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Growth of carbon nanofibers and related structures by combined method of plasma enhanced chemical vapor deposition and aerosol synthesis

Michal Guláš[a,b,*], Mária Čaplovičová[c], Miroslav Michalka[d], François Le Normand[b], Marius Rayar[a], Peter Macko[a], Pavel Veis[a]

[a]*Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, F2, 84248 Bratislava, Slovakia*
[b]*Group Surfaces and Interfaces, IPCMS, UMR 7504 CNRS, Bat 70, 23, rue du Loess, 67034 Strasbourg Cedex, France*
[c]*Department of Mineral Deposits, Faculty of Natural Science, Comenius University, Mlynská dolina, G, 84215 Bratislava, Slovakia*
[d]*International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovakia*

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Abstract

Growth of carbon nanofibers and nanotubes by combination of aerosol synthesis and plasma-enhanced catalytic chemical vapor deposition with alcohol as carbon precursor is presented. Only a hollow cathode glow discharge (HCGD) is used as gas activation process without any specific heating of the substrate. Specially designed hollow cathode enables the evaporation of catalyst directly on the substrate for catalytic growth. Product of physical vapor deposition process was examined by energy dispersive X-ray spectrometer (EDS). Spectroscopic features of the plasma were monitored by optical emission spectroscopy (OES). Carbon deposition was examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Catalytic nanofibers and multi-walled carbon nanotubes with outer diameters 20–60 nm have been observed.

Keywords: Plasma-enhanced chemical vapor deposition; Carbon nanotubes; Aerosol synthesis; Hollow cathode glow discharge; Optical emission spectroscopy

1. Introduction

Carbon nanofibers (CNFs) and related structures as carbon nanotubes (CNTs) are great point of interest. Their remarkable mechanical, thermal and electrical properties are often pointed out [1–3]. Due to their exceptional properties their preparation methods are subject of many studies. In general, three ways of CNFs and CNTs synthesis are generally used: electric arc discharge, laser ablation [4–7] and chemical methods. The chemical methods can be divided into chemical vapor deposition (CVD) [8–10] and aerosol synthesis [11]. In the arc discharge and laser ablation methods, CNTs are obtained after condensation of a hot carbon gas, while in the catalytic chemical methods the growth of a CNT is determined by the presence of a catalyst [12]. These catalysts, usually metal nanoparticles such as Fe, Co or Ni, cause the catalytic adsorption and the dehydrogenation of hydrocarbons. The advantages of CVD technique, besides large-scale production of CNTs, are the relatively low temperature, less than 1100 K, needed for CNTs synthesis and the controlled and localized growth. This temperature could even be lowered using activation of the incoming gas mixture by plasma (plasma-enhanced catalytic CVD or PE CCVD) created with radio frequency discharge [13], DC discharge [14], microwave discharge

*Corresponding author at: Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, F2, 84248 Bratislava, Slovakia. Tel.: +421 2 602 95 106; fax: +421 2 654 12 305.
E-mail address: gulas@fmph.uniba.sk (M. Guláš).

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[15], with hot-filaments associated or not, with plasma CVD (PE HF CCVD) [16,17]. Alcohol as a precursor gas (ACCVD) [18] also allows decreasing the temperature to around 1000 K. In aerosol synthesis, the catalyst particles are formed *in situ* during the CNF synthesis and the whole process takes place in the gas phase [11].

In this article, the growth of CNFs and related structures is presented by combined method of plasma enhanced catalytic CVD (PE CCVD) with alcohol as carbon precursor and aerosol synthesis. As called combined method consist of aerosol process, where carbon precursor and catalytic particles are both in gas phase, and CVD process, where growth of nanofibers occurs on the substrate.

A hollow cathode glow discharge (HCGD) is used as the gas activation process. HCGD behaves essentially as a strong ionization environment which is produced by fast electrons in the cathode region of a glow discharge [19]. Studies in the literature on the plasma characteristics during PE CCVD of CNTs are rather seldom, whereas properties of the applied discharge (electron temperature, electron and ion densities and kinetic energy) could be helpful for achieving better knowledge of the plasma influence on the controlled growth of CNTs: density, size, growth rate, growth direction. Thus, it is found that the plasma intensity is an important factor for the alignment of the nanotubes [20–22].

2. Experimental set-up

The scheme of PE ACCVD experimental apparatus for the CNFs growth consists of three main parts: an apparatus for mixing the inlet gas, equipment for spectroscopic measurements and the CVD reactor.

Ethanol (C_2H_6O) and isopropyl alcohol (C_3H_8O) were used as a carbon source, and adding of argon as a carrying gas enabled estimation of the plasma parameters. Decomposed OH radicals etched carbon atoms with a dangling bond, thus impurities such as amorphous carbon, and carbon nanoparticles might be suppressed even at relatively low reaction temperature [18]. During the discharge, the spectroscopic features of the plasma were monitored by optical emission spectroscopy (OES). The emitted discharge light came out from the reactor through quartz window. Consequently, it was focused on the input slit of spectrometer prisms (ISP-51). Diffracted image was taken by CCD chip of an adapted Audine camera. The spectrum picture was accumulated for several hundreds periods depending on signal intensity. Also the SD2000 Ocean Optics Miniature Fiber Optic Spectrometer with two spectrometer channels in dual housing for wide scan measurements and Andor Mechelle ME 5000 with intensified camera Andor IStar have been used. The CVD reactor was composed of a quartz tube with an inner diameter of 18 mm ended by brass flanges at both sides. First flange B included non-corroding steel hollow cathode (outer diameter 6 mm, length 100 mm) and the gas inlet (saturated vapor). The anode, the quartz window for OES, gas outlet and pressure gauge were placed in the right flange A. The sample, an Al_2O_3 or Si substrate, were located inside the hollow cathode. The structure of the hollow cathode is complex and is shown in more details in Fig. 1. It consists of three concentric cylinders 100 mm long. Outer and inner cylinders are made up of stainless steel. Between these metal cylinders, Al_2O_3 cylinder is placed with an outer diameter of 4 mm and an inner diameter of 3 mm (Fig. 1).

A rotary pump pumped the reaction chamber down and the ethanol or isopropyl alcohol vapors (vapor pressure of 58.5 and 41.2 mbar, respectively [23]) and argon as a carrying gas were supplied to the quartz tube from a room temperature alcohol reservoir. Keeping the vacuum pump on, the pressure in the quartz tube varied from 10 to 90 mbar. By controlling the argon flow (33–145 sccm), the total pressure was able to vary. A 0–1100 V power supply (VEB Statron 4222) with current 0–50 mA was employed to maintain the required voltage and current for the HCGD. Uniform plasma had been ignited at around 750 V. The discharge had been kept between the ceramic cylinder and the metal cylinders at the end of hollow cathode. During the process of synthesis and the HCGD the atomic lines of H and radicals C_2, CH and argon lines had been monitored. After cooling down, the end of the cathode Al_2O_3 ceramic and Si sample were observed. Carbon deposition was examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as well. These methods were employed for evaluation of the morphology, the microstructure and the internal structure of CNFs. Analyses were performed on a LEO1550 field emission scanning electron microscope at an acceleration voltage of 15 kV in secondary electrons mode. We used InLens secondary electron detector to achieve high resolution. For TEM examination of CNTs, transmission electron microscope JEOL JEM 200CX operating at 200 kV was used. Energy dispersive X-ray spectrometer (EDS) NORAN with Ge crystal was employed for the determination of the chemical composition of catalyst nanoparticles.

3. Results and discussion

3.1. Catalyst evaporation process

As mentioned above, the inlet gas did not contain the catalyst in gas phase as it is conventional for aerosol methods. The catalyst was acquired by physical vapor deposition (PVD) *by sputtering* from hollow cathode at the beginning of each experiment. During the discharge in argon and alcohol vapor atmosphere, the cathode placed in vacuum chamber was heated electrically to more than 1000 K. After ignition of the electric discharge, the high-energy argon ion bombardment ejects away the material of the cathode, so that the ejected atoms or molecules can condense on a substrate. This leads to *in situ* formation of