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

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Abstract

Carbon nanostructures present leading field in nanotechnology research. 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. The 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. Special attention will be given to microwave discharges and atmospheric pressure glow discharge (APG). Our group has successfully synthesized multi-walled carbon nanotubes directly on substrate or in volume by microwave plasma torch. We were able to growth several tens of micrometers high layer of nanotubes in time less than 1 minute, without any external heating source. The carbon nanotubes layer could be also grown on substrates without a buffer layer or with predefined patterns. Lately APG discharge became an attractive method to growth single-walled carbon nanotubes with good alignment. Critical factor for growth of carbon nanotubes is the catalyst. Properties of buffer layer between substrate and catalyst and catalytic particles size considerably influence final product and are key to control of nanotube properties and growth conditions such as temperature and gas mixture. In the end of the article a possibility to synthesize graphene with atmospheric pressure discharges is discussed.

Introduction

Carbon with its many allotropes became major player in nanotechnological research. From 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 nano research was electrified by carbon structures. Fullerene took the Nobel prize in 1996, carbon nanotubes are taking regularly first spot on number of published articles in field of nanotechnology to even more surprising and fascinating properties such a quantum Hall effect and electrons obeying Dirac equation of graphene. Synthesis of carbon nanostructure was closely related to plasma processes. Carbon nanotubes, similarly to fullerenes, could be synthesized by 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 the aligned CNTs was reported by thermal, plasma enhanced and hot filament CVD methods [6]. Plasma enhanced CVD (PECVD) refers to the case where a plasma source is used to create a discharge. The introduction of the catalyst divides the CVD methods into the group of bulk production techniques using catalyst in the gas phase, 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.
Carbon nanotubes synthesis by PECVD at atmospheric pressure

Recently, atmospheric pressure discharges have become 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 d.c. 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 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), i.e., 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 regards the dielectric barrier discharges (DBDs), Kyung, Lee et al. investigated filamentary DBD discharges at kHz frequencies for the deposition of supported CNTs. They tested multipin electrode covered by the dielectric plate [13] and capillary dielectric barrier [14] configurations. The most successful application of DBD, in this case of its glow mode called 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 CNFs in radio frequency (r.f.) APG, he showed the growth of vertically aligned SWNTs [15] in r.f. APG using He/H₂/CH₄ feed.

Our group has grown CNTs in the atmospheric pressure microwave plasma torch directly on substrate. The microwave plasma torch 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 a three stub matching unit. 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 deposition chamber 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 reactive mixture of hydrogen and methane is added by a concentric opening instead of the set of holes in the outer housing.

![Fig. 1. Experimental apparatus scheme.](image1)

![Fig. 2. Deposition chamber detail.](image2)

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 80 mm.
The substrate for MWNTs growth, silicon piece with the dimensions 10x15 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 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. The used substrates for deposition are Si, Si/SiO₂ or Si/Al₂O₃ with the iron catalyst layer. Example of a such deposited carbon nanotube layer can be found on Fig. 3. Deposited samples were studied by scanning and transmission electron microscopy and Raman spectroscopy.

![Fig.3. MWCNTs deposited on Si/SiO₂/Fe substrate by microwave plasma torch.](image)

**Catalyst role at the nanotube growth**

For the carbon nanotube growth it is necessary to obtain nanometer scale catalytic particles. Except a wide range of chemical methods, the catalytic particles can be directly generated by decomposition of organometalic 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 case of integration on the Si substrates. Application of buffer layer between catalyst and substrate can hinder unwanted reaction and significantly enhance carbon nanotube growth. 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 [23] or generated nanotubes with given electrical properties [24-25]. Usage of Al₂O₃ buffer layer with combination of small amount H₂O vapor also lead
to discovery of so called super-growth technique [26], which can be use to grow several millimetres high nanotube forest in the matter of minutes.

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

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**References**
COMPOSITE MATERIALS REINFORCED BY SHORT (NANO) FIBRES – COMPUTATIONAL SIMULATIONS

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Abstract. Composites reinforced by short fibres/tubes are often defined to be materials of future with excellent electro-thermo-mechanical (ETM) properties. The aspect ratio (length to diameter) of the short fibres is often 10³:1-10⁶:1, or even more. Because of these properties very large gradients are localized in all ETM fields along the fibres and in the matrix. These fields define the interaction of the fibres with the matrix, with the other fibres and with the boundaries of the domain/structure. Method of Continuous Source Functions (MCSF) was developed by authors [1, 2] to simulate the interaction. Although the Carbon Nano-Tubes (CNT) have diameter of several nano-meters, their length is much larger and so, methods of continuum mechanics can be used also for the simulation of CNT with the matrix material. Main aim of our paper is to show some results of computational simulation for the interaction of fibres with the matrix and their contribution to increase stiffness, conductivity, strength and other properties of the composite material in micro- and macro-dimensions.

Computational simulations and results

In the MCSF the interaction of matrix with fibres is solved as homogeneous continuum with material matrix properties and with 1D continuous source functions placed along fibre axes to simulate the continuity conditions in discrete points along the fibre/matrix boundaries (Fig. 1). The source functions are unit forces, dipoles and couples in statics. The force is vector function and the dipoles and couples are tensors obtained from the force as corresponding derivatives. The dipole is derivative of the force in the force direction and the couple in perpendicular direction to the force. In thermal problems the basic source is a unit heat source, i.e. it is scalar function and heat dipoles are derivatives of the heat source in corresponding direction, i.e. it is a vector function.

Fig. 1 Distribution of source functions and collocation points
It is supposed that the fibres have much higher stiffness, strength and conductivity than the matrix. Because of large aspect ratio also bending stiffness of fibres is negligible comparing to its axial stiffness. The micro-dimensions of the structure allow using multi-scale simulations in which the material properties are executed on micro-models and then they are homogenized for macro-model. Following continuity conditions are introduced between the fibre and the matrix:

In mechanics displacements are supposed to be constant in each fibre in the first iteration step. Moreover, because of the interaction between fibres, it is also necessary to prescribe displacements and strains to be equal in opposite points in cross-sections. The source functions located inside the fibre define resulting force acting in each cross section and from it one can obtain stresses and strains along the fibre, which can be used for corrections taking into account finite stiffness of the fibre in the next iteration steps.

Similarly constant temperatures are assumed in each fibre in the first iteration step and also additionally equal temperatures are prescribed on opposite sides of fibre cross-sections. The source functions inside fibres define in this case the heat flow in the fibre and taking into account its final conductivity, the continuity conditions are corrected in the next iteration steps.

Rigid body displacements of fibres and temperature changes by the interaction of fibres and matrix are obtained by satisfaction of force equilibrium and thermal energy conservation by source functions in each fibre.

Largest gradients in all potential fields are in the end parts of fibres. Their contribution to the interaction with the matrix is strongest. In mechanical problems, it is introduced by shear stresses and in thermal problems by the heat flow through the fibre/matrix interface (Fig. 2).

There is, however, also very strong interaction between neighbour fibres. Most important contribution to this interaction is close to the ends of closest fibres (see Fig. 3).
In a Control Volume Element (CVE) we have many fibres interacting together. Computational model has to take into account all these interactions in order to evaluate correctly mechanical and thermal properties of the composite material. Increase/decrease of temperature of fibres in a CVE of randomly distributed fibres is given in the Fig. 4. The CVE is in thermal field which correspond to the field of homogeneous material of the matrix with temperatures equal to corresponding coordinates in fibre axis direction. Diameter of fibres is equal to 2 and their length 200. Fibres which would intersect with other fibre, or are very close to another fibre are excluded from the computational model and so, there is no increment of the temperature in corresponding fibres in the Figure 4.

Behaviour of all mechanical, thermal, or electro-magnetic fields is similar, however, as the basic field variable in thermal field is scalar valued temperature, in mechanical field the displacement is vector having three components in 3D space, there are also three times more equations to be solved after the numerical discretization of the problem.
If the fibres are curved similar numerical procedure can be used as numerical evaluation is used in our models. CNT are able to decohere and recohere in the end parts of fibres/tubes in the end parts, where there are very large shear stresses (Fig. 5). The region of very large shear stresses is usually very small and the decohesion/recohesion does not influence force transmission in other parts of fibres very much. The recohesion and recohesion is introduced by transmission of work from mechanical to thermal form and in dynamics by damping effect which is very important for some applications (turbine blades for aerospace engine, etc.).

Fig. 5 Shear forces along fibre boundary (overlapping with neighbour fibres)

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References
The Slovak Centre of Scientific and Technical Information – SCSTI (http://www.cvtisr.sk) is the national information centre and specialized scientific library of the Slovak Republic focused on all branches of technology and selected areas of natural and economic sciences. It is the state-owned institution with task to gather, process and provide science-related information and build complex information systems for research and development (R&D). The institution was established in 1938, while the most of the time in its more than 70-year history was known as the Slovak Technical Library, which always belonged to pioneers in the process of new library technologies’ implementation. The change of the name to the Slovak Centre of Scientific and Technical Information in 1996 should have meant also the extension of standard library services to other activities; however, the full development of non-library services has actually started only since 2007. Currently, the Slovak Centre of Scientific and Technical Information is the directly-managed organisation of the Ministry of Education of the Slovak Republic. It provides a wide range of library services including online catalogues, presence and absence loan services, etc. Besides that, the SCSTI offers also the possibility to loan books from other Slovak and foreign libraries, through the interlibrary loan services. In order to enable the easier and efficient orientation of users searching the information resources on the Internet, the specialised SciTech navigator has been developed, which contains the information about free accessible resources and systems on the Internet. For the benefit of library community, apart from educational activities, the Centre publishes specialized expert publications and the periodical “ItLib-information technologies and libraries”, as well as administrates the Internet portal InfoLib, which is focused on area of libraries and information science. Based on mutual agreements, the SCSTI hosts depository libraries of the EU, the OECD and the EBRD, the Centre of Patent Information – PatLib of the European Patent Office, as well as the Sales Office of the EU Publisher – Publications Office of the EU. The SCSTI builds and operates also the EURO:i:portal focusing on the issue of European integration.

New tasks of the SCSTI

NCP SaT – National Centre for Popularisation of Science and Technology in Society

In 2007, a new department called the National Centre for Popularisation of Science and Technology in Society (NCP SaT) has been created by the Ministry of Education of the SR within the SCSTI, with the aim to fulfil the tasks related to implementation of the Strategy of science and technology popularisation in society, which was approved by the government of the Slovak Republic in February 2007. The mission of the NCP SaT is to raise wider public
awareness of science, technologies and research results, while targeting mainly on the young generation; to promote the work of scientists and attract young people for studies at universities with orientation on technical and natural sciences. The NCP SaT attempts to initiate and create a forum for discussions among researchers about the achieved R&D results and the importance of active participation of the Slovak R&D organisations in international science and technical co-operation. Following this objective, the NCP SaT organises a number of events on a regular basis. The most important and popular ones are: “Science in the centre” – a cycle of science cafes meaning the informal meetings of scientists with experts and wider public in the SCSTI premises; “Scientific confectioners” – co-organised with the so called Young Slovak Researchers Association aimed at involving the elementary and secondary school students and their teachers in a relaxed way in the scientific discussions with well-known scientists; and “The week of science and technology in Slovakia” – where the SCSTI supports the Ministry of Education of the SR in organisation of main and accompanying events, conferences and competitions. In addition to these activities, the NCP SaT organises continuously lectures at schools, as well as exhibitions focused on science promotion.

The SCSTI has also been authorised by the Ministry of Education of the SR to ensure the operation of the Central information portal for research, development and innovation (CIP RDI), which is one of the main information, managerial and supervisory tools of the state scientific and technical policy. CIP RDI provides information related to the state support of science, financing, relevant official documents, selected statistical data, implementation of European regulations, international science co-operation, R&D results, public calls for research projects, as well as records of all research, development and innovation projects and tasks financed partially or in total from public sources, together with the evaluation of their socio-economic outcomes. The portal contains the following data since the year 2000:

- Calls for proposals for research related projects;
- More than 600 organisations from area of science and research;
- Database of more than 4,000 implemented research projects;
- Database of more than 1,000 experts from various science fields;
- Characteristic of more than 3,000 laboratories and research facilities.

Furthermore, the CIP RDI serves as a tool for the:

- Effective organization and implementation of the agenda called “Science and Society” in Slovakia;
- Valuation of state and regional potential in area of research, development and innovation;
- Follow-up the effectiveness of public funds provided for R&D support.

Currently, the CIP RDI is being augmented with new functions, mainly in terms of effective handling with projects throughout their life-cycle and interconnection with other R&D related information systems. Moreover, the improvement of English version of the portal will be finished soon and thus the portal will become an effective support tool also for foreign researchers, entrepreneurs and venture investors interested in the Slovak R&D. The portal can be visited at the following link: https://www.vedatechnika.sk
National information system promoting research and development in Slovakia – Access to electronic information resources – NISPEZ

The access to electronic information resources (EIR) is the basic prerequisite for the knowledge-based society development. Until 2008, the research and scientific community in Slovakia accessed the electronic information resources (EIR) through academic libraries at individual universities, which had to submit each year the development projects to the Ministry of Education of the SR in order to obtain means for subscriptions. The Slovak Academy of Sciences obtained and paid for licensed EIR for its researchers from its own budget line. By the end of 2008, the SCSTI started an implementation of the national project called NISPEZ, which is financed from the EU structural funds – European Regional Development Fund (ERDF), Operational programme Research and development. The main objective of the project is to ensure the access to electronic information resources in the field of research and development for the science community and university students in Slovakia. The end of the project is planned for June 2014 and the total amount of grant provided is 19.881.676,23 EUR. In this long-term period of 5 years, it will handle the co-ordinated purchase and access provision to EIR for research and development in Slovakia, creation of the database of Slovak EIR and also augmenting of CIP RDI with new functions focused on interconnection with other information systems on research and development, while respecting the EU standards, especially data model CERIF (Common European Research Information Format). Within the NISPEZ project, the access (for academic and research community in Slovakia) to the following databases is being provided: ACM / Association for Computing Machinery; Art Museum Image Gallery; Gale Virtual Reference Library: Art; IEEE/IET Electronic Library (IEL); Knovel Library; ProQuest Central; REAXYS; (originally Beilstein-CrossFire Direct); ScienceDirect; SCOPUS; SpringerLink; Web of Knowledge; and Wiley InterScience.

Data centre for research and development – DC-R&D

The SCSTI currently implements another national project within the Operational programme Research and development (ERDF) called “Infrastructure for Research and Development – the Data centre for research and development”. The main project objective is to build a data centre, which will store, process and provide access to information that is needed by Slovak scientific organisations while carrying out their R&D activities. Within the project, progressive ICT infrastructure for research and development area will be built, with purpose to store and provide data used by researchers, while ensuring a high level of accessibility and security. At the same time, the infrastructure for electronic communication in area of science and research will be created. The total amount of grant provided from EU structural funds for this project implemented in period 2009 – 2014 is 33.133.963,58 EUR.
The SCSTI and the technology transfer support

During 2009, there are first offices focused on technology transfer support being established at Slovak universities and research institutions. However, since the technology transfer (TT) is a relatively new issue in Slovak conditions (similarly as in other eastern-European countries), there is an obvious need for assuring the co-ordination of activities of individual centres, support their development and thus create an effective system for TT support at national level. The key part of the system should, according to the decision of the Ministry of Education of the SR, be the Slovak Centre of Scientific and Technical Information together with local TT centres established at universities and R&D organisations. With regard to this new task, the SCSTI has established a Technology transfer department, which will be further developed and transformed mainly within another EU structural funds’ project implemented by the SCSTI.

The SCSTI has recently finished the preparation of the above-mentioned national project called “National infrastructure for technology transfer support in Slovakia – NITT SK”, which has been submitted to the programme’s Managing authority. The project beginning is planned for June 2010, while the implementation should be finished in December 2014; nevertheless, the SCSTI has the ambition to continue with TT support activities also after the project termination. Again, the project will be financed from the EU structural funds (ERDF) within the Operational programme Research and development. The planned total budget of the project is nearly 8,5 million EUR and the main objective is to create and implement the national support system for transferring the knowledge and technologies gained by R&D activities to socio-economic praxis, with the aim to contribute to knowledge-based economy development. The project intention is to propose and implement the national infrastructure for technology transfer support, and thus contribute directly to more intensive and efficient state support of research and development. The national system will support those R&D activities that reflect the real needs of entrepreneurial sector, which will result in increased application of R&D results and technologies in industry. At the same time, it will support the creation of long-term partnerships between academy and industry, which will help not only to academics themselves, but it will contribute to the sustainable development of the whole, knowledge-based society. The NITT SK project will be implemented nation-wide at the whole territory of the SR, while the primal target group of the project will be the science community coming from public sector. The project will be focused on achieving the following three specific objectives:

• Building-up the Technology transfer centre at the SCSTI, in order to ensure the systematic technology transfer support at national level;
• Support the science community in the process of technology transfer through utilisation of existing ICT capacities and resources for research and development;
• More efficient transfer of technologies and scientific knowledge to economy and society through the science promotion.

The SCSI transformation towards progressive approaches in the field of access, organisation and provision of scientific information, as well as orientation on new tasks and support services is a long-lasting process, which is significantly accelerated due to an effective use of means provided within the EU structural funds.