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Carbon nanotubes synthesis time versus their layer height

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ABSTRACT

Purpose: The purpose of the article is to present an approach for the optimisation of a synthesis process of Vertically Aligned Multi-Walled Carbon Nanotubes (VAMWCNTs) with Catalytic-Chemical Vapour Deposition (CCVD) on a silicon substrate.

Design/methodology/approach: Scanning and transmission electron microscopy was applied for showing the structure and morphology of the synthesised multi-walled carbon nanotubes.

Findings: The article presents and characterises nanostructural carbon materials fabricated with the CCVD method using an Fe catalyst deposited on a silicon substrate. SEM and TEM examinations have confirmed that a vertical layer of a CNTs "forest" growing on a silicon substrate containing a metallic catalyst is obtained and enabled to select optimum time for their growth process.

Practical implications: Vertically aligned multi-walled carbon nanotubes can be applied in numerous fields of technology, especially in scanning probes, photovoltaic cells, anisotropic conductive materials, semiconductors, membranes, chemical and biological sensors, field emitters in nanoelectronics and in molecular electronics.

Originality/value: An approach is presented of optimising the synthesis time of VAMWCNTs with a metallic catalyst using CCVD with an EasyTube® 2000 device by FirstNano.

Keywords: Nanomaterials; VAMWCNTs; CCVD; SEM; TEM

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MATERIALS

1. Introduction

Vertically aligned carbon nanotubes deposited on a given substrate are a new attractive engineering material. Their advantages include, most of all, a good aspect ratio, homogenous orientation and high purity. These days there is often a need for controlled fabrication of vertically aligned carbon nanotubes (VAMWCNTs), in particular in such applications as: scanning probes, photovoltaic cells, lithium-ion batteries, anisotropic conductive materials, semiconductors, membranes, chemical and biological sensors, field emitters in nanoelectronics, flat panel displays and molecular electronics [1-6]. Several technologies have been developed enabling to synthesise vertically aligned

carbon nanotubes on various substrates, and the most popular methods include: High-Pressure Carbon Monoxide Process (HIPco) [7], Fluidized Bed Catalytic Chemical Vapour Deposition (FB-CVD) [2], Catalytic-Chemical Vapour Deposition (CCVD). CCVD is the most effective method at present, however, costly substrate materials and deposition devices still must be used, which is a disadvantage of the method reducing its practical industrial applicability. The aim of the research carried out globally is to develop a technology allowing for repeatable mass synthesis of a layer of vertically aligned carbon nanotubes [3-4,8]. The catalytic decomposition of hydrocarbon (e.g. CH_4, C_2H_4, C_6H_6, C_2H_2, C_6H_{12}) at a high temperature (600-1200°C) on a surface of a metallic catalyst nanoparticle, e.g. Fe, Ni, Mo, Co [3,9-12]. Catalytic pyrolysis is controlled by selecting appropriately the size and type of the catalyst, hydrocarbon gas, temperature and process time. It is hence possible to fabricate vertically oriented single-walled and multi-walled carbon nanotubes on various substrates, e.g. glass, ceramics or a silicon wafer with deposited buffer layers and a thin layer of a metallic catalyst. The key issue for the practical utilisation of nanostructural carbon materials is to control carbon nanotubes' growth and morphology. There are several essential parameters influencing the kind and form of the final product, including, most of all: the type and flow rate of hydrocarbon gas, inert gas, hydrogen; 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 the working chamber (vertical or horizontal) [1,3-4,9-10,13-15].

The authors' intention was to fabricate vertically aligned carbon nanotubes growing on a silicon substrate. Process time is a key parameter influencing the height of a nanostructural material layer [4,13]. The purpose of the article is to present an approach for optimising the synthesis process time of VAMWCNTs with Catalytic-Chemical Vapour Deposition (CCVD) on a silicon substrate.

2. Materials and methodology

Multi-walled carbon nanotubes were synthesised with Catalytic-Chemical Vapour Deposition using an EasyTube® 2000 device on a silicon substrate containing a catalyst in the form of a thin film (2 nm of Fe) and two buffer layers of Al_2O_3 and SiO_2. Fig. 1 shows a diagram showing a graphical concept of selection of carbon nanotubes' synthesis parameters for ensuring a maximum height of layers.

A system for synthesising carbon nanotubes (Fig. 2a) consists of a quartz process pipe situated in a horizontal oven in which temperature sensors are located in 3 zones: at the start, at the centre and the end of the oven. Initial conditions must be ensured to carry out each of the experiments, by: (i) closing the oven, (ii) pumping off the gases to achieve an appropriate pressure value in the working chamber, (iii) checking the leak-tightness of the installation, (iv) heating the oven in the presence of Ar flowing with the speed of 5 SLPM[1] to the set temperature, (v) stabilising the temperature in each of heating zones with the tolerance of +/- 2°C. A silicon waffle is inserted into the so prepared heated oven for 15 minutes, in the presence of H_2 flowing at a rate of 300 SCCM[2] and Ar flowing at a rate of 1 SLPM. A source of carbon, in the form of C_2H_4 flowing at a rate of 300 SCCM, is introduced in another phase into the working chamber in which Ar and H_2 shield gases are still flowing. In a series of experiments, C_2H_4 was applied for, respectively, 15, 30 and 45 minutes. The following activities are made at the end after stopping to supply C_2H_4: the feeder was removed together with a specimen from the oven, the specimen was removed, the system was purged with the presence of Ar flowing for 5 minutes at a rate of 5 SLPM, the oven was gradually cooled down to 200°C, the system was purged again and the process was finished. An additional experiment was undertaken after performing the planned series of experiments and selecting the optimum time of synthesis enabling to

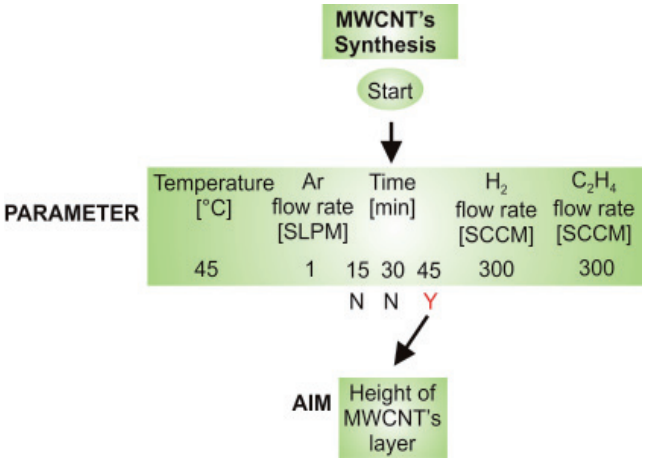

Fig. 1. Diagram showing a graphical concept of selection of carbon nanotubes' synthesis parameters for ensuring a maximum height of their layers

[1] Standard Litre per Minute, where 1 SLPM = 1,68875 Pa·m^3/s
[2] Standard Cubic Centimetres per Minute, where 1 SCCM = 0,0016 Pa·m^3/s

fabricate the highest layer of nanotubes, and the experiment differed from the previous ones in that a silicon waffle was placed on the feeder in a quartz boat as shown in Figure 2b. Table 1 presents the VAMWCNTs synthesis process parameters for all the experiments.

The nanostructures obtained were observed using electron microscopes: a scanning and transmission microscope. SEM images were made using a scanning electron microscope SEM Supra 35 by Carl Zeiss equipped with the X radiation spectrometers: an energy dispersion EDS and wavelength WDS spectrometer 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 with low beam voltage and with a very small distance of the preparation examined to the electron gun (working distance).

The TEM images were made using a transmission electron microscope STEM TITAN 80-300 by FEI fitted with an electron gun with FEG field emission, a condenser spherical aberration corrector, STEM scanning system, light and dark field detectors, HAADF (High Angle Annular Dark Field), and EFTEM energy image filter and an EDS spectrometer. The preparations for transmission electron microscopy investigations were prepared by dispergating the carbon nanotubes obtained in ethanol using an ultrasound washer, and then by depositing them using a pipette with droplets onto a copper mesh covered with a carbon film. The material deposited as a droplet was dried with free air at room temperature.

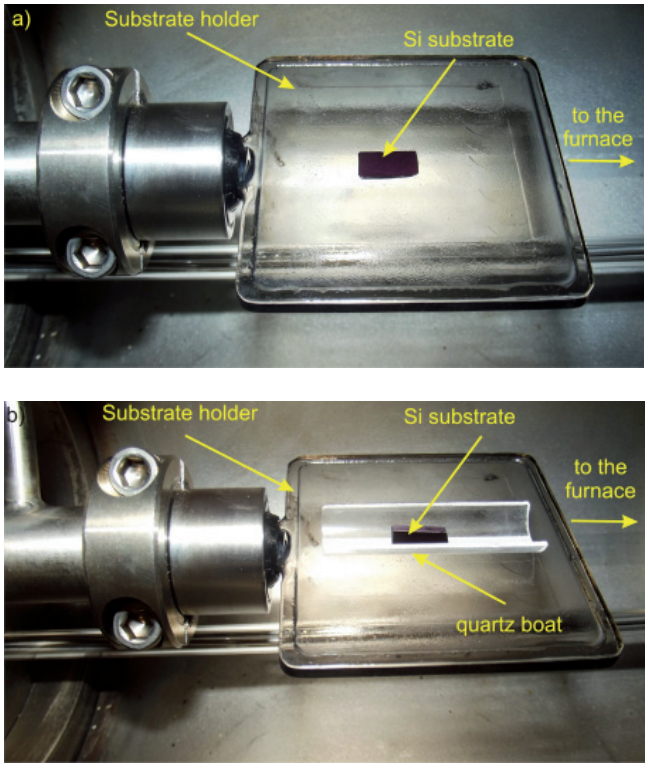

Fig. 2. Two options of placement of specimens in the oven: a) a specimen placed directly on a feeder, b) a specimen placed on a feeder additionally in a quartz boat

Table 1.
VAMWCNTs synthesis parameters for all the experiments carried out

Sample	Temperature, °C	Time, min	H_2, SCCM	C_2H_4, SCCM	Ar, SLPM	Catalyst
1	750	15	300	300	1	2 nm Fe
2	750	30	300	300	1	2 nm Fe
3	750	45	300	300	1	2 nm Fe
4	750	45	300	300	1	2 nm Fe (in a quartz boat)

3. Results and discussion

A layer of homogenous vertically aligned carbon nanotubes growing on a silicon substrate covered with a Fe catalyst was achieved as a result of the synthesis. The photos of multi-walled carbon nanotubes synthesised using an EasyTube® 2000 system for the following process parameters: temperature of 750 °C, synthesis time of 15-45 minutes, H_2 flow rate of 300 SCCM, C_2H_4 flow rate of 300 SCCM, Ar flow rate of 1 SLPM, resulting from own observations carried out with Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) are presented in, respectively, Figures 3-12 and 13-14.

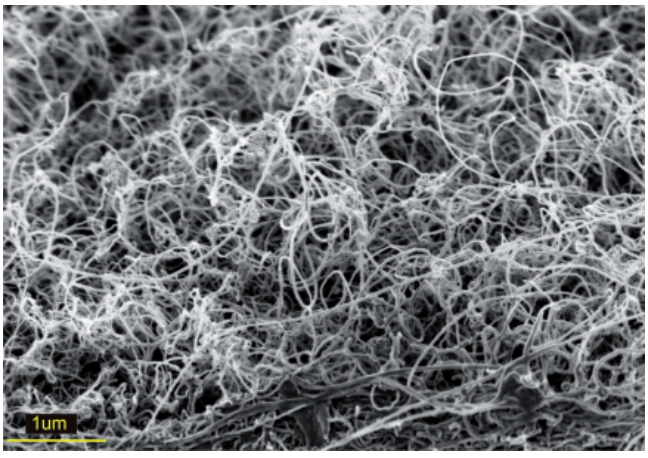

Fig. 3. SEM image of randomly arranged carbon nanotubes; mag. 50 000x

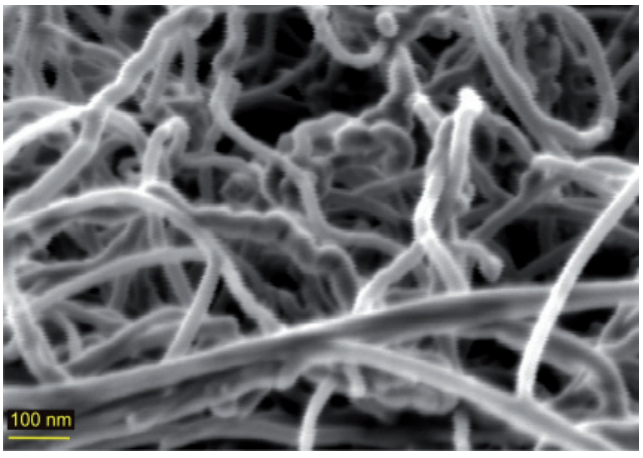

Fig. 6. SEM image of randomly arranged carbon nanotubes; mag. 300 000x

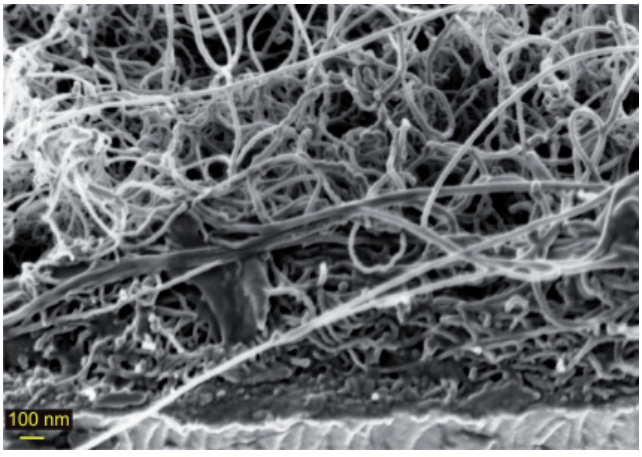

Fig. 4. SEM image of randomly arranged carbon nanotubes; mag. 100 000x

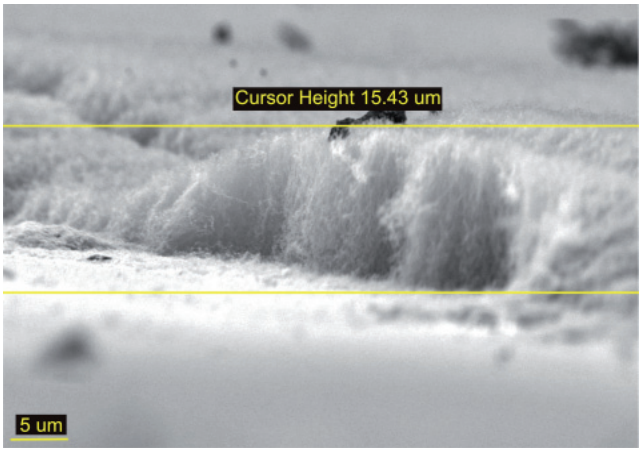

Fig. 7. SEM image of vertically aligned carbon nanotubes; synthesis time 15 min; mag. 4300x

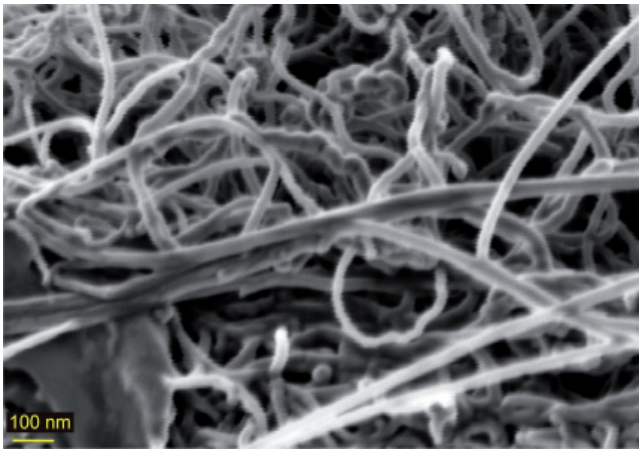

Fig. 5. SEM image of randomly arranged carbon nanotubes; mag. 200 000x

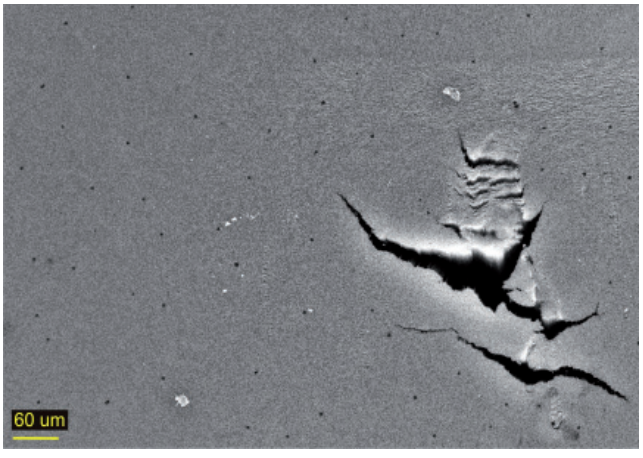

Fig. 8. SEM image of vertically aligned carbon nanotubes; synthesis time 45 min; top view; mag. 400x

Figures 3-6 present randomly oriented carbon nanotubes magnified, respectively, by 50 000x, 100 000x, 200 000x and 300 000x, which had been previously removed from the silicon substrate. When VAMWCNTs are removed from a silicon substrate, the nanotubes observed are entangled and randomly oriented.

Figures 7-12 show a full imaging range of a vertical layer of carbon nanotubes, starting with a layer of nanotubes synthesised within 15 minutes (Fig. 7) through a top view (Fig. 8-9) and side view (after rotating a specimen by 90°) (Fig. 10) of a layer manufactured within 45 minutes, ending with results of an experiment carried out using a quartz boat (Fig. 11-12). The observations made allow to conclude that the thickest layer of nanotubes was obtained in the case where the synthesis time was longest and was 45 minutes. A full, uniform coverage of the silicon substrate was obtained in this case with a layer of carbon nanotubes, and the layer of nanotubes has a maximum height of 185 μm. In the case where a specimen is additionally placed in a quartz boat, the layer height is doubled and reaches 370 μm.

The examinations carried out with a transmission electron microscope (TEM) allowed to achieve much higher magnification, therefore allowing to observe the clusters of carbon nanotubes produced using the EasyTube® 2000 device by FirstNano (Fig. 13). The HRTEM mode allowed to observe particular graphene layers forming the nanotubes structure (Fig. 14). The results of TEM examinations assert that the diameter of carbon nanotubes fabricated through CCVD using an Fe catalyst is approx. 10-18 nm.

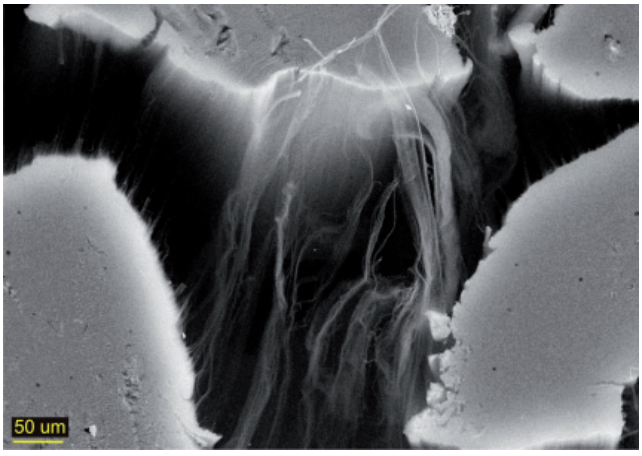

Fig. 9. SEM image of vertically aligned carbon nanotubes; synthesis time 45 min; top view; mag. 500x

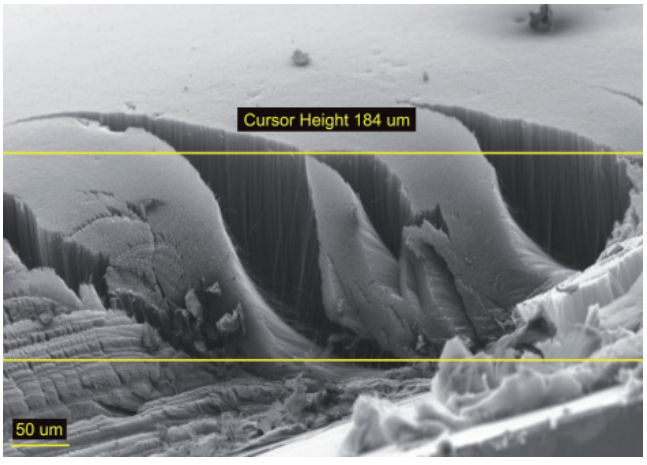

Fig. 10. SEM image of vertically aligned carbon nanotubes; side view (after rotating a specimen by 90°); mag. 285x

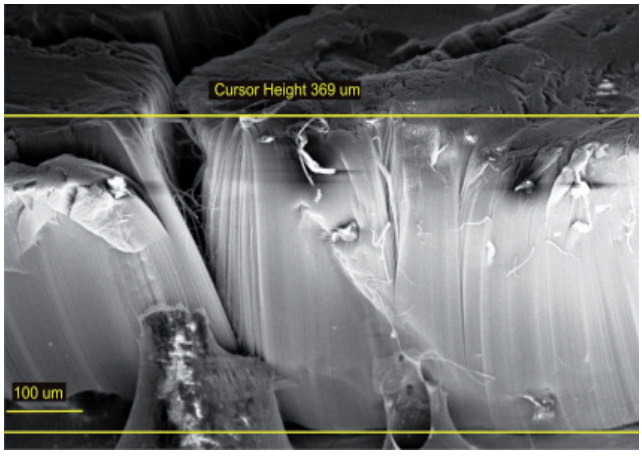

Fig. 11. SEM image of vertically aligned carbon nanotubes synthesised in a quartz boat; mag. 350x

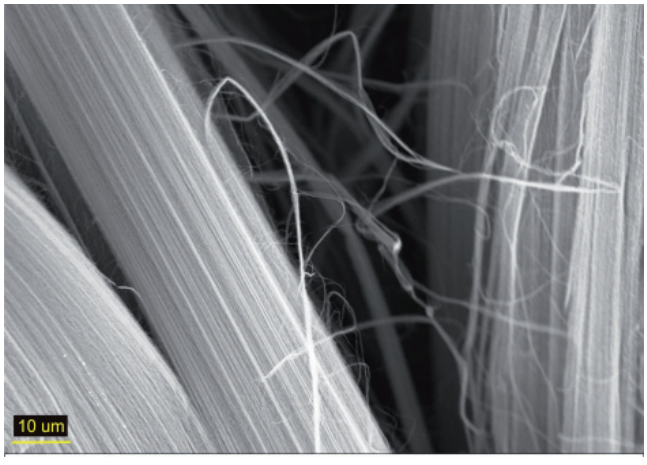

Fig. 12. SEM image of vertically aligned carbon nanotubes synthesised in a quartz boat; mag. 3000x

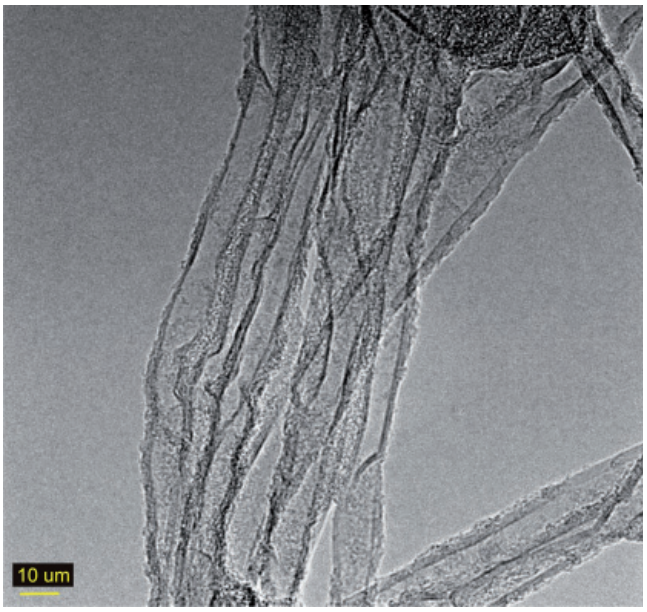

Fig. 13. TEM image of MWCNTs; mag. 145 000x

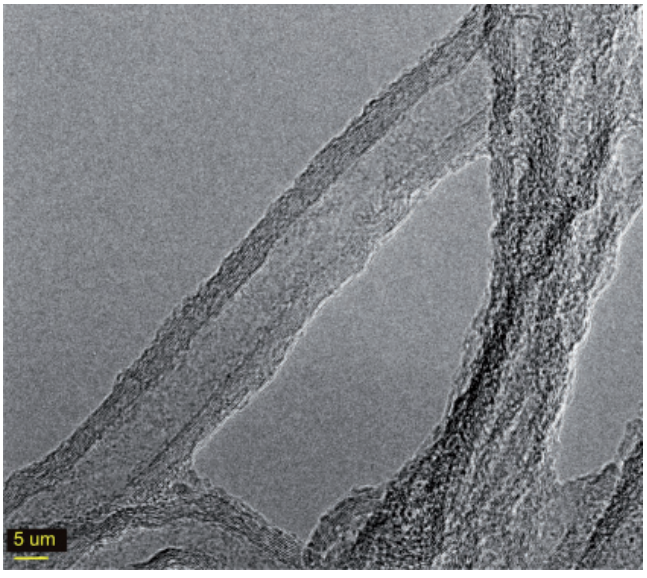

Fig. 14. HRTEM image of MWCNTs; mag. 185 000x

4. Conclusions

The VAMWCNTs synthesis experiments undertaken together with scanning and transmission electron microscopy examinations allowed to determine optimum parameters of producing high-quality multi-walled carbon nanotubes on a silicon substrate using the CCVD method with the EasyTube® 2000 system. The optimum synthesis time is 45 minutes with the other set parameters being constant. A full, uniform coverage of the silicon substrate was obtained with the such set time in this case with a vertically aligned layer of carbon nanotubes with the maximum height of 185 μm. Due to a shorter growth process time of VAMWCNTs of, respectively, 15 and 30 minutes, the layer of nanotubes is lower and non-uniform, and the growth of nanostructures takes place locally only in some random parts of the silicon substrate. A twice higher layer of nanotubes of maximum about 370 μm is achieved by applying a quartz boat in the process with the same synthesis time. The authors of the article are continuing the research to analyse the impact of individual process parameters on the form and quality of the final product. Ultimately, the materials fabricated will be used by the Authors of the article to manufacture nanocomposites consisting of carbon nanotubes and nanoparticles of noble metals [16-18] and will be used as an active layer of chemical and biochemical substance sensors, including environmentally obnoxious gases.

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References

[1] A.D. Dobrzańska-Danikiewicz, D. Łukowiec, D. Cichocki, W. Wolany, Carbon nanotubes manufacturing using the CVD equipment against the background of other methods, Archives of Materials Science and Engineering 64/2 (2013) 103-109.

[2] Q. Zhang, M.Q. Zhao, J.Q Huang, Y. Liu, Y. Wang, W.Z. Qian, F. Wei, Vertically aligned carbon nanotube arrays grown on a lamellar catalyst by fluidized

bed catalytic chemical vapor deposition, Carbon 4/7 (2009) 2600-2610.
[3] S. Rahmanian, A.R. Surayaa, R. Zahari, E.S. Zainudin, Synthesis of vertically aligned carbon nanotubes on carbon fiber, Applied Surface Science 271 (2013) 424-428.
[4] A.D. Dobrzańska-Danikiewicz, D. Cichocki, M. Pawlyta, D. Łukowiec, W. Wolany, Synthesis conditions of carbon nanotubes with the chemical vapor deposition method. Physca Status Solidi B, 251 (2014) 2420-2425. doi: 10.1002/pssb.201451178.
[5] A.P. Terzyk, B. Kruszka, M. Wiśniewski, Will a nanotube forest grow around us? Chemical News 65/1-2 (2011) 111-135.
[6] A.K. Chatterjee, Maheshwar Sharon, Rangan Banerjee, Michael Neumann-Spallart, CVD synthesis of carbon nanotubes using a finely dispersed cobalt catalyst and their use in double layer electrochemical capacitors, Electrochimica Acta 48 (2003) 3439-3446.
[7] T. Gökçen, C.E. Dateo, M. Meyyappan, Modeling of the HiPco process for carbon nanotube production. II. Reactor-scale analysis, Journal for Nanoscience and Nanotechnology 2/5 (2002) 535-544.
[8] N. de Greef , L. Zhang , A. Magrez , L. Forró, J.-P. Locquet, I. Verpoest, J.W. Seo, Direct growth of carbon nanotubes on carbon fibers: Effect of the CVD parameters on the degradation of mechanical properties of carbon fibers, Diamond & Related Materials 51 (2015) 39-48.
[9] M. Kumar, Y. Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production, Journal of Nanoscience and Nanotechnology 10 (2010) 3739-3758.
[10] J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, Methods for carbon nanotubes synthesis-review, Journal of Materials Chemistry 21 (2011) 15872-15884.
[11] A.-C. Dupuis, The catalyst in the CCVD of carbon nanotubes – a review, Progress in Materials Science 50 (2005) 929-961.
[12] L. Qu, F. Du, L. Dai, Preferential Syntheses of Semiconducting Vertically Aligned Single-Walled Carbon Nanotubes for Direct Use in FETs, Nano Letters 8/9 (2008) 2682-2687.
[13] B. Bahrami, A. Khodadadi, Y. Mortazavi, M. Esmaieli, Short time synthesis of high quality carbon nanotubes with high rates by CVD of methane on continuously emerged iron nanoparticles, Applied Surface Science 257 (2011) 9710-9716.
[14] O. Fedorovskaya, L.G. Bulusheva, A.G. Kurenya, I.P. Asanov, N.A. Rudina, ,K.O. Funtov, I.S. Lyubutin, A.V. Okotrub, Supercapacitor performance of vertically aligned multiwall carbon nanotubes produced by aerosol-assisted CCVD method, Electrochimica Acta 139 (2014) 165-172.
[15] W. Deng, X. Chen, Z. Liu, A. Hu, Q. Tang, Z. Li, Y. Xiong, Three-dimensional structure-based tin disulfide/vertically aligned carbon nanotube arrays composites as high-performance anode materials for lithium ion batteries, Journal of Power Sources 277 (2015) 131-138.
[16] A.D. Dobrzańska-Danikiewicz, D. Łukowiec, D. Cichocki, W. Wolany, Carbon nanotubes decorating methods, Archives of Materials Science and Engineering 61/2 (2013) 53-61.
[17] A.D. Dobrzańska-Danikiewicz, D. Łukowiec, Synthesis and characterization of Pt/MWCNTs nanocomposites, Physica Status Solidi B 250/12 (2013) 2569-2574.
[18] A.D. Dobrzańska-Danikiewicz, W. Wolany, G. Benke, Z. Rdzawski, The new MWCNTs–rhenium nanocomposite, Physica Status Solidi B 251/12 (2014) 2485-2490.