

SYNTHESIS OF CARBON NANOTUBES IN MW PLASMA TORCH WITH DIFFERENT METHODS OF CATALYST LAYER PREPARATION AND THEIR APPLICATIONS

Lenka ZAJÍČKOVÁ^a, Ondřej JAŠEK^a, Petr SYNEK^a, Marek ELIÁŠ^a, Vít KUDRLE^a, Magdaléna KADLEČÍKOVÁ^b, Juraj BREZA^b, Renáta HANZLÍKOVÁ^c

^a*Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*

^b*Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovak Republic*

^c*Institute of Scientific Instruments v.v.i., Academy of Sciences of the Czech Republic, Královopolská 147, 612 64 Brno, Czech Republic*

Abstract

The microwave plasma torch (2.45 GHz) was used for the synthesis of carbon nanotubes from the mixture of CH₄/H₂/Ar or C₂H₂/H₂/Ar on different substrates with iron catalyst. Iron catalyst was prepared by vacuum evaporation of iron on Si, Si/SiO_x or Si/AlxO_y substrates or by deposition of iron oxide nanoparticles on Si/SiO_x substrate by decomposition of Fe(CO)₅ in gas feed. Such prepared substrates were used for growth of carbon nanotubes. Reconstruction of the iron catalyst layer into nanoparticles was also studied in dependence on substrate buffer layer, gas atmosphere and temperature. Samples were studied by scanning and transmission electron microscopy and Raman spectroscopy. Synthesis resulted in rapid growth of MWNTs on all samples but the density, purity and nanotube diameter distribution varied. Such prepared carbon nanotube layers were used for sensing applications.

1. INTRODUCTION

Carbon nanotubes (CNTs) [1] are a driving force for current advances in nanotechnology, both on applied and fundamental levels. The selection of the ideal growth process depends on the application. For development of composites and other structural applications, the merit is the ability to produce "tons a day" at reasonable price. In contrast, the ability to achieve controlled growth (of specified thickness) on patterns is important for applications in nanoelectronics, field emission, displays, and sensors. They can be prepared by arc discharge [1,2], laser ablation [3] and chemical vapor deposition (CVD) [4] methods. For industrial applications, such as flat panel displays or field emitters, it is desirable to produce vertically aligned CNT films with uniform properties. The preparation of the aligned CNTs was reported by thermal, plasma enhanced and hot filament CVD methods. Most of these techniques work at low pressure requiring vacuum systems. However for industrial applications it would be desirable to work at atmospheric pressure. In our work atmospheric pressure microwave plasma torch is used for deposition of carbon nanotubes [5]. Surface bound catalyst and floating catalyst methods were used for generation of iron catalyst nanoparticles (NPs) for nanotube growth. Surface bound catalytic particles are generated on the substrate by reconstruction of thin layer film by pretreatment in various conditions. In the floating catalyst method decomposition of iron pentacarbonyl Fe(CO)₅ in microwave plasma torch is used to generate iron nanoparticles which are collected on the substrate and used later for the deposition of carbon nanotubes. The size of these particles and the carbon containing gas used for the CNT growth control the final distribution of CNT diameters [6] and morphologies of carbon nanotubes/nanofibres [7]. The restructuring of ultrathin metallic films for the catalysis of CNT growth is usually obtained by heating the films in N₂, H₂ or NH₃ [8] or plasma treatment [9]. Thin films

have a high surface-to-volume ratio and the heating results in the development of holes and, eventually, particles [10]. The particles can coalesce during continuous heating due to Ostwald ripening or surface migration [11], thus modifying the final distribution of catalyst particles. This process is strongly dependent on the heating time and gas environment [12], the thickness of the pristine catalytic layer [13] and its surface morphology [14]. In addition to this, the interaction with the material under the catalyst is of importance especially in case of integration on the Si substrates. At temperatures of CNTs growth, the metal catalyst can react with Si substrate and as-prepared particles change from pure metal to metal silicide. It is still a matter of debate how the formation of metal silicides affects particle catalytic activity [8]. It was found that application of a buffer layer between the silicon supporting substrate and metal catalyst significantly improves the catalytic function of created particles and consequently the CNTs growth because the formation of metal silicides is suppressed [15]. Most successfully used materials of the buffer layer are SiO_2 or Al_2O_3 . It was shown lately by several authors that careful reconstruction of catalyst layer under special conditions can be used to substantially lower deposition temperature of carbon nanotubes [7] or generated nanotubes with given electrical properties [16,17]. Usage of Al_2O_3 buffer layer with combination of small amount H_2O vapor also lead to discovery of so called super-growth technique [18] which can be used to grow several millimeters high nanotube forest in the matter of minutes. Here we report a high flexibility of the atmospheric pressure microwave plasma torch to use various types of catalyst for growth of carbon nanotubes.

2. EXPERIMENTAL

The successful growth of CNTs in the atmospheric pressure microwave plasma torch by our group was reported elsewhere [5]. The apparatus consists of microwave generator working at the frequency of 2.45 GHz and standard rectangular waveguide transmitting the mw power through a coaxial line to a hollow nozzle electrode. Ferrite circulator protects the generator against the reflected power by rerouting it to the water load. The matching of the plasma load to the line impedance is achieved by the combination of a movable short plunger and a line stretcher as described in [19]. In the last experiments, a stub tuner is mounted to the waveguide for easiest load matching. Working gas mixture flows through the central conductor of the coaxial line and the nozzle electrode. The central conductor is held in place by a boron nitride ceramics. The outer conductor of the coaxial line is terminated by a flange. Detailed drawing of the current set-up is in Fig. 1. The standard deposition mixture consists of argon, methane and hydrogen. The coaxial line and the electrode accommodate a dual gas flow. The design of the experiment is modified with respect to previously published papers [19, 20] in order to achieve Berger stability of torch discharge. Argon passes through the center whereas the reactive mixture of CH_4/H_2 is added by a concentric opening instead of the set of holes in the outer housing. The plasma torch is enclosed by a quartz tube, 200 mm in length, and duralumin shielding is wrapped around the tube. The diameter of the quartz tube is increased from originally 40 to actual 80 mm.

The substrate for MWNTs growth, silicon piece with the dimensions $10 \times 15 \text{ mm}^2$, was fixed on the quartz holder in the variable distance from the torch nozzle Fig.2. It was heated by a heat exchange with hot gas and surface recombination. Therefore, its temperature was determined by power input, gas mixture and its distance from the nozzle. The mw power applied for the deposition of CNTs was 400 W. Argon flow rate was changed from 700 to 1500 sccm. Hydrogen flow rate was between 285 and 430 sccm, methane flow rate was 42 sccm. The catalyst was 1-15 nm thick iron film prepared by vacuum evaporation. If not specified

otherwise the iron film was deposited on SiO_x buffer layer prepared by plasma enhanced chemical vapor deposition (PECVD) in low pressure radio frequency capacitive coupled discharge from the mixture of hexamethyldisiloxan (HMDSO) and oxygen. The radio frequency (13.56 MHz) power applied for the deposition was 100 W. The pressure in the reactor and the percentage of HMDSO in the mixture were 5 Pa and 20 %, respectively. Second type of the buffer layer consisted of native oxidized Al (further labeled as Al_xO_y) was prepared by vacuum evaporation of 10 nm Al layer on the silicon substrate and exposing the samples to ambient conditions for native oxide formation.

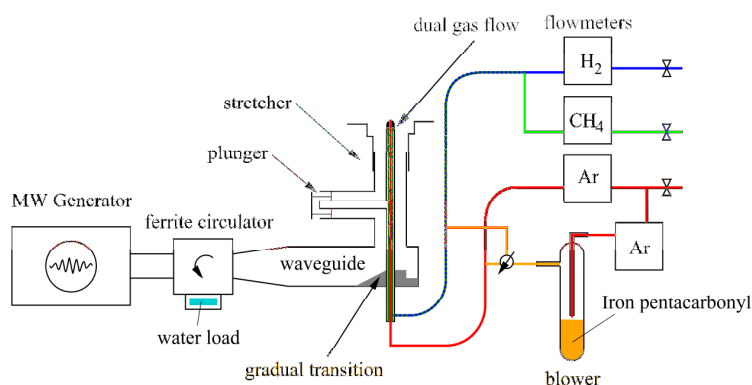


Fig. 1. Experimental apparatus scheme.

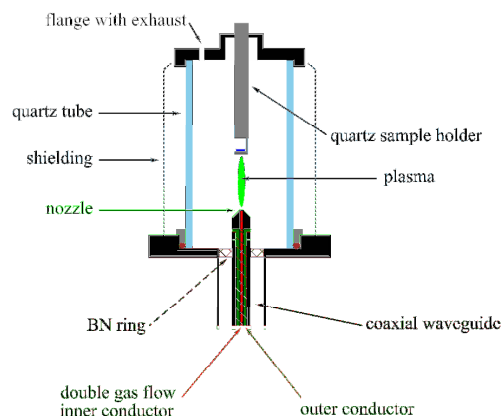


Fig. 2. Deposition chamber detail.

Study of reconstruction of catalyst thin film was performed in Gaseous Electronic Cell (GEC) reactor. GEC reactor is equipped turbomolecular pump and a resistively heated electrode (Boraletic heater element) . The temperature of the electrode can reach up to 1100 °C. Due to the poor thermal contact between the heater and sample, the real sample temperature was about 200 °C lower than electrode itself as measured by pyrometer. Heated electrode temperature was monitored by the thermocouple (K type). The gas flows are controlled by electronic flow controllers.

The substrate temperature could be monitored during the deposition by Raytek Thermalert TX pyrometer (temperature range 500 - 2000 °C). Deposited CNTs and prepared nanoparticles on the substrates were analyzed by CNTs were investigated with a field emission scanning electron microscope (FE-SEM) JOEL 6700F using three different detectors of electrons. The conventional E-T scintillation PMT system mounted aside from the electron beam detected all the electrons producing a "lower electron image" (LEI). The second system detected true secondary electrons at the semi-in-lens position, i.e. in the direction of the objective lens, producing a highly resolved "secondary electron image" (SEI). The third detector (AUX1), the yttrium-aluminum garnet (YAG) single crystal scintillator at the semi-in-lens position, collected backscattered electrons. The SEI micrographs provide good quality highly resolved images. Therefore, they were often used for detailed studies of CNTs. The LEI and AUX1 micrographs provide less resolved images with partial information about distribution of different elements because heavier elements appear brighter. They were used to distinguish carbon material from iron catalyst. Transmission electron microscopy (TEM) was carried out with the Phillips microscope CM12 (tungsten cathode) using a 120 kV electron beam. Copper grids coated with a carbon support film were used to prepare the samples. The sample powder was dispersed in ethanol, the suspension was treated in an ultrasonic bath for 10 minutes, and then the copper grid was dipped into it. Raman spectroscopy was performed using Renishaw inVia Raman microscope. The laser wavelength and power were 632.8 nm and 50mW, respectively.

3. RESULTS AND DISCUSSION

3.1. Surface-bound catalyst method

We have previously reported growth on CNTs on the Si/SiO_x/Fe system substrates[5] and study of catalytic particle formation through pretreatment process in capacitive plasma discharge[21] and microwave plasma torch [20,22]. In this work the possibility to growth carbon nanotubes in microwave plasma torch using other buffer layer are investigated and compared. Samples used in surface bound catalytic thin film growth were silicon wafer substrates 10x15 mm², <100> orientation. Used substrates can be divided into two groups according to used buffer layer. Buffer layers used were SiO_x and Al_xO_y and also substrate without buffer layer are used. Thin layer of iron (1 - 5 nm) was vacuum evaporated on the top of each sample as catalyst. Samples were treated in vacuum, Ar and H₂ atmosphere (10 Pa) for 15 minutes (5 minutes temperature stabilization period + 10 minutes at constant temperature) at elevated temperature (heated electrode temperature 750 °C or 850 °C). After 15 minutes heating was shut off and samples were cooled down at vacuum. SEM micrographs of prepared samples were analyzed for the particle size distribution. Micrographs in Fig.3 show Si/SiO_x/Fe(2,5 nm) type samples treated in vacuum (Fig.3a), Ar (Fig.3b) and H₂ (Fig.3c).

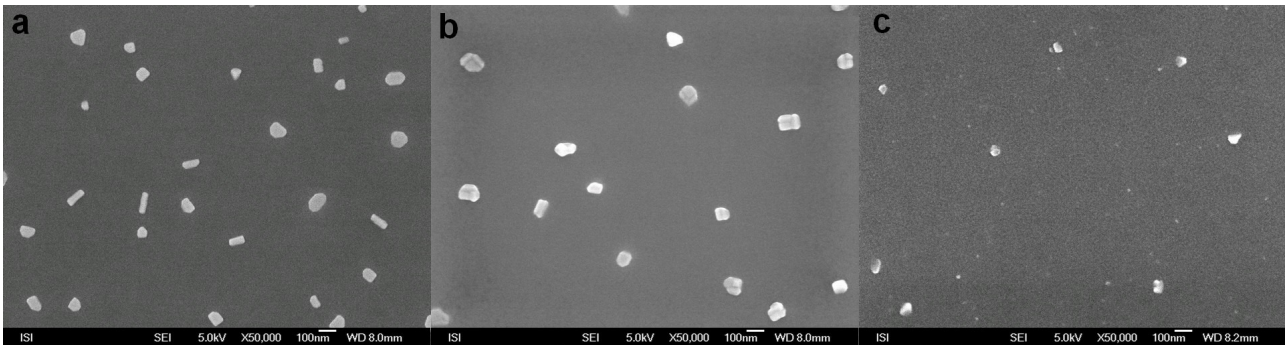


Fig. 3. Si/SiO_x/Fe substrates pretreatment under a) vacuum b) Ar and c) H₂ atmosphere at 750 °C.

The analysis show large particles with diameters over 100 nm in all cases. Particles created in argon and hydrogen atmosphere show crystal faces structure. In the case of the hydrogen atmosphere also small particles with the diameter between 10 and 20 nm can be found on the substrate. When the higher temperature (850 °C) was used in the pretreatment process, the particles with smaller diameter around 10 nm could be also found on the substrate. Results of the second set of experiments with Si/ Al_xO_y /Fe(2,5 nm) samples can be seen on the micrographs in Fig.4. As can be seen using Al_xO_y buffer layer resulted in much finer particles structure with diameters in the rage of 5-20 nm. In the case of hydrogen atmosphere the particles diameter size distribution could be narrowed with prevailing particles in the nanometer range. Treatment at the 850 °C shifted the particles diameter size to slightly lower values. Such pretreated samples, including sample without buffer layer, were then used for carbon nanotube growth in the microwave plasma torch to assess the ability of our system to use catalytic particles created by ex-situ methods. The results of the depositions can be seen in the Fig. 5. The deposition was carried out in the mixture of Ar/H₂/CH₄ with flowrates of 1540/430/42 sccm, respectively. The deposition time was 60 s, microwave power 400 W and the deposition temperature was between 700 and 750 °C.

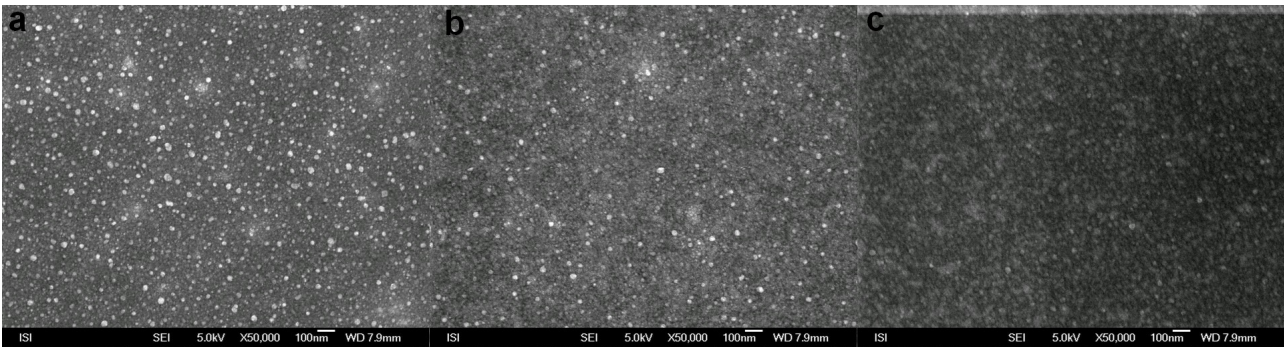


Fig. 4. Si/Al_xO_y/Fe substrates pretreatment under a) vacuum b) Ar and c) H₂ atmosphere at 750 °C.

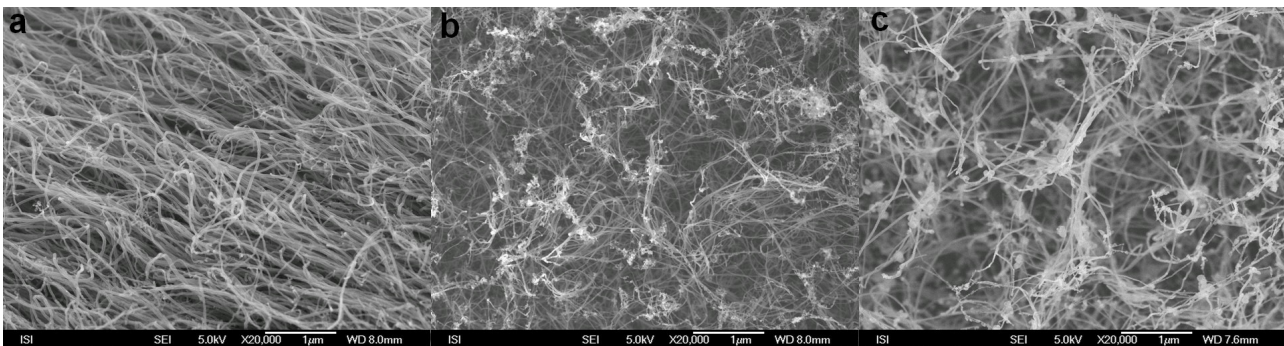


Fig. 5. Deposition of carbon nanotubes using a) SiO_x b) Al_xO_y and c) without buffer layer.

The deposition on the Si/Al_xO_y/Fe type sample resulted in smaller diameter CNTs in comparison with nanotubes deposited on the Si/SiO_x/Fe samples. This is in the agreement with the generally accepted model of the carbon nanotube growth where the nanoparticle size is correlated with CNT diameter. Analysis of sample without buffer layer also showed remarkable ability of the plasma torch system to synthesize nanotubes on such a system. This lead to the possibility to produce CNTs directly on conductive Si and use them as electron-emitting electrode of the gas pressure sensor [23].

3.2. Floating catalyst method

In the floating catalyst method the atmospheric pressure microwave plasma torch gas feed was modified by adding a blower with Fe(CO)₅ and Ar flow (10 sccm) into the centralchannel gas line. The generated nanoparticles were then collected on the silicon substrate placed in the collection zone near the upper flange. With microwave power 360 W iron oxide nanoparticles (Fe₃O₄ magnetite and γ-Fe₂O₃ maghemite) could be produced and collected on the Si/SiO_x substrate Fig. 6. The multi-walled carbon nanotubes deposited on such prepared substrate with microwave plasma torch in the mixture of Ar/H₂/CH₄ (1540/430/42 sccm) can be seen in Fig.7. Raman spectra (Fig 8.) showed a peak at 189 cm⁻¹ on the as-deposited sample which suggests the presence of SWNTs. In this case it would correspond to the radial breathing mode (RBM) of SWNT with the diameter of 1.3 nm [24]. The first-order Raman spectra in high frequency region shows typical SWNT-splitting of the G band in which the upper frequency component ω_G⁺ is found at about 1590 cm⁻¹ for all types of SWNTs whereas the frequency of ω_G⁻ depends on the metallic/semiconducting character of SWNT and its diameter. Besides the peaks corresponding to CNTs, there were few weak peaks related to iron oxides. They were probably related to the iron oxide nanoparticles not involved in nanotube growth.

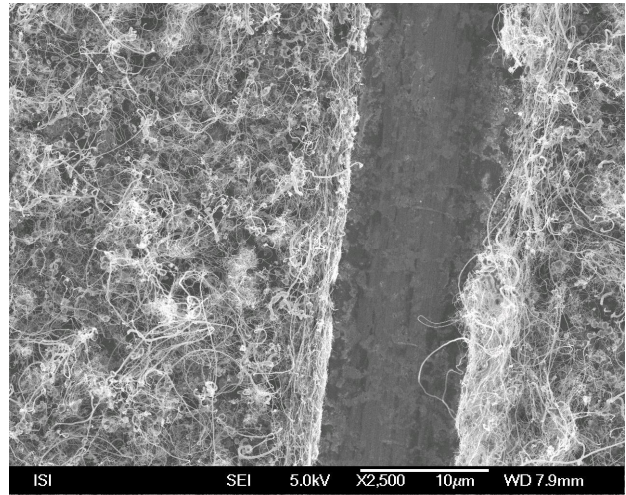
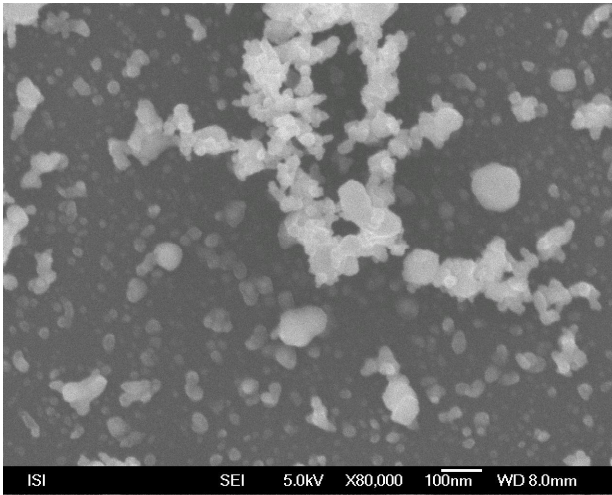


Fig. 6. SEM micrograph of deposited iron oxide NPs.

Fig. 7. SEM micrograph of deposited CNTs.

These peaks were identified belonging to magnetite at 669 cm^{-1} and hematite at 225 , 244 , 291 , 411 and 619 cm^{-1} and much lower signal of CNTs. The peak at around $1320\text{--}1340\text{ cm}^{-1}$ is difficult to assign because it can be a convolution of second-order feature of hematite reported at 1322 cm^{-1} [25] and D-band of disordered carbon.

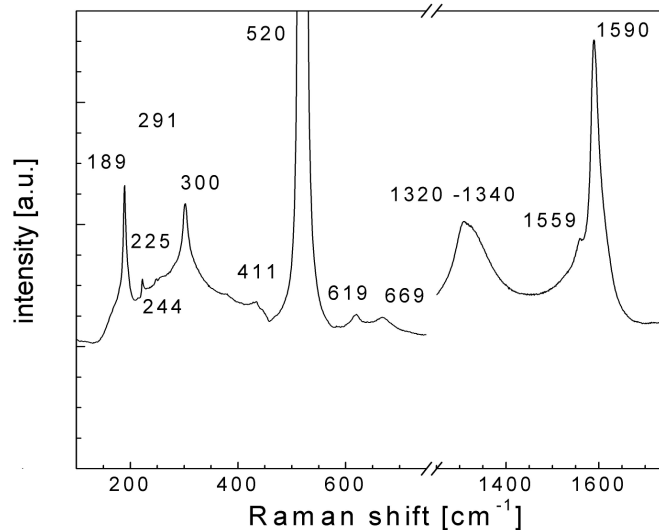


Fig. 8. Raman spectra of deposited CNTs and NPs.

Such deposited CNT layers were also intended to create a gas sensor based on the changes of electrical resistance measured between two planar electrodes connected by CNTs. Such prepared CNTs gas sensor showed significant resistance change response to NH_3 .

4. CONCLUSIONS

The microwave plasma torch operating at the atmospheric pressure was successfully applied to the fast deposition of multi-walled nanotubes (MWNTs) on the substrate without necessity of any vacuum or heating equipment. Different ways to generate in situ and ex-situ catalytic nanoparticles for the carbon nanotube growth were tested. Dense straight standing nanotubes were successfully prepared on silicon substrates with or even without barrier SiO_x layer and oxidized Al layer. Therefore, it was possible to produce CNTs directly

on conductive Si and used them as electron-emitting electrode of the gas pressure sensor. The CNTs grown in microwave torch were also intended to create a gas sensor based on the changes of electrical resistance measured between two planar electrodes connected by CNTs. Such prepared sensors could detect NH₃ gas.

5. ACKNOWLEDGEMENT

This work was supported by the Czech Ministry of Education under the project MSM 0021622411, by the Grant Agency of the Czech Republic, contracts 202/07/P523, 202/08/0178 and by the Academy of Sciences of the Czech Republic, contract KAN311610701.

LITERATURE

- [1] IIJIMA, S., *Nature*, 1991, 354, 56.
- [2] EBBESEN, T.W., AJAYAN, P.M., *Nature*, 1992, 358, 220.
- [3] THESS, A., LEE, R., NIKOLAEV, P. et.al., *Science*, 1996, 273, 483.
- [4] MEYYAPPAN, M., DELZEIT, L., CASSELL, A. et.al., *Plasma Sources Sci. Technol.*, 2003, 12, 205.
- [5] JAŠEK, O., ELIÁŠ, M., ZAJÍČKOVÁ, L. et al., *Materials Science and Engineering C*, 2006, 26, 1189.
- [6] DAI H., *Surf. Sci.*, 2002, 500, 218-241.
- [7] CANTORO M., HOFMANN S., PISANA, S. et.al., *Nanoletters*, 2006, 6, 1107-1112.
- [8] ESCONJAUREGUI, S., WHELAN, C. M., MAEX, K., *Nanotechnology*, 2007, 18, 015602.
- [9] KABIR, M. S., MORJAN, R. E., NERUSHEV, O. A. et.al., *Nanotechnology*, 2005, 16(4), 458-466.
- [10] JIRAN, E., THOMPSON, C. V., *Thin Solid Films*, 1992, 208, 23-28.
- [11] WEN, J., EVANS, J. W., BARTELT, M. C. et.al., *Phys. Rev. Lett.*, 1996, 76(4), 652-655.
- [12] PISANA, S., CANTORO, M., PARVEZ, A. et.al., *Physica E*, 2007, 37, 1-5.
- [13] CANTORO, M., HOFMANN, S., PISANA, S. et.al., *Diam. Relat.Mater.*, 2006, 15(4-8), 1029-1035.
- [14] LIU, H., CHENG, G., ZHAO, Y. et.al. , *Surface and Coatings Technology*, 2006, 201(3-4), 938-942.
- [15] DE LOS ARCOS, T., VONAU, F., GARNIER, M. G. et.al., *Appl. Phys. Lett.*, 2002, 80(13), 2383.
- [16] CHIANG, W.-H., SANKARAN, R. M., *Nature Materials*, 2009, in print, doi:10.1038/nmat2531.
- [17] HARUTYUNYAN, A.R., CHEN, G., PARONYAN, T.M. et al., *Science*, 2009, 326, 116-120.
- [18] HATA, K., FUTABA, D., MIZUNO, K. et.al., *Science*, 2004, 306, 1362-1364.
- [19] ZAJÍČKOVÁ, L., ELIÁŠ, M., JAŠEK, O. et.al., *Plasma Phys. Control. Fusion*, 2005, 47, B655-B666.
- [20] ZAJÍČKOVÁ, L., ELIÁŠ, M., JAŠEK, O. et.al., *Plasma Processes and Polymers*, 2007, 4, S245-S249.
- [21] ELIÁŠ, M., JAŠEK, O., JANČA, *Czech. J. Phys., Suppl. C*, 2004, 54, 2004, 853.
- [22] JAŠEK, O., ELIÁŠ, M., ZAJÍČKOVÁ, L. et al., *J. Phys. Chem. Solids*, 2007, 68, 738-743.
- [23] FICEK, R.; VRBA, R.; JAŠEK, O et.al., *In Proceedings of Third International Conference on Systems*. Cancun: IEEE Computer Society, 2008., s. 93-96.
- [24] DRESSSELHAUS, M., DRESSSELHAUS, G., JORIO, A. et.al., *Carbon*, 2002, 40, 2043.
- [25] DE FARIA, D., Silva, S., DE OLIVEIRA, M., *J. Raman Spectrosc.*, 1997, 28, 873