Research Article Open Access

Leszek A. Dobrzański, Marek Szindler*, Mirosława Pawlyta, Magdalena M. Szindler, Paulina Boryło, and Błażej Tomiczek

Synthesis of Pt nanowires with the participation of physical vapour deposition

DOI 10.1515/phys-2016-0017

Received October 12, 2015; accepted March 30, 2015

Abstract: The following paper presents the possibility of formation of Pt nanowires, achieved by a three-step method consisting of conformal deposition of a carbon nanotube and conformal coverage with platinum by physical vapour deposition, followed by removal of the carbonaceous template. The characterization of this new nanostructure was carried out through scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

Keywords: nanotechnology; nanomaterials; nanowires; physical vapour deposition

PACS: 61.46.+w, 61.46.Np, 61.46.-w

1 Introduction

Nanotechnology is currently the fastest growing interdisciplinary field of science. It combines scientific disciplines such as physics, chemistry, biology, biotechnology, medicine, pharmacy, informatics and materials engineering. One of the main factors causing so much interest in the world of nanotechnology is that the field focuses on materials at the molecular level, which often have properties radically different from the same starting materials at normal size [1–3]. Nanomaterials are characterized as having at least one of their dimensions be less than 100 nm, and at the same time having completely different properties from their micro- and macroscopic equivalents. Carbon nanotubes are one of the most intensively studied types of nanomaterials. They take the form of open or closed cylinders with a diameter from one to several tens of nanometers, and a length of up to several centimeters. Nanotubes are characterized by unusual physicochemical characteristics; they are as hard as diamonds, are flexible, elastic, resistant to tearing and crushing, and are very good conductors of heat, thus offering the prospect of their wide use in many fields of technology [4–6]. On the other hand, in recent years, there has also been a wide interest in the organic counterparts of nanotubes, cylindrically shaped and called nanowires. As expected, small diameter nanowires show distinctly different optical, electric or magnetic properties from the bulk material. Already there have been developed first concepts for the construction of LEDs [7–9], transistors [10, 11] and logic components [12, 13] using these nanomaterials. Nanowires were for the first time observed using a scanning tunneling microscope in 1987 by Gimzewski and Moller [14]. In 1993, electrical conductivity quantization in nanowires made from gold using STM at room temperature and atmospheric pressure [15] was investigated for the first time. Further studies showed that nanowires can be formed in much simpler systems: between a pair of vibrating wires (1995) [16] and between relay contacts (1997) [17]. There have also been attempts to produce metallic nanowires by electrochemical methods, including the use of porous molds and nanolithographic methods [18–22]. Some interesting information about the formation of Pt nanowires by atomic layer deposition on highly ordered pyrolytic graphite can be found in the literature [23]. There has also been research on synthesis of a 3D network of Pt nanowires by atomic layer deposition on a carbonaceous template [24]. Reviews of the literature indicate that many methods are known for producing metal nanowires, but none of the publications indicate a method for preparing nanowires by usage of carbon nanotubes as the preform with the method of physical vapour deposition as the metal source. Such a method is described in this article.

Leszek A. Dobrzański, Mirosława Pawlyta, Magdalena M. Szindler, Paulina Boryło, Błażej Tomiczek: Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str., 44-100 Gliwice, Poland
***Corresponding Author: Marek Szindler:** Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str., 44-100 Gliwice, Poland, E-mail: marek.szindler@polsl.pl

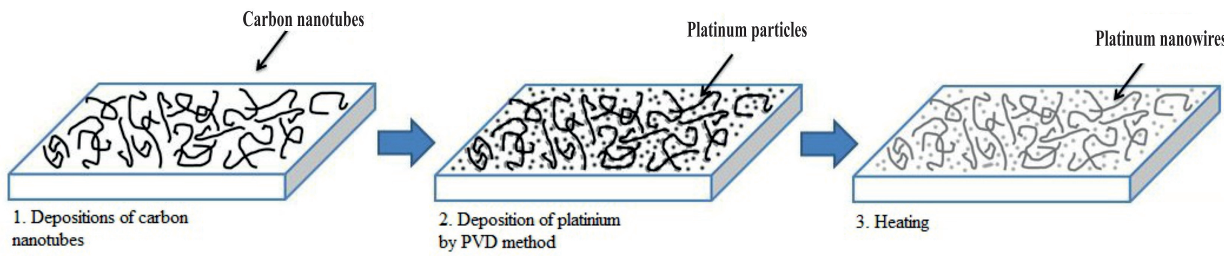


Figure 1: Scheme of three-step process for preparing metal nanowires.

2 Materials and methodology

Multi-wall carbon nanotubes were dispersed in anhydrous ethyl alcohol using a sonicator. Then, using a pipette, they were deposited on a BK7 glass substrate and on a polished silicon substrate. On such prepared substrate, a layer of platinum was deposited using a PVD coater (sputtering time - 2 s, current - 50 mA, voltage - 50 V). During the sputtering deposition, using the material safety data sheets delivered by the manufacturer and at the determined voltage and current, it is possible to control the amount of platinum deposited thereon. This article presents mainly the results for the parameters for which the best results were obtained. After sputtering, the prepared materials were heated at 700°C for 90 minutes. A diagram of the proposed three-step process for the preparation of metal nanowires is shown in Figurere 1.

Visualization of the morphology of the surface of the platinum nanowires was carried out by the use of a Zeiss Supra 35 scanning electron microscope. The accelerating voltage was 3-5 kV. In order to obtain images of the surface topography, a detection of secondary electrons by the detector In Lens was used. The detailed structural studies were conducted using a Titan 80-300 scanning-transmission electron microscope S/TEM from the FEI Company. For this purpose, prepared platinum nanowires were deposited on the special copper mesh substrate used in electron microscopy. The whole study was complemented by x-ray crystallography.

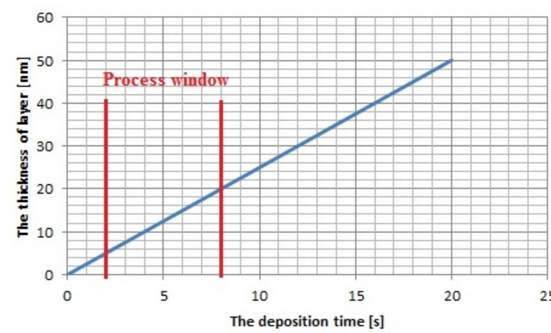


Figure 2: The effect of deposition time on thickness of the deposited layer by sputtering method.

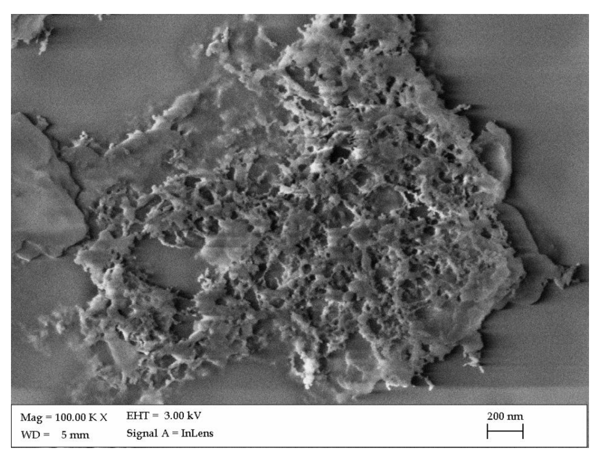
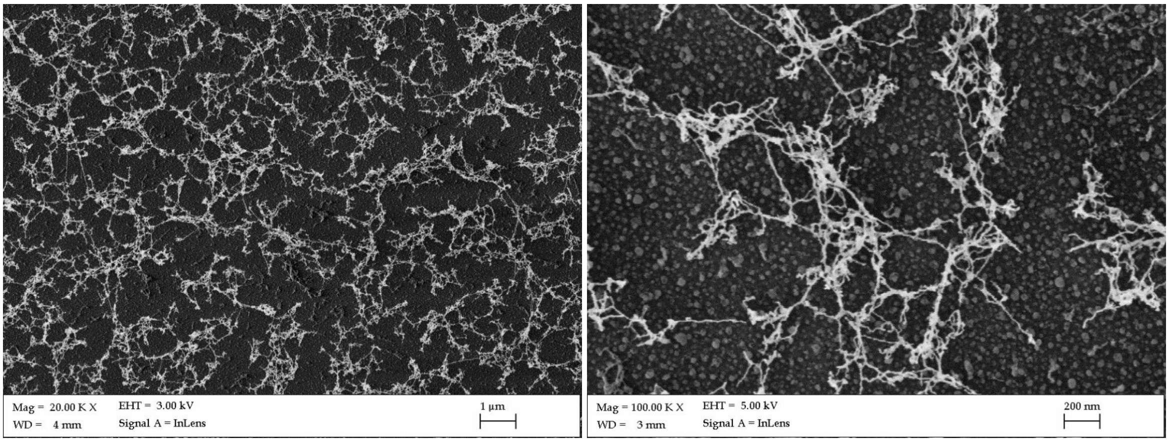


Figure 3: An example of large platinum agglomerates.

3 Results and discussion

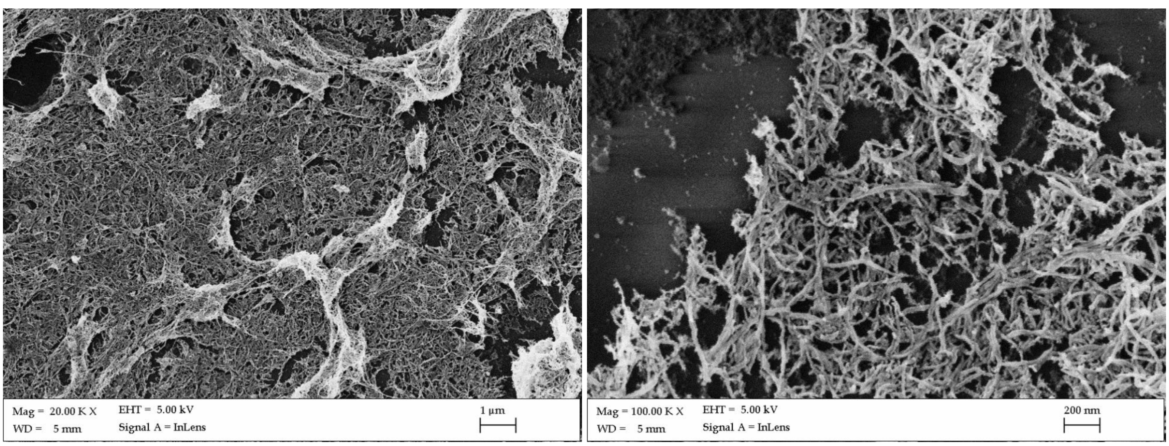
One of the important factors affecting the synthesis of Pt nanowires using the presented method is the thickness of the deposited platinum layer on the carbon nanotubes. In the sputtering method, it is possible to control the thickness of the deposited layer at determined values of voltage and current by changing only the time of sputtering. This allows the determination of the so-called process window (Figure 2).

The platinum kept more or less the shape of the nanotubes if the deposition thickness was contained within the range of 5-20 nm. At a smaller thickness, only small clusters of platinum on the substrate were observed, and at higher thicknesses, large platinum agglomerates were observed (Figure 3). This article focuses on the results for the parameters for which the best synthesis of the plat-



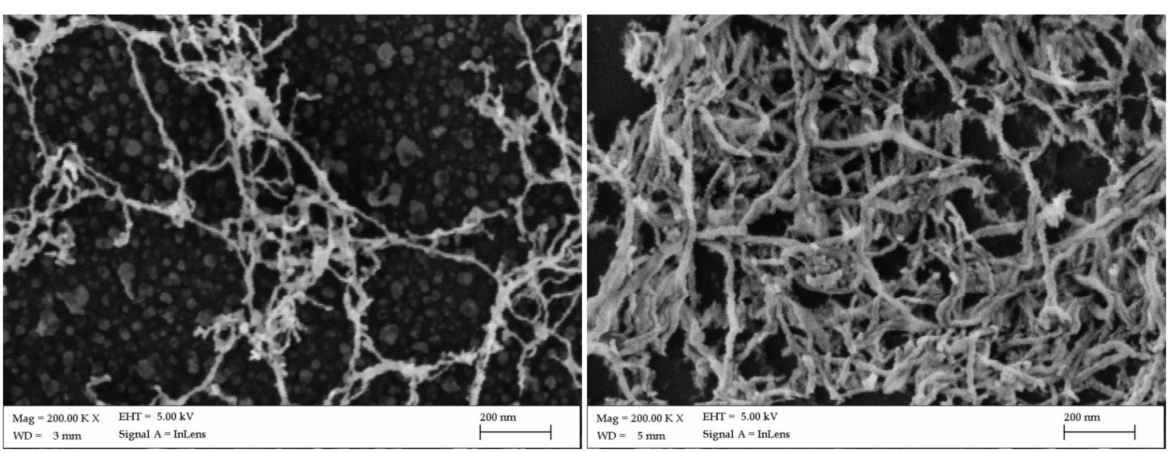
a) b)

Figure 4: SEM image of platinum nanowires manufactured on a polished silicon substrate, at a magnification of: a) 20 000; b) 100 000.



a) b)

Figure 5: SEM image of platinum nanowires manufactured on a glass substrate, at a magnification of: a) 20 000; b) 100 000.



a) b)

Figure 6: SEM image of platinum nanowires manufactured on: a) a polished silicon substrate, at a magnification of 200 000; b) a glass substrate, at a magnification of 200 000.

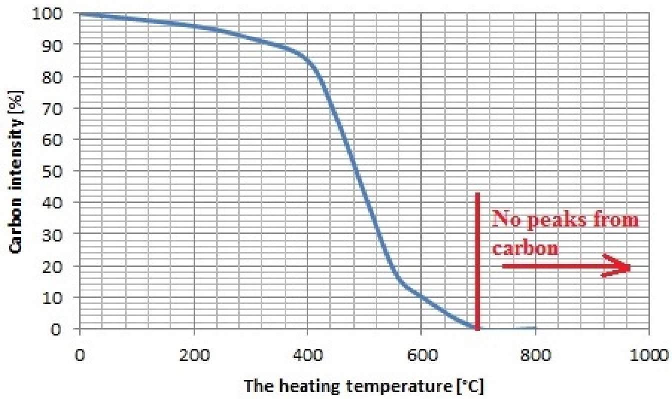
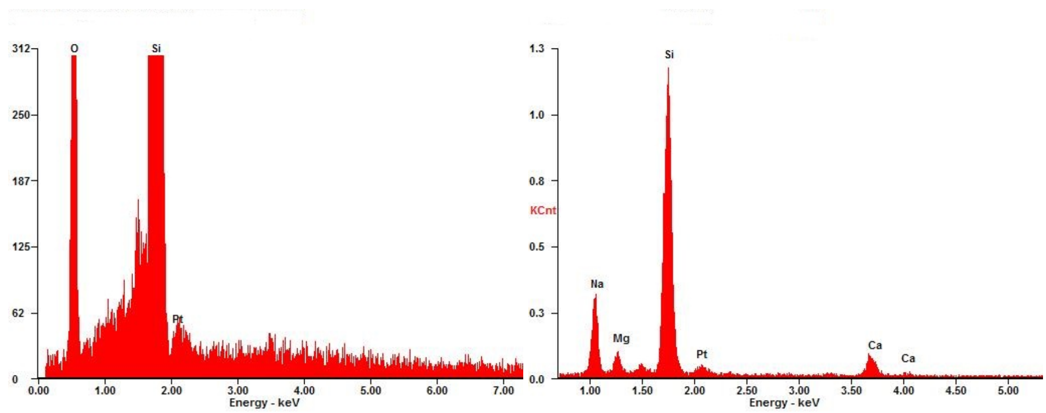
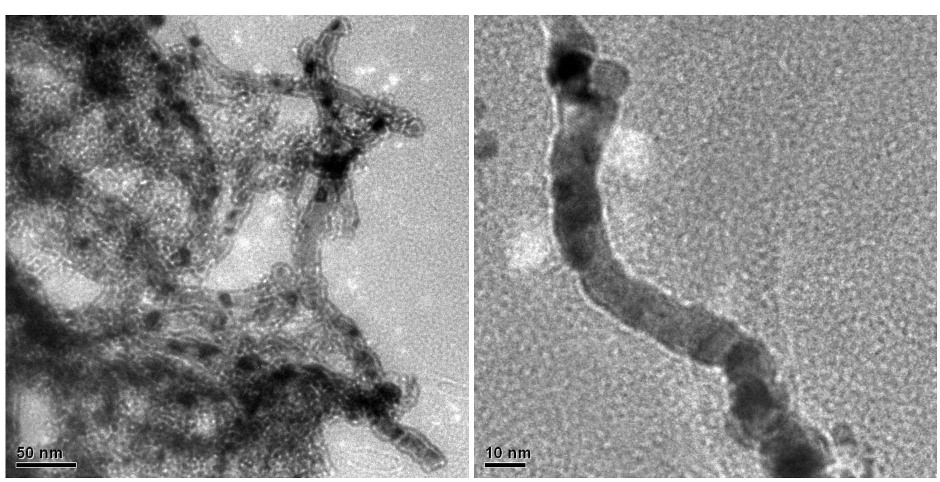


Figure 7: Carbon content registered by using EDS on carbon nanotubes, covered by platinum and heated at different temperatures.



a) b)

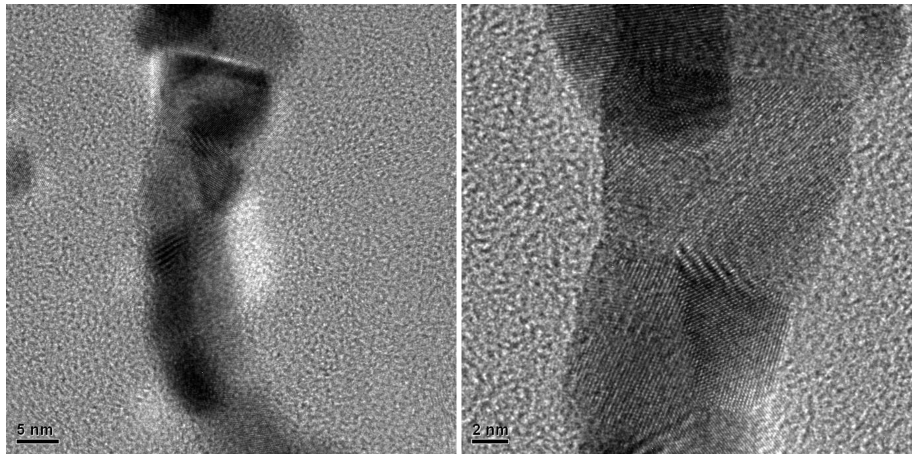
Figure 8: EDS spectrum of platinum nanowires manufactured on: a) a polished silicon substrate; b) a glass substrate.



a) b)

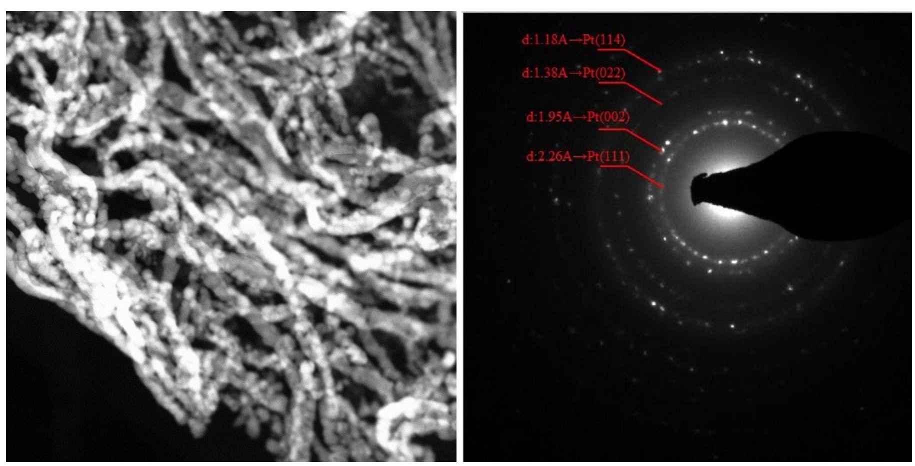
Figure 9: The TEM image of the: a) platinum nanowires; b) single platinum nanowire, formed on a glass substrate.

inum nanowires were obtained. Analysing the surface of the sample at magnifications from 20 000 to 100 000, a mesh of tangled nanowires (Figure 4 and Figure 5) can be observed. Only at a magnification of about 200 000 was it possible to analyse the diameter and length of the nanowires obtained on the platinum (Figure 6). Using Im-



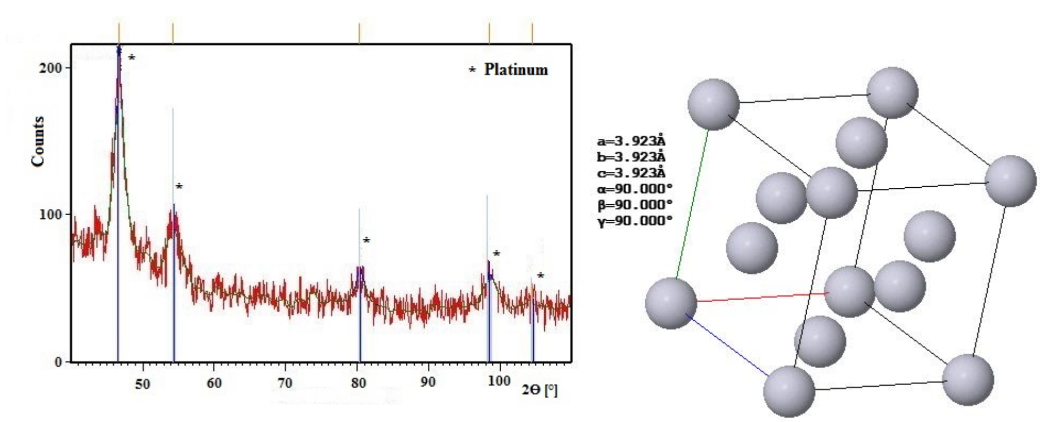
a) b)

Figure 10: The HRTEM image of the single platinum nanowire formed on a glass substrate (a) and a fragment of this single platinum nanowire (b).



a) b)

Figure 11: The HAADF image of the platinum nanowires (a) and the SAED pattern (b).



a) b)

Figure 12: The diffraction pattern of platinum nanowires using the constant angle of incidence method (a) and the face centred cubic crystal structure of platinum (b)

age J software, it was determined that the diameter of the metal nanowires produced is between 10 and 30 nm. To confirm that the observed nanowires are platinum and to check that the heat treatment was performed properly to dispose of the carbon nanotubes, qualitative chemical composition study using Energy Dispersive Spectrometry (EDS) was performed. An important factor affecting the synthesis of the Pt nanowires is the temperature during heating. Reduction of the carbon content with increasing heating temperature was registered using EDS and shown in Figure 7, with 100% taken as the intensity of carbon for nanotubes covered with platinum registered before heat treatment. Heat treatment at a temperature of up to 400°C caused only a slight decrease in intensity of carbon. This may suggest that only amorphous carbon and functional groups were degraded, but not the nanotubes themselves. A significant decrease in carbon content was registered above 400°C, indicating decomposition of the actual carbon nanotubes.

For samples heated at 700°C, spectra with the reflections typical for platinum (2.127keV) and the others from the substrate were registered (Figure 8). Not registering peaks from the carbon confirmed that the heating process was carried out successfully. In the spectrum of nanowires formed on a polished silicon substrate (Figure 8a), there is a recorded peak coming from oxygen. This may suggest that some silicon oxide is present on the surface of the substrate, which was confirmed by big, visible irregularities (Figure 6a) on the polished silicon.

Detailed results of surface morphology and structural studies were performed using the S/TEM. The recorded images in TEM documents the occurrence of nanowires (Figure 9). Additionally, images in HRTEM mode document the polycrystalline structure of the nanowires (Figure 10). For research purposes the STEM imaging mode was also used. The Titan 80-300 microscope is equipped with three coaxial detectors dedicated to STEM mode: Bright Field–BF, Annular Dark-Field–ADF and High-Angle Annular Dark-Field–HAADF (Figure 11a). Selected area electron diffraction (SAED) patterns were registered. The SAED pattern shows a clear appearance of diffraction rings from the Pt, confirming the removal of the carbon nanotubes subsequent to heating (Figure 11b).

The structural studies were complemented by X-ray examinations (Figure 12a). The platinum nanowires were characterized by a constant angle of incidence. To solve the diffractogram, JCPDS files were used, according to which were assigned the appropriate Miller indices. For the first peak, for which 2θ is 46.69°, the index is (111), for the second peak at 54.25°, the index is (002), for 80.35° the index is (022), for 98.44° the index is (113) and for 104.48° the index is (222). The crystal structure for the platinum was identified as face centred cubic (Figure 12b).

4 Conclusions

Review of the literature indicates that there have not been any reports on a method for preparing nanowires by using carbon nanotubes as the preform and the method of physical vapour deposition as the metal source. Our findings confirm that this proposed method can be used to produce nanowires from noble metals such as platinum. The results obtained by the authors of this paper provide a promising perspective for research and indicate that this is an attractive direction in the search for new solutions to manufacturing nanomaterials.

Acknowledgement: This work has been implemented within the framework of the project entitled “Determining the importance of the effect of the one-dimensional nanostructural materials on the structure and properties of newly developed functional nanocomposite and nanoporous materials”, funded by the Polish National Science Centre in the framework of the “OPUS” competitions, headed by Prof. Leszek A. Dobrzański. The project was financed by the National Science Centre granted on the basis of the decision number DEC-2012/07/B/ST8/04070.

References

[1] Kelsall R.W., Hamley I.W., Nanoscale Science and Technology, Wiley & Sons, England, 2005.
[2] Karkare M., Nanotechnology: Fundamentals and Applications, I.K. International Publishing House, New Delhi 2008.
[3] Ramsden J., Nanotechnology: An Introduction, Elsevier, Amsterdam, 2011.
[4] Monthioux M., Kuznetsov V.L., Who should be given the credit for the discovery of carbon nanotubes? Carbon, 2006, 44, 1621-1623.
[5] Tersoff J., Ruoff R.S., Structural properties of a carbon-nanotube crystal, Phys. Rev. Lett., 1994, 73, 676-679.
[6] Guo T., Nikolaev P., Thess A., Colbert D.T., Smalley R.E., Catalytic growth of single-walled nanotubes by laser vaporisation, Chem. Phys. Lett., 1995, 243, 49-54.
[7] Duan X. *et al.*, Inidium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices, Nature, 2001, 409, 66-69.
[8] Cui Y., Leiber C.M., Functional nanoscale electronic devices assembled using silicon nanowire bulding blocks, Science, 2001, 291, 851-853.

[9] Kim J.R. *et al.*, Rectifying diode made on individual GaN nanowire, Physica E, 2003, 18, 225-226.

[10] Tans S.J. *et al.*, Room-temperature transistor based on a single carbon nanotube, Nature, 1998, 393, 49-52.

[11] Martel R. *et al.*, Single and multi-wall carbon nanotube field-effect transistors, Appl. Phys. Lett., 1998, 73, 2447-2449.

[12] Bachtold A. *et al.*, Logic circuits witch carbon nanotube transistors, Science, 2001, 294, 1317-1320.

[13] Huang Y. *et al.*, Logic gates and computation from assembled nanowire bulding blocks, Science, 2001, 294, 1313-1317.

[14] Gimzewski J.K., Möller R., Transition from the tunneling regime to point contact studied using scanning tunneling microscopy. Phys. Rev. B, 1987, 36, 1284-1287.

[15] Pascual J.I. *et al.*, Ouantum Contact in Gold Nanostructures by Scanning Tunneling Microscopy, Phys. Rev. Lett., 1993, 71, 1852-1855.

[16] Agrat N., Rodrigo J.G., Vieira S., Conductance steps and guantization in atomic-size contacts, Phys. Rev. B, 1993, 47, 12345-12348.

[17] Costa-Kramer J.L. *et al.*, Nanowire formation in macroscopic metallic contacts: guantum mechanical conductance tapping a table top, Surface Science, 1995, 342, L1144-L1149.

[18] Ohgai T. *et al.*, Electrochemical fabrication of metallic nanowires and metal oxide nanopores, Materials and Manufacturing Processes, 2007, 22, 440-443.

[19] Adeela N. *et al.*, Fabrication and temperature dependent magnetic properties of nickel nanowires embedded in alumina templates, Ceramics International, 2015, 41, 12081-12086.

[20] Untied C. *et al.*, Fabrication and characterization of metallic nanowires, Phys. Rev. B, 1997, 56, 2154-2160.

[21] Karen P., Organization of matter into one-dimensional units on designed media, Open Phys., 2011, 9, 360-368.

[22] Esmaeil D., Rahim G., Hojjat S., 3D quantum mechanical simulation of square nanowire MOSFETs by using NEGF method Open Phys., 2011, 9, 472-481.

[23] Han-Bo-Ram L., Sung Hyeon B., Thomas F.J., Stacey F.B., Growth of Pt Nanowires by Atomic Layer Deposition on Highly Ordered Pyrolytic Graphite, Nano Letters, 2013, 13, 457-463.

[24] Deng S. *et al.*, Synthesis of a 3D network of Pt nanowires by atomic layer deposition on a carbonaceous template, Nanoscale, 2014, 6, 6939-6944.