Deposition of vertical carbon nanosheets by MPECVD at atmospheric pressure

S Marinov, V Vachkov and Zh Kiss’ovski
Faculty of Physics, St. Kl. Ohridski University of Sofia,
5 J. Bourchier Blvd., Sofia 1164, Bulgaria

E-mail: kissov@phys.uni-sofia.bg

Abstract. The deposition process is studied of vertical carbon nanosheets by microwave (MW) plasma-enhanced chemical vapor deposition (PECVD) at atmospheric pressure. A coaxial MW plasma source with a surface-wave discharge at 2.45 GHz produces plasma in a gas mixture (Ar/H₂/CH₄) in the processing chamber. The emissive spectra of the plasma column in pulsed regime of the source are registered by an iHR550 spectrometer. The light from the plasma column is collected by a lens system connected to the spectrometer by an optical fiber. The dependence of the gas temperature in the plasma column on the absorbed MW power is obtained from the recorded OH-band and CN-band spectra by using the LIFBASE program. The plasma density is estimated from the Stark broadening of the Hβ-line, while the electron temperature is estimated by the line-ratio method using argon lines. The composition of the outlet gases from the chamber is measured and analyzed by an Agilent Micro gas chromatograph. The results obtained demonstrate the high efficiency of the methane decomposition process in the hot region of the plasma column (Tg ~ 3000 K). The deposition of vertical carbon nanosheets is carried out at fixed plasma parameters and controlled substrate temperature. Cu plate and Ni-foam are used as substrates. The carbon nanostructures formed on the metallic substrates are studied by SEM; the dependence is thus obtained of their morphology on the plasma parameters, gas temperature and substrate temperature. The structures are confirmed as graphene sheets via Raman spectroscopy. The results demonstrate the viability of our system for deposition of vertical carbon sheets at atmospheric pressure.

1. Introduction

The carbon nanostructures (CNS) possess unique electrical, mechanical and optical properties making them an excellent choice for various applications. Depending on the number of nanoscale dimensions, the CNS are classified as 0D (nanoparticles), 1D (nanowires, nanotubes), 2D (nanowalls, nanosheets) or 3D structures. Carbon nanowalls and vertically standing few-layer graphene sheets are of great interest due to their specific properties and morphology (intersecting vertical sheets with sharp edges and high specific surface area).

Carbon nanowalls (CNW) have potential applications in microelectronics as sensors, field emitters and electrodes for supercapacitors. Promising methods for graphene production are the plasma-enhanced chemical vapor deposition (PECVD) [1-3] and the free standing method [4-7]. A variety of gas-discharge plasmas (DC, RF or MW) can be used for this purpose. Synthesizing CNS at atmospheric pressure in Ar/CH₄ or N₂/H₂/CₓHᵧ gas mixtures allows for shorter deposition times and easier
technological implementation compared to the typically used low-pressure CVD methods. The MW discharges are usually characterized by a high-density plasma and relatively high gas temperature, which provides efficient decomposition of hydrocarbons and production of C_2H_4 radicals and C_2.

In this study, an MW plasma reactor is used for CNS deposition at atmospheric gas pressure under controlled conditions. The plasma parameters are determined and the structures deposited are analyzed by SEM.

2. Experimental set-up and diagnostics
The experimental setup (figure 1) has been discussed in other publications [8, 9] and has undergone a few modifications which will be explained below.

![Experimental setup](image)

**Figure 1.** Experimental setup.

A low-power MW discharge in a ceramic tube is used to create plasma in a gas mixture of Ar, CH_4 as a precursor and additional H_2 to improve the deposition process. An MPG-4M generator is used to feed a signal at 2.45 GHz to an MW plasma exciter through a coaxial line. The MW exciter includes alumina ceramic as a dielectric medium and also as a surface-wave discharge tube. The plasma source and the substrate holder are placed in a quartz vessel with metal flanges filled with a gas mixture of Ar, H_2 and CH_4. The discharge is ignited by the MW exciter and the substrate (nickel foam, Cu-plate) is heated by both the plasma jet and an additional heater. Monitoring and control of the substrate temperature are performed via a thermocouple electronic system. The reflected and forward power is measured by an HP 437B Power Meter through a Pasternack PE 2219-30 directional coupler; the data received from it is used to achieve a better matching of the plasma source by a Maury 1878C triple stub. The pulse parameters of the MW signal are measured by a Tektronix TDS 360 oscilloscope.

The setup has two main improvements over the one used previously [8, 9]. First, an Agilent Technologies 490 Micro gas chromatograph is used to measure the outlet gases from the process chamber. Second, the emissive spectra of the plasma flame are measured by both an HR Ocean Optics spectrometer and a new Horiba iHR550 imaging spectrometer. The light from the plasma flame is collected by a collimator and fed to the spectrometers through an optical cable. The data obtained is used to determine the rotational gas temperature using the LIFBASE program to fit and compare simulated OH and CN-bands to the experimental ones [10]. The electron temperature and electron density are obtained using the line-ratio method [12] and the H_β line broadening [13]. Also, the presence of certain bands in the plasma spectrum is used to determine that the successful production is taking place of reactive species usually associated with the deposition process.

3. Results
Using the LIFBASE software, we fitted the simulated to the experimental spectra to determine the gas temperature (T_e) of the plasma [10]. The parts of spectrum used were the OH (A – X) 0-0 band (305 nm – 315 nm) and the CN (B^2Π – X^2Π) 0-0 band (387.2 nm – 388.4 nm) [11]. Due to the necessity
for controlled environment and pre-treatment of the substrate, the processing chamber was initially filled with Ar/H\(_2\) gas mixtures. The oxygen amount in the chamber strongly decreased as the pre-treatment time and the heater temperature were increased; the OH emission band intensity decreased accordingly. After CH\(_4\) was added to the gas mixture and the methane was pyrolyzed in the plasma column, the CN band intensity increased; this was used to determine the gas temperature.

In the deposition process of vertical nanosheets, a gas mixture Ar/H\(_2\)/CH\(_4\) with volume ratios 180/4/1 was used. In this process, the argon is a working gas for the plasma source, H\(_2\) serves as a catalyst and CH\(_4\) is decomposed in the plasma column and is the source of hydrocarbon, C and C\(_2\) species.

The spectra were used to measure the rotational gas temperature at different substrate/plasma exciter distances (5 – 10 mm) and at different input MW power (6 – 14 W). The results show that as the power is increased and the tube-substrate distance is decreased, the gas temperature rises from 2800 K up to 3800 K. The presence of the intensive swan band in the measured spectra at gas temperatures above 3000 K confirms that the methane decomposition and C\(_2\) radicals production are efficient (figure 2).

The argon lines from the spectra were used to determine the electron temperature (\(T_e\)) and electron density (\(n_e\)) via the line ratio method [12] and the H\(_0\) line broadening [13] as a second method to obtain \(n_e\). During the deposition of graphene nanostructures under the conditions quoted, the plasma parameters were determined to be \(n_e \approx 4.5 – 6\times10^{20} \text{ m}^{-3}\) and \(T_e \approx 1.1\) eV.

The graphene nature of the deposited nanostructures as a thin layer on the nickel-foam wires was confirmed by Raman spectroscopy (figure 3) showing the 2D, D+D' and 2D' peaks.

SEM imaging was used to study the nanostructures’ morphology. It shows that the structures are carbon nanowires when a low power (6 – 9 W) and a large substrate/plasma exciter distance (10 mm) are used. Increasing the power (10 – 14 W) and decreasing the distance changes the morphology of the structures into vertical carbon nanosheets (figure 4). Decreasing the distance even further (< 5 mm) leads to stronger plasma etching processes and removes most depositions from the substrate. The average deposition time for these structures is 8 min; exceeding this time results in the deposition of a thick carbon layer with no visible nanostructures.

Both types of structures required a sufficiently high substrate temperature in the deposition process, which was maintained by a cartridge heater; controlling the temperature within the 600 – 700 \(°C\) resulted in a successful deposition.
Figure 4. SEM image of: A) carbon deposited on nickel-foam wires, B) carbon nanowires deposited at 8 W and 10-mm distance from the exciter, C) image from the top of vertical carbon nanosheets deposited at 12 W and 7 mm distance from the exciter, D) image at an angle of vertical carbon nanosheets deposited at 12 W and 7 mm distance from the exciter.

4. Conclusions
The results are presented of PECVD using an MW plasma source on nickel foam substrate. They demonstrate the validity of the method for controlling the deposition process allowing production of different graphene nanostructures. The key advantage of the described method is the possibility to deposit nanosheets and nanowires at atmospheric pressure. The power requirements of up to 14 W guarantee the cost-effectiveness of the devised system.

Acknowledgements
This work is supported by European research project PEGASUS, H2020, NIS-SU N3257.

References
[1] Bo Z, Mao S, Han Z J, Cen K, Chen J and Ostrikov K (Ken) 2015 Emerging energy and environmental applications of vertically-oriented graphenes Chem. Soc. Rev. 44/8 2108-21
[2] Cai M, Outlaw R A, Butler S M and Miller J R 2012 A high density of vertically oriented graphenes for use in electric double layer capacitors Carbon 50 5481-8
[3] Yuan W and Shi G 2013 Graphene-based gas sensors J. Mater. Chem. A 1/35 10078-91
[4] Bundaleska N, Tsyganov D, Dias A, Felizardo E, Henriques J, Dias F M, Abrashev M,
Kissovs'ki J and Tatarova E 2018 Microwave plasma enabled synthesis of free standing carbon nanostructures at atmospheric pressure conditions Phys. Chem. Chem. Phys. 20 13810-24

[5] Tatarova E et al 2017 Towards large-scale in free-standing graphene and N-graphene sheets Sci. Reports 7 10175

[6] Tatarova E et al 2014 Microwave plasmas applied for the synthesis of free standing graphene sheets J. Phys. D: Appl. Phys. 47/38 385501

[7] Tatarova E, Henriques J, Luhrs C C, Dias A, Phillips J, Abrashev M V and Ferreira C M 2013 Microwave plasma based single step method for free standing graphene synthesis at atmospheric conditions Appl. Phys. Lett. 103/13 134101

[8] Kiss'ovski Zh, Djermanova N, Mitev D and Vachkov V 2014 Substrate temperature control in a system for deposition of carbon nanostructures at atmospheric pressure J. Phys.: Conf. Series 514/1 012007

[9] Mitev D, Dimitrov Zh and Kiss’ovski Zh 2016 Plasma reactor for deposition of carbon nanowalls at atmospheric pressure J. Phys.: Conf. Series 768/1 012017

[10] Luque J, Crosley D R 1999 LIFBASE: Database and Spectral Simulation Program (Version 1.5) SRI International Report MP 99

[11] Nassar H 2012 CN violet system spectrum used as a molecular pyrometer and the influence noise to signal ratio on the temperature values J. Phys.: Conf. Series 370/1 012050

[12] Kiss’ovski Zh, Ivanov A, Iordanova S and Koleva I 2011 Plasma parameters of a small surface-wave discharge at atmospheric pressure obtained by line-ratio method J. Phys. D: Appl. Phys. 44/20 205203

[13] Qian M, Ren C, Wang D, Zhang J and Wei G 2010 Stark broadening measurement of the electron density in an atmospheric pressure argon plasma jet with double-power electrodes J. Appl. Phys. 107/6 063303