of, respectively, 15 and 30 minutes, the layer of nanotubes is non-uniform, and the growth of nano-materials takes place locally in the central part of the substrate only.



a) SEM image of vertically arranged carbon nanotubes manufactured by CCVD method on the silicon substrate (side view, specimen rotated under 90°); the synthesis time of 45 min. [87], b) SEM image of vertically arranged carbon nanotubes manufactured by CCVD method on the silicon substrate; the synthesis time of 45 min



FIGURE 1.15

a) SEM image of vertically arranged carbon nanotubes manufactured by CCVD method on the silicon substrate placed in a quartz boat; the synthesis time of 45 min. [90], b) SEM image of vertically arranged carbon nanotubes manufactured by CCVD method on the silicon substrate placed in a quartz boat; the synthesis time of 45 min. [98]

This phenomenon is probably caused by insufficient activity time of a catalyst and a less effective rate of ethylene decomposition, leading to a low growth rate of nanotubes [18, 100]. In the case of an experiment during which a silicon substrate was placed in a quartz boat, the height of the layer of nanotubes is highest and is about 370 μ m. Figure 1.16 shows microscope images of randomly oriented carbon nanotubes. In order to prepare a specimen, the nanotubes were removed mechanically from a silicon wafer on which they were growing. By removing the vertically arranged MWCNTs from a silicon substrate, the nanostructural carbon material observed is entangled and

randomly oriented. The measurements of several diameters of carbon nanotubes were also made (Fig. 1.16b), with the value ranging between 15 nm and 20 nm.



FIGURE 1.16

a) SEM image of randomly oriented carbon nanotubes manufactured with CVD method; the material removed from silicon substrate, b) SEM image of randomly oriented carbon nanotubes manufactured with the CCVD method; the material removed from silicon substrate

Atomic forces microscopy was used for analysing the silicon substrate surface topography before and after the synthesis process. AFM images were made with an atomic forces microscope AFM XE 100 by Park Systems. The maximum size of the scanned area was 1 mm x 1 mm, operated in noncontact mode. The experiments made enabled to observe the topography of the silicon substrate surface before (Fig. 1.17a) and after (Fig. 1.17b) MWCNT synthesis. The MWCNT were perpendicular to the substrate surface and nanotubes are arranged parallel to each other.

The object of AFM investigations were silicon plates onto which carbon nanotubes were synthesised for 15, 30 and 45 minutes. The other process parameters for all the three experiments were constant. The nanotubes were produced at 750 °C following earlier optimisation. The C_2H_4 and H_2 flow rate was 300 SCCM, and 1 SLPM for the Ar. AFM suggests that the highest layer of nanotubes was obtained when the synthesis time was longest and was 45 min. A full, uniform coverage of the silicon substrate with a carbon material was obtained in this case, and a layer of nanotubes in this case has the maximum relative height of 762 to 692 nm. In the other case, corresponding to a synthesis process carried out for 15 and 30 min, the substrate is covered with them non-uniformly due to insufficient time of nanotubes growth, and their growth takes place only locally.



a) AFM 3D image of surface topography of silicon substrate before the synthesis process of multi-walled nanotubes; the maximum relative height of 3.618 [nm] [87], b) AFM 3D image of surface topography of silicon substrate after the synthesis process of multi-walled nanotubes; the maximum relative height of 762.692 [nm] [87]

Determination of MWCNTs quality using Raman spectroscopy

The degree of defects of the obtained carbon nanotubes' structure was examined using a Raman in using a Renishaw Reflex Raman Spectrometer fitted with a Leica confocal Research Grade microscope. The samples were viewed in the reflected and transmission mode. Measurements were recorded using a Long Working Distance lens with x20 magnification. The nanotube samples were deposited onto glass substrates. A comparative analysis of the obtained D, G and 2D spectra characteristic for multi-walled nanotubes was subsequently carried out. The ratio of the G band to D band confirms the degree of defects of the structure, and also the purity of the fabricated materials [101,102,104]. The presence of Radial Breathing Mode (RBM) bands in the spectra, characteristic for single-walled nanotubes, was not recorded during the experiment performed, which also confirms the fact that the carbon nanotubes fabricated are multi-walled. Examinations were also carried out with Raman spectroscopy to determine the effect of H₂ on the quality of carbon nanotubes and the level of impurities of the material obtained.

Table 1.3 shows the results of the matched curves for the Raman spectra obtained, made with Fityk software which uses distribution into 4 Lorentz functions and 2 Gauss functions [101] in relation to the D and G bands and the value of the relationship I_e/I_d . Figure 1.18 presents typical Raman spectra of multi-walled carbon nanotubes fabricated at different hydrocarbon flow rates. A multiwalled carbon nanotube spectrum is characterised by the occurrence of the following bands: the D band corresponding to the degree of nanotubes structure disorder (approx. 1345 cm⁻¹), the G band corresponding to the degree of nanotubes graphitisation (approx. 1576 cm⁻¹) and the 2D band corresponding to stresses (approx. 2685 cm⁻¹), the value of which is similar for all the rates of hydrogen flow, and is negligible for the considerations made, as it delivers no information about the studied material's purity. The shape of D and G modes and the ratio of their I_d/I_e intensity indicates that multi-walled carbon nanotubes were synthesised. The Raman spectra presented in the figures below were created for multi-walled carbon nanotubes fabricated with the CCVD method at 750 °C for 45 minutes in the presence of the following gases: C_2H_4 flowing at a rate of 300 SCCM, Ar flowing at a rate of 1 SLPM and H_2 , the flow rate of which was a variable parameter and was, respectively: 200, 300 and 500 SCCM. The higher the value of the I_g/I_d relationship, the better is the quality of the study material (fewer defects). The results of the examinations presented in Table 1.3 point out that the value of the I_d/I_g relationship is highest in case of a hydrogen flow rate equal to 200 and 300 SCCM. It should therefore be asserted that by using such rates in a synthesis process, a material with the highest purity will be ensured. The presence of the D3 band (\approx 1500 cm-1) coming from the

TABLE 1.3

Results of investigations of carbon nanotubes using a Raman spectroscope for the D and G band

H ₂	Rama	anshift	[cm⁻¹]	Intensity [a.u.]			Ig/Id
[SCCM]	G	D	D3	G	D	D3	
200	1574	1344	1470	9798	6260	592	1.56
300	1573	1339	1463	3347	2986	164	1.12
500	1572	1339	1470	2332	2628	174	0.88



Raman spectra for multi-walled carbon nanotubes fabricated by CCVD method with different hydrogen flow rate of 200, 300 and 500 SCCM

fraction of amorphous carbon was additionally confirmed in the investigations undertaken. Table 1.2 shows the results of the matched curves for the obtained Raman spectra made with Fityk software using distribution into 4 Lorentz functions and 2 Gauss functions for the D3band [48]. The height of the D3 band is lower in the case of the flow rate of H₂ of 300 SCCM, which confirms the highest purity of the so fabricated material. The results are the same as the results of S/TEM microscope observations.

Presence confirmation of MWCNTs by X-ray phase analysis

An X-ray phase analysis of the specimens was performed with a TUR-M62 diffractometer using filtered radiation of a copper tube lamp (Cu λ =1.54050·10-10) with a 35 kV voltage supply and a 20 mA filament current. Measurements were made within the angle range, 20 = 20 to 90°, the step is 0.01°, and counting time is 5s. Figure 1.19 presents the results of an X-ray XRD phase analysis as an X-ray diffraction pattern of the fabricated carbon nanotubes. The occurrence of reflexes for the 20 reflection angle value of 25.9°, 42.9°, 53.3° and 78.7° was seen. The material was identified by comparing the observed reflexes with a diffraction pattern of carbon nanotubes available from the International Centre for Diffraction Data (ICDD), possessing information concerning the situation of

diffraction lines and their relative intensity. It was confirmed, based on the results of an X-ray qualitative phase analysis, that the studied material contains carbon nanotubes without the content of a metallic catalyst, which confirms the high purity of the synthesised nanotubes. Table 1.4 shows the list of the recorded peaks corresponding to reflexes coming from the planes (002), (100), (004), (110). A material synthesised with the following parameters was examined, i.e. the temperature of 750 °C, the synthesis time of 45 minutes and the flow rate of H₂ of 300 SCCM for the constant flow rate of other gases of, respectively, for C₂H₄ – 300 SCCM, and for Ar – 1 SLPM.



FIGURE 1.19

X-ray diffraction pattern of carbon nanotubes

TABLE 1.4

A list of the recorded peaks corresponding to reflexes coming from particular planes

Material	Reflection angle of 2θ	Miller's indicators (hkl)
Carbon nanotubes Reference code: 00-058-1638	25.919	002
	42.959	100
	53.292	004
	78.721	110

Thermogravimetric research results of manufactured MWCNTs

The purity of carbon nanotubes was examined with a TG-DTA Q-1500 derivatograph by MOM Budapest. Nanotubes manufactured using the following optimum process conditions were examined: the temperature of 750 °C, the synthesis time of 45 minutes and the flow rate of H_2 of 300 SCCM.



FIGURE 1.20

Thermogravimetric TG curve of the produced multi-walled carbon nanotubes

A thermogravimetric curve was created during incineration of the nanotubes in the atmosphere of air with a heating rate of 10°C/min. within the temperature range of 20-950 °C (Fig. 1.20). Two distinctive areas were spotted within the temperature range of 300-450 °C and 450-700 °C. The undertaken analysis of TGA, DTG and DTA has revealed that the I endothermic reaction related to amorphous carbon oxidisation in the specimen, corresponding to a preparation mass loss of about of 5%, was recorded while heating a nanotube material within the temperature range of 300-450 °C. The temperature range of 450-700 °C is associated with the II endothermic reaction corresponding to carbon nanotubes oxidisation and is characterised by a mass loss of 89.6 %. Above 750 °C, a TG curve becomes flattened due to oxidisation of nanotubes with the highest thermal stability. A preparation left after a thermogravimetric analysis has the mass of 2.24 mg, which corresponds to catalyst content in the tested specimen of 5.4 % of its total mass. The outcomes presented pertain to a raw material which, if necessary, can be subjected to further processing to purify and functionalise it.

Conclusions

Multiple diverse experimental systems for synthesis of carbon nanotubes exist at present. The majority of laboratory methods allow to produce maximally gram quantities of the product. Considering the fabrication methods of multi-walled carbon nanotubes, CVD methods show greatest development prospects and a possibility of industrial-scale applications. This is connected, among others, with the highest efficiency and lowest energy consumption when fabricating pristine carbon nanotubes as compared to high-temperature methods. An analysis of microscope images and the results of experiments concerning the influence of process conditions on the form and quality of the final product are essential to evaluate the efficiency and performance of a given type of a CVD method. It is very difficult to attempt to compare the results of studies concerning a synthesis of carbon nanotubes due to a large number of variants of CVD methods and the conditions in which particular nanotubes synthesis processes are performed. The experiments carried out using an author's approach to the optimisation of MWCNTs synthesis conditions together with examinations performed using TEM, SEM, AFM, Raman spectroscopy, XRD and TGA analysis have enabled to determine the optimum fabrication parameters of high-quality multiwalled carbon nanotubes on a silicon substrate using the CCVD method and to characterise the structure of the carbon materials obtained. The optimum process parameters include the process temperature of 750 °C, the synthesis time of 45 minutes and the flow rate of H_2 of 300 SCCM for the constant flow rate of other gases of, respectively, for C_2H_4 - 300 SCCM and for Ar – 1 SLPM. The results of experiments obtained for the flow rate of H_2 of 200 and 300 SCCM are very similar, for this reason the next experiments are planned to be performed for the hydrogen flow rate of 200-300 SCCM, in order to determine a flow rate allowing to manufacture nanotubes with the highest quality.

Process temperature has influence on the length of the synthesised MWCNTs, and the rate of hydrogen decomposition is growing with temperature. If the rate of C_2H_4 decomposition is fast, the catalyst may be deactivated, the growth of nanotubes inhibited, metallic impurities may remain and short MWCNTs may be produced. The synthesis process time influences the height of the nanotubes layer and its uniform distribution over a silicon substrate, in addition, if a silicon substrate is placed in a quartz boat, a higher layer of material is produced with the same growth time employed. A flow rate of H_2 is essential for the quantity of impurities (notably amorphous carbon). If the amount of H_2 is insufficient, carbon substrates may be created without the fraction of carbon nanotubes, and when the flow rate of H_2 is too high, the catalyst may be deactivated and a larger amount of amorphous material may settle. A carbon deposit can be removed by heating a material at a temperature of above 500-600 °C. The characteristic of a carbon material using XRD has confirmed that carbon nanotubes are created, the fraction of a metallic catalyst was not additionally observed. A material analysis using Raman spectroscopy confirms its good quality. Multi-walled carbon nanotubes formed with the optimum selected parameters are homogeneous, long (about 200 nm), with the diameter of about 15-20 nm. The outcomes obtained with a TGA analysis also confirm that the material analysed is pure, i.e. deprived of large contents of metallic impurities and amorphous carbon deposits.

The authors of the chapter are continuing their research work in scope of further optimisation of synthesis conditions of the CCVD process, in particular for selection of a concentration of hydrocarbon gas, usage of quartz boats in a synthesis process and the place where a silicon substrate is situated in a feeder. The research team has been conducting investigations comprising also: a TGA analysis for more accurate determination of material purity, functionalisation of the obtained materials to improve the possibility of creating nanocomposite materials, examinations

using Fourier Transform Infrared Spectroscopy (FTIR) to confirm the obtained function groups on the surface of carbon nanotubes subjected to prior functionalisation, decoration of carbon nanotubes with Rh, Re, Pd, Pt nanoparticles and their mutual combination, a chemical composition analysis by X-ray Photoelectron Spectroscopy (XPS), and also investigations into electric properties of nanocomposites consisting of carbon nanotubes and different nanoparticles of noble metals.

Acknowledgements

The works have been implemented within the framework of the ELCONANO project headed by Prof. A.D. Dobrzańska-Danikiewicz, funded by the Polish National Science Centre in the framework of the "OPUS" competitions. The project was awarded a subsidy under decision DEC-2011/03/B/ST8/06070. DawidCichocki is a holder of scholarship from the project "Scholarship and Internship Fund for the development of knowledge transfer in the region" co-financed by the European Union under the European Fund.

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