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Plasma synthesis of carbon nanotubes for electrical and electronic engineering

Streszczenie. *W artykule przedstawiono mikrofalowy system plazmowy do syntezy nanorurek węglowych. Jako docelowe zastosowanie tego systemu przewiduje się wytwarzanie nanorurek węglowych w postaci wymaganej do projektowania nowej generacji urządzeń elektrycznych i elektronicznych (**Plazmowa synteza nanorurek węglowych dla inżynierii elektrycznej i elektronicznej**)*

Abstract*. In this paper the microwave plasma system for synthesis of carbon nanotubes is presented. The target of the system is the ability to produce carbon nanotubes in the form required to design a novel generation of electric and electronic devices.*

Słowa kluczowe: plazma mikrofalowa, nanorurki węglowe
Keywords: microwave plasma, carbon nanotubes

Introduction

The world demand for nanomaterials to be used in the new advanced products is annually growing with the rate over 60%. Energy sector, Electronics and Health Care seem to be the largest markets.

Micro mechatronics is one of the areas that have made remarkable progress recently. There are micro sensors and actuators for automotive technology, avionics technology, bio-medical technology, consumer electronics, and many others. There is a number of electric and electronic devices waiting for new nanomaterials.

Generally there are two approaches for carbon nanotubes (CNT's) synthesis the first one using solid carbon (arc and laser ablation methods) and the second one using hydrocarbon fuel with or without catalyst (chemical vapour deposition method – CVD and plasma enhanced chemical vapour deposition method – PECVD).

The paper describes a new CNT's synthesis method that employs plasma not being hybridized with any furnace. It allows producing CNT's in the powder form or making deposits on substrates such as silica, metals and on refractory insulators. This can be applied to some electronic devices such as electron emitters, transistors, heat sinks and to many electrical devices specifically used in energy storage and mechatronics. Conditions required for CNT's synthesis in microwave plasma are specified. Also the process parameters and plasma jet temperature measurements are here presented.

CNT's Synthesis

The carbon arc discharge method is the easiest way to produce carbon nanotubes as it is rather simple to undertake. This method creates nanotubes through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product [1].

One of the main challenges to achieve optimal performance of the product is to develop a continuous synthesis process as possible and in the form of uniform layer of carbon nanotubes deposited on the substrate. Currently, a method commonly used for this purpose is the method of CVD. It consists of a furnace for heating of carbon containing substances in the pyrolysis process. In this furnace the catalytic synthesis of nanometer-scale tubes of graphene structure takes place. Carbon atoms and molecules can be supplied with acetylene, benzene, ethylene, methane, propylene, carbon monoxide and other carbon-containing gases, as well as from the solid material (e.g. ferrocene), which is lead to the evaporation or materials in liquid (e.g. iron pentacarbonyl) that can be introduced into the furnace in the form of an aerosol. Catalysts are mainly iron, cobalt and nickel. Synthesis takes place in a noble gas flow at temperatures ranging from 700 to 1600K.

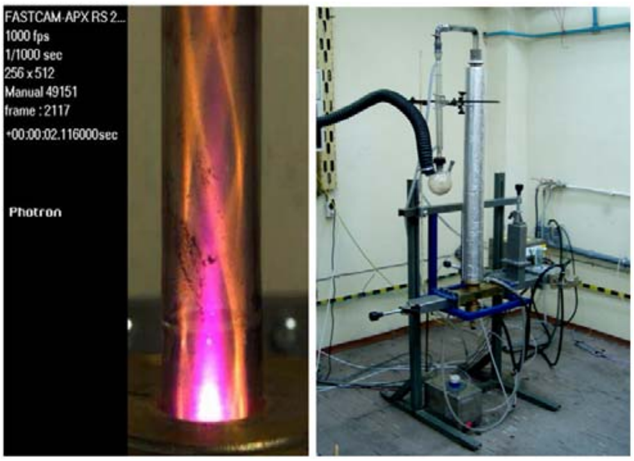

Fig. 1. The microwave plasma – left and the setup for synthesis of carbon nanotubes- right

Leading investigators [2] suggest recently that microwave plasma may be used as an activator of the synthesis process of carbon nanotubes. It can be applied at the entrance to the furnace CVD. Then the tube furnace can be used to ensure the conditions necessary for the synthesis process. However the microwave plasma takes also part in preparation (activation) of catalytic gas and mixing it with carbon carrying gas.

In order to optimizing the synthesis process the first studies we conducted in a hybrid system: microwave plasma plus a CVD tube furnace. Then the furnace was removed and the quartz tube was thermally insulated (Fig. 1 – right photo).

Our studies have shown that the microwave plasma may itself lead to the synthesis of carbon nanotubes without the use of CVD furnace. The vertical geometry of the quartz reactor tube causes symmetrical heating of the inner volume by gas flowing through the microwave plasma. It has also positive impact on the homogeneity of the product, preventing the local overheating of the quartz tube.

In order to compare the heating ability of the two systems the spectral measurements of plasma temperature and the thermocouple measuring the temperature distribution inside a quartz reactor along its axis were employed.

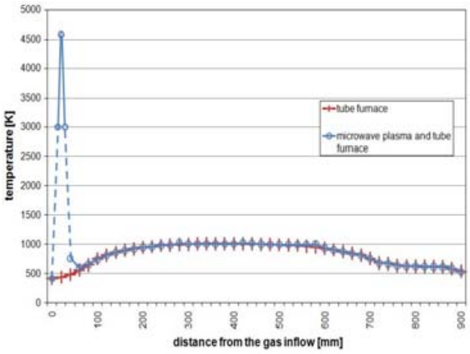

Fig. 2. Temperature distribution along the quartz tube axis for the tube furnace working alone and for the furnace with microwave plasma for the conditions as follows: the 1-st furnace zone (0-300mm) and the 2-nd one (300-600mm) were set on 1000K, the 3-rd furnace zone (600-900mm) was not heated, gas flows Ar =10 l/min, N_2 =10 l/min, microwave power set on 1680W.

The temperature distribution along the axis of the hybrid reactor is shown in Fig. 2. It should be noted that the edge of the furnace tube in zone 1 was cooled with water. For this reason, the gas temperature at the beginning of the axis (0) was relatively low (about 450K). The measurements show that the presence of plasma did not give a visible impact in the distribution of gas temperature in zone 2 and 3 of the furnace tube. Microwave plasma is used, in this case, for the activation of iron from iron pentacarbonyl. In the second approach, which is the goal of our studies the tube furnace has been removed and replaced with thermal insulation (Fig. 1a). A series of spectral and thermocouple temperature measurements along quartz reactor axis for different process parameters were done.

The measurement results presented in Fig. 2 prove that the microwave power is sufficient for the synthesis reaction temperature.

Materials for Electrical & Electronic Devices

General view

It is impossible to review here all the branches of electrical and electronic engineering in which carbon nanotubes might be successfully applied. We mention only some examples and focus on the most promising applications. For example in the field of mechatronics CNTs can be used as actuators for synthetic muscle. It can be possible with them to transform electric energy into mechanical effects. Actuators based on sheets of single-walled carbon nanotubes can generate higher stresses than natural muscle and higher strains than high-modulus ferroelectrics. Like natural muscles, the macroscopic actuators are assembled of millions of individual nano scale actuators. Compared to some other actuators, which require about 30V to function, the nanotube material being developed requires approximately 1 V for actuation and about 4 V at most [3].

In the area of sensors it has been demonstrated [3] an infra red (IR) light detector with higher sensitivity than existing technology. The device, known as an IR bolometer, is made by suspending a 0.5mm wide layer of single-walled CNTs over a 3.5mm gap between two electrical contacts. This layer is heated by incident IR radiation, causing its resistance to change.

It is also possible to use CNTs as gas detector because of the existing interaction between nanotube and gas molecules. The gas can be ionized at voltages that are up to 65% lower than in traditional sensors [3].

Nanotweezers can be made by using nanotubes. They are attached to independent electrodes. The voltage applied to the electrodes might open and close the free ends of the nanotubes [4].

Nowadays there is a trend in the field of electronics, from micro to nano devices, since it is clearly foreseen that the economic success lies in miniaturization. Therefore, micro electro-mechanical systems (MEMS) have started receiving a great deal of attention. MEMS are the integration of mechanical elements and electronics on silicon substrates by utilizing film growth and material etching techniques. MEMS devices are extremely small in size, for example, electrically driven motors smaller than the diameter of a human hair can be realized.

Carbon Nanotube based Field Effect Transistors (CNTFET), nanotube based logic inverters and organic-chain diodes, switches, and memory cells have been already demonstrated [3] what can lead to early stage logic devices for future computer architectures. The CNTFET structure is similar to the conventional isolated gate transistors. The CNTFET uses a nanotube that is laid across two gold contacts acting as the source and drain, the nanotube essentially becomes the current carrying channel. To produce a specific chip one must connect a huge amount of carbon nanotubes to appropriate contact. To achieve it is necessary to connect nanotubes placed in predefined locations or put the nanotubes in some pre-existing array of interconnections.

A new type of switching device is a single electron transistor (SET) that uses controlled electron tunneling to amplify current. The first successful approach was demonstrated by C. Dekker from Delft University of the Netherlands [3]. The SET has been made by introducing sharp bends in the nanotube using an atomic force microscope.

A nano scale transistor that can be switched between "on" and "off" with a single electron and working efficiently at room temperature will probably become an important component in molecular electronics. The bending causes the tube to buckle, with the two buckles separated by 20 nm. Due to electrostatic forces the buckles serve as barriers on either side of a "conducting island" into which electrons can tunnel one at a time, when an appropriate voltage is applied to the "gate" underneath the island. The whole device was only 1nm wide and 20 nanometers long, altogether less than 1/500th the distance across a human hair.

For large-scale applications, SETs will have to be fabricated more efficiently. Dekker and co-workers suggest that it might be possible to induce buckles in many nanotubes at once by using a patterned substrate or by chemically creating defects in the side wall of the nanotube. So this would solve the problem with mass production, what is the main challenge up to date.

Energy conversion and storage

Application of nanotechnology to the fields of Solar Energy and Energy Saving is a very much required commercial action of the current times. Day by day received and reviewed published research results allow to understand, to recognize and to discuss the most promising nanotechnology application to Solar Cells, Hydrogen Fuel Cells, Rechargeable Batteries and Supercapacitors.

In the Table 1 there are specified the main energy conversion systems and products in which CNTs and related nanomaterials can be used.

Silicon crystalline photovoltaic cells are expensive and they are able to convert maximum 25% of energy absorbed. Nanotechnology offers alternative materials with conversion efficiency 15% but with low cost. These are dye sensitized thin film materials called Graztel cells. They can absorb more the light of particular colour and with wide range of colours that increases their efficiency. These cells are very promising because they are made of low cost material - TiO_2. With polymer additives will be possible to fabricate large areas of flexible low cost light absorbing surfaces able to capture and to convert significant amounts of solar energy.

Table 1. Nanomaterials for energy conversion

Energy Conversion Applications			
Solar photo voltaics	Electrochemical	H_2 conversion	Thermoelectricity
Energy Conversion Products			
Thin film cells	Batteries	Fuel cells	Thermoelectrical devices
Nanomaterials for Energy Conversion			
TiO_2	CNTs	CNTs	Si-Ge nanowires

Possibilities of electrochemical energy conversion using carbon nanotubes in various systems, such as lithium batteries, hydrogen storage, are presently investigated.

Carbon nanotubes are interesting discharging hosts for Li-ion batteries because of their structure and chemical bonding. Nanotubes might have a higher saturation composition than graphite as guest species can intercalate in the interstitial sites and between the nanotubes. Therefore, carbon nanotubes are expected to be suitable high energy density anode materials for Lithium-ion batteries. [3]

The CNTs can be considered as hydrogen containers. It is because of CNTs high surface area, abundant pore volume and due to their cylindrical and hollow geometry, and nanometer-scale. It has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect. Gas phase intercalation of hydrogen in CNTs concerns the adsorption of H_2, called physisorption instead of chemisorption (involving H+ and chemical bonds). This adsorption of H_2 on the surface of CNTs is a consequence of the field force at the surface of the solid, which attracts the molecules of the gas or vapour. The storage is due to the physical forces [3].

Table 2. Nanomaterials for energy storage

Energy Storage Applications		
Rechargeable batteries	Hydrogen storage	Supercapacitors
Energy Storage Products		
Rechargeable batteries	Fuel cell storage material and catalyst	Supercapacitors
Nanomaterials for Energy Storage		
CNTs	CNTs & Nano magnesium and titanium	CNTs

Thermoelectricity can be required in power supply or cooling devices depending on the use of Seebeck or Peltier effect. Nanowires sufficiently decrease the size of the thermo device and exhibit much higher charge carriers mobility, lower thermal conductivity what leads to higher figure of merit ZT. It is possible to reach very high density of nanowoires in one layer in the order of 1 million wires per square centimeter [3].

In the Table 2 there are specified the main energy storage systems and products in which CNTs and related nanomaterials can be used.

The advantages of using nanotubes for energy storage are their small dimensions, smooth surface topology and perfect surface specificity. It is shown that for these applications, the electrochemical properties of multi-walled CNTs and single walled CNTs are essentially dominated by their mesoporous character.

CNTs may upgrade the most efficient electrochemical energy sources –rechargeable batteries.

CNTs spontaneously form bundles that are called nanoropes. These bundles are kept together by Van der Waals forces. Several experiences were made, and proved that CNTs have a better reversible capacity concerning lithium discharging with regard to porous graphite. So, CNTs bundles seem to be attractive host materials for reversible energy sources. They could also be low-cost, high-performance anode materials for rechargeable lithium-ion batteries since they show an excellent reversible capacity and cycle ability during lithium insertion and extraction. Due to the ability of high Li-ions intercalation the carbon and metallic nanotubes can increase several times the battery power and capacity of energy.

There are several possibilities for the hydrogen to be stored in carbon nanotubes. For hydrogen storage in closed CNTs the structure has two possible sites: inside the tubes and in the interstitial sites between the tube. In case of a long single walled CNTs closed with fullerene-like end caps, the hydrogen can only get access to the tube interior via the hexagons of the graphite-like tube wall. An opened tube with removed caps gives an easier access for the hydrogen molecules to the tube. Typically, the tubes are very long and therefore a good diffusivity of the hydrogen inside the tube will be required in order to fill the whole tube volume. Cutting the rope in shorter pieces may therefore help to improve hydrogen storage and its kinetics [3]. Contrast in results is very high: there is a range from 0 to 67 wt%. A possible reason is that hydrogen storage is only optimised for a very specific and narrow distribution of CNTs of distinct types and diameters. Although theoretical calculations predict that a range of 2-14 wt% hydrogen adsorption in carbon nanotubes is possible, they do not clearly distinguish between chemisorptions and physisorption [3].

Supercapacitors, also known as electrochemical double-layer capacitors, store energy as an electrical field, making them more efficient than standard batteries, which get their energy from chemical reactions. They are next-generation devices with a possibility of being applied to an auxiliary power supply, and the combined use with photovoltaic equipment and an electro mobile. It is because they are able to combine the energy storage properties of batteries with the power discharge characteristics of capacitors. Supercapacitors can be applied in: the hybrid power supply for electric mobiles, electric power storage of wind power, electric power storage of photovoltaic sources, memory backup power supplies, such as a notebook PC and a cellular phones.By using highly porous carbon material with a surface area up to 2000 m^2/g as electrodes of commercial supercapacitors it can be achieved the value of energy density (6Wh/kg) that is much greater than the energy density of a conventional capacitor or a lithium ion battery. In addition, carbon is a relatively cheap, low density, environmentally friendly and highly polarisable material which makes application even more attractive. [3]

Due to its tiny size, the nanotubes supply a gigantic superficial area, in which the energy can be stored and released later. The new supercapacitors can store energy in a density of 30 kW/kg, compared with 4 kW/kg of the most advanced ultracapacitors available commercially nowadays.

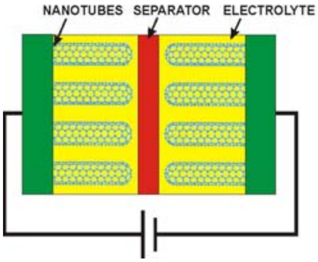

Fig. 3. Design principle of a double layer electrochemical supercapacitor employing CNTs

Presently commercial supercapacitors use yet electrodes made of activated carbon, which is extremely porous and therefore has a very large surface area. However, the pores in the carbon are irregular in size and shape, which reduces efficiency. The newly applied vertically aligned nanotubes in the supercapacitor have a regular shape, and a size that is only several atomic diameters in width. It results in significantly more effective surface area, which equates to increased storage capacity [3]. In Fig. 3 the design principle of double layer electrochemical supercapacitor employing CNTs is presented. It consists of two metallic electrodes with vertically implanted “forests” of CNTs, separated by a membrane saturated in electrolyte. The separator allows mobility of the charged ions but forbid the electronic conductance. With an electric field applied to elelctrodes each electrode – electrolyte interface represents a capacitor so the complete cell can be considered as two capacitors in series. The total is rolled or folded into a cylindrical or rectangular shape and stacked in a container.

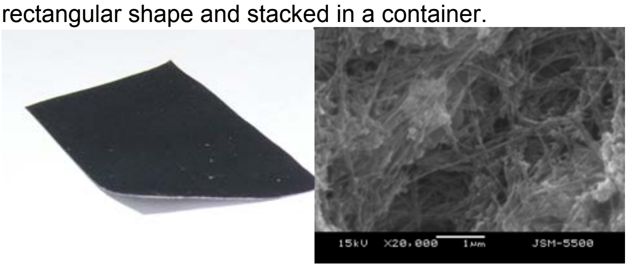

Fig. 4. Sample of supercapacitor membrane covered with CNTs (digital photo and SEM of carbon nanotubes covering capacitor membrane).

The supercapacitors have the advantages as follows: rapid charge and discharge, can be cycled millions of times, allows low/high temperature operation, compared with the usual aluminium electrolytic capacitor, it has about 1 million times higher capacity and high energy density. The materials and processes are less dangerous than in standard batteries, good reversibility, light weight, low toxicity of materials used, high cycle efficiency (95% or more) [3]. There are also some limitations such as cells have low voltages and they have high self-discharge.

The presented here microwave plasma system is able to produce CNTs that are captured as they are flying into containers or deposited on a surface. To increase the active area of the electrolytic capacitor the CNTs can be deposited on the electrodes or/and on the separating membrane. Fig.4 shows flexible membrane for supercapacitor that has been covered with CNTs in our laboratory.

There are randomly oriented nanotubes which are shown in SEM image. Using the microwave plasma system we are also able to make vertically oriented carbon nanotubes on silicon substrate. The sample of CNTs forest removed from the substrate is shown as a photo from AFM in Fig. 5.

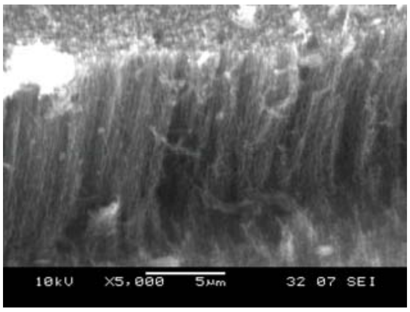

Fig. 5. SEM image of the slice vertically oriented carbon nanotubes obtained with microwave plasma on silicon substrate [6]

Such excellent CNTs architecture allows rapid ion transport in the interspaces and within the tubes. The specific electrode working area increases if CNTs are having multiwall geometry. Present research in this field concentrate on development of scalable deposition techniques and catalyst optimization to control the CNTs shape. In the nearest future the continuous process will be developed.

Conclusion

Some examples of carbon nanotubes as promising material to be applied in different electrical, electronic and mechatronic devices are presented. New microwave plasma system for synthesis of CNTs has been demonstrated. Some samples of synthesized CNTs that are directed on energy conversion and storage have been shown. This paper might be also an offer to conduct joint research with regard to obtain new products of electrical engineering and electronics employing carbon nanotubes.

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