

SYNTHESIS OF CARBON NANOSTRUCTURES BY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION AT ATMOSPHERIC PRESSURE

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Carbon nanostructures present the leading field in nanotechnology research. A wide range of chemical and physical methods was used for carbon nanostructures synthesis including arc discharges, laser ablation and chemical vapour deposition. Plasma enhanced chemical vapour deposition (PECVD) with its application in modern microelectronics industry became soon target of research in carbon nanostructures synthesis. Selection of the ideal growth process depends on the application. Most of PECVD techniques work at low pressure requiring vacuum systems. However for industrial applications it would be desirable to work at atmospheric pressure. In this article carbon nanostructures synthesis by plasma discharges working at atmospheric pressure will be reviewed.

Key words: carbon nanostructures, plasma enhanced chemical vapour deposition, atmospheric pressure

1 INTRODUCTION

Carbon with its many allotropes became major player in nanotechnological research. From the discovery of fullerenes [1], through carbon nanotubes [2] to the latest, but hopefully not last surprise, addition of graphene [3], stable 2-dimensional carbon structure, the nanoresearch was electrified by carbon structures. Fullerene took the Nobel Prize in 1996, carbon nanotubes are taking regularly the first spot in a number of published articles in the field of nanotechnology to even more surprising and fascinating properties such the quantum Hall effect and electrons obeying Dirac equation of graphene. Synthesis of the carbon nanostructure was closely related to plasma processes. Carbon nanotubes, similarly to fullerenes, could be synthesized by an arc discharge [2], laser ablation [4] and chemical vapour deposition (CVD) [5] 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 aligned CNTs was reported by thermal, plasma enhanced and hot filament CVD methods [6]. Plasma enhanced CVD (PECVD) refers to the case where CVD is combined with plasma processes. The introduction of the catalyst divides the CVD methods into the group of bulk production techniques using catalyst in the gas phase, the so-called floating catalyst methods, and surface-bound CVD with supported catalyst either in the form of catalyst nanoparticles [7] or ultrathin films [8]. Most of these techniques work at low pressure requiring vacuum systems. However for industrial applications it would be desirable to work at atmospheric pressure.

2 CARBON NANOTUBES SYNTHESIS BY PECVD AT ATMOSPHERIC PRESSURE

Recently, atmospheric pressure discharges have been studied by some research groups because of their relatively simple set-up without expensive vacuum systems. Some publications deal with the synthesis of CNTs using dc plasma arc jet or torch ignited in flow gas between two electrodes. This approach is close to the arc discharge method because it is based on evaporation of solid carbon introduced as one of the electrodes and/or powder [9]. The catalyst can be integrated into a graphite electrode or introduced into the gas phase. Generally, these methods produce soot with certain portion of unaligned single and multi-walled CNTs. The experiments with microwave (mw) torches are focused on the floating catalyst approach (ferrocene, iron pentacarbonyl), *ie*, also bulk production of unaligned CNTs [10]. On the other hand, the mw torch has been successfully used by our group for high speed synthesis of vertically aligned supported CNTs [11–12]. With regard the dielectric barrier discharges (DBDs), Kyung, Lee *et al.* investigated filamentary DBD discharges at kHz frequencies for the deposition of supported CNTs. They tested a multipin electrode covered by a dielectric plate [13] and capillary dielectric barrier [14] configurations. The most successful application of DBD, in the case of its glow mode called the atmospheric pressure glow (APG), was performed by Nozaki. Besides the growth of unaligned CNTs of low quality in APG driven at 125 kHz and the growth of CNTs in radio frequency (rf) APG, he showed the growth of vertically aligned SWNTs [15] in rf APG using He/H₂/CH₄ feed.

Our group has grown CNTs in the atmospheric pressure microwave plasma torch directly on substrate. The

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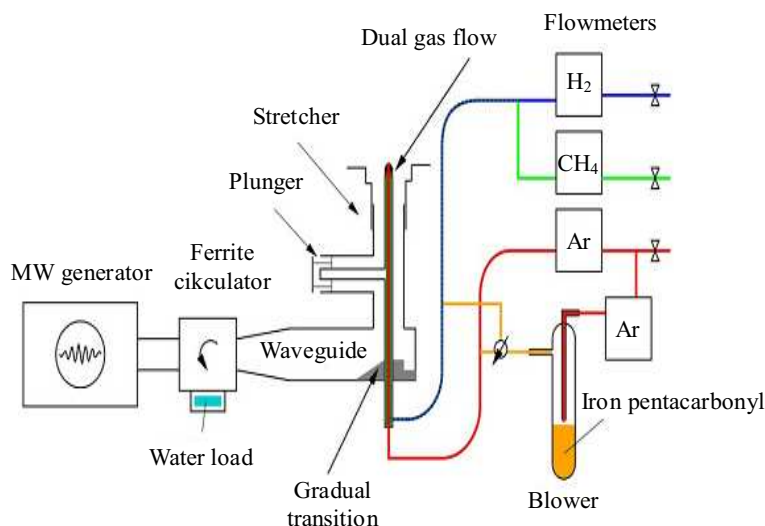


Fig. 1. Experimental apparatus scheme

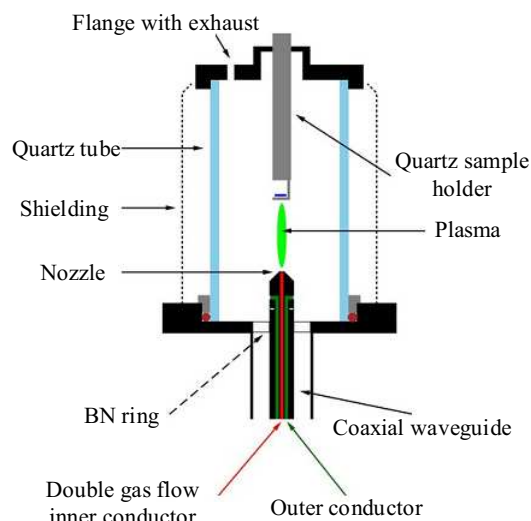
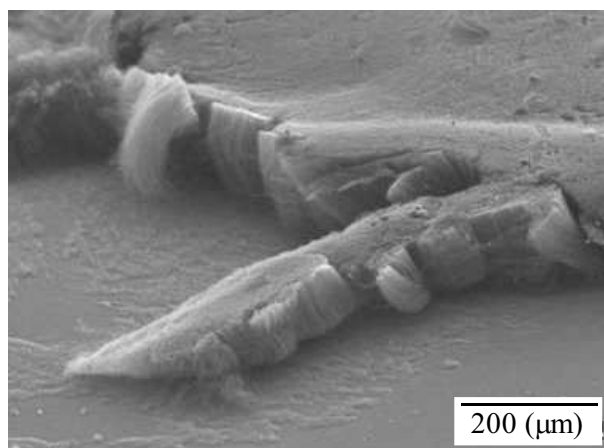


Fig. 2. Deposition chamber detail

Fig. 3. MWCNTs deposited on Si/SiO₂/Fe substrate by microwave plasma torch

microwave plasma torch apparatus consists of a microwave generator working at a frequency of 2.45 GHz and standard rectangular waveguide transmitting the mw power through a coaxial line to a hollow nozzle electrode. A ferrite circulator protects the generator against the reflected power by rerouting it to a water load. The matching of the plasma load to the line impedance is achieved by a three stub matching unit. A 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, detail of the deposition chamber in Fig. 2. The standard deposition mixture consists of argon, methane and hydrogen. The coaxial line and the electrode accommodate a dual gas flow. Argon passes through the centre whereas the re-

active mixture of hydrogen and methane 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 a duralumin shielding is wrapped around the tube. The diameter of the quartz tube is 80 mm. The substrate for MWNTs growth, silicon piece with the dimensions 10 × 15 mm², was fixed on the quartz holder in the variable distance from the torch nozzle. It was heated by a heat exchange with hot gas and surface recombination. Therefore, its temperature was determined by the power input, gas mixture and its distance from the nozzle. The mw power applied for the deposition of CNTs was 400 W. The argon flow rate was changed from 700 to 1500 sccm. The hydrogen flow rate was between 285 and 430 sccm, the methane flow rate was 42 sccm. The catalyst was a 115 nm thick iron film prepared by vacuum evaporation. The used substrates for deposition are Si, Si/SiO₂ or Si/Al₂O₃ with an iron catalyst layer. An example of a such a deposited carbon nanotube layer is shown in Fig. 3. Deposited samples were studied by scanning and transmission electron microscopy and Raman spectroscopy.

3 CATALYST ROLE AT THE NANOTUBE GROWTH

For the carbon nanotube growth it is necessary to obtain nanometre scale catalytic particles. In addition to a wide range of chemical methods, the catalytic particles can be directly generated by decomposition of an organometallic compound (floating catalyst method) or by reconstructing thin layer of catalyst (surface bound catalyst method). The restructuring of ultrathin metallic films of catalysis for CNT growth is usually obtained by heating the films in N₂, H₂ or NH₃ [16] or plasma treatment [17]. Thin films have a high surface-to-volume ratio and the heating results in the development of holes and,

eventually, particles [18]. The particles can coalesce during continuous heating due to Ostwald ripening or surface migration [19], thus modifying the final distribution of catalyst particles. This process is strongly dependent on the heating time and gas environment [20], the thickness of the pristine catalytic layer [21] and its surface morphology [22]. In addition to this, the interaction with the material under the catalyst is of importance especially in the case of integration on Si substrates. Application of a buffer layer between the catalyst and substrate can hinder unwanted reaction and significantly enhance the carbon nanotube growth. It was shown lately by several authors that careful reconstruction of the catalyst layer under special conditions can be used to substantially lower the deposition temperature of carbon nanotubes [23] or generated nanotubes with given electrical properties [24–25]. Usage of an Al_2O_3 buffer layer in combination with a small amount of H_2O vapour also has lead to the discovery of the so-called super-growth technique [26], which can be used to grow a several millimetres high nanotube forest within minutes.

4 GRAPHENE SYNTHESIS BY PECVD AT ATMOSPHERIC PRESSURE

Lately a method producing a graphene sheets in atmospheric pressure microwave reactor by decomposition of ethanol was published [27]. This method produced graphene sheet in the gas phase without the need of a substrate with the same quality as methods like micromechanical cleaving or graphite oxide reduction. Graphene sheets were synthesized by passing liquid ethanol droplets into argon plasma. The graphene sheets were characterized by transmission electron microscopy, electron energy loss spectroscopy, Raman spectroscopy, and electron diffraction.

Acknowledgement

We would like to thank M. Kadlečíková from the Slovak Technical University Bratislava for Raman spectroscopy measurements, J. Buršík from the Institute of Physics of Materials, ASCR Brno for SEM and TEM analysis and the team of the Institute of Scientific Instruments, ASCR, Brno for HRSEM analysis. This work was supported by the Czech Ministry of Education under the projects MSM 0021622411 and by the Grant Agency of the Czech Republic contracts P205/10/1374, 202/08/0178, and 104/09/H080 and by the Academy of Sciences of the Czech Republic, contract KAN311610701.

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Received 30 June 2010

This work was presented at Nanoved & Nanotech & Techtransfer 2010, International Conference on Nanoscience, Nanotechnology, Nanomaterials, Nanomedicine and Transfer 16-19 May 2010, Bratislava, Slovakia.