Deposition of carbon nanostructures on metal substrates at atmospheric pressure

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Abstract. The microwave-plasma-enhanced CVD of carbon nanostructures at atmospheric pressure allows shorter deposition times and reduces the complexity of the experimental set-up. In our study, the substrate temperature was varied in a wide range (300 – 700 °C) using microwave plasma heating, as well as an additional heater. The distance between the substrate and the plasma flame was also varied in order to establish the conditions for an efficient deposition process, the latter being carried out at specific argon/hydrogen/methane gas mixtures. Optical measurements of the plasma flame spectrum were conducted to obtain the gas temperature and the plasma density and to analyze the existence of reactive species. The carbon nanostructures deposited on the metal samples were investigated by SEM. The relation between the morphology and the gas-discharge conditions is discussed.

1. Introduction

The carbon nanostructures (CNS) attract great interest with their unique electrical, mechanical and optical properties. CNS provide a new route to exploring the novel physics of two-dimensional materials. There are several types of CNS, the most intensively investigated ones being graphene, carbon nanotubes, nanoflakes, nanoribbons, nanowalls and vertically-standing few-layer graphene sheets [1]. Vertical few-layer graphene (FLG) sheets and carbon nanowalls (CNW) draw attention with their properties and specific morphology – intersecting vertical walls with sharp edges and a high surface-to-volume ratio. CNWs have potential applications in microelectronics as sensors, field emitters and supercapacitors [2-4]. Various methods can be used for preparation of graphene – exfoliation, chemical vapor deposition, epitaxial growth, supersonic spraying, intercalation etc. Vertical graphene structures are mainly synthesized by plasma-enhanced chemical-vapor deposition (PECVD). The deposition of FLGs and CNW is conducted usually at a low gas pressure in vacuum chambers, which results in a long period of deposition. A variety of gas discharge plasmas (DC, RF and microwave) are used for CNS deposition. CNSs are also successfully prepared at atmospheric pressure in a normal glow discharge [4] in Ar/H\textsubscript{2}/C\textsubscript{x}H\textsubscript{y} or N\textsubscript{2}/C\textsubscript{x}H\textsubscript{y} gas mixtures. The microwave discharges are usually characterized by high-density plasma and relatively high gas temperature, which allows for efficient decomposition of hydrocarbons. Microwave plasmas are also used for PECVD of carbon nanostructures and, especially, for synthesis of carbon nanotubes [5].
In this study, a novel plasma reactor was used for carbon nanostructures deposition at atmospheric gas pressure. A low-power microwave discharge in a quartz vessel [6] was used to create plasma in argon gas, with CH$_4$ as a precursor and additional H$_2$-gas to improve the deposition process. The chemical composition and diversity of radicals in the plasma jet were investigated by optical emission spectroscopy. The spectra obtained were used to determine the gas temperature, the plasma parameters and the presence of reactive species which are usually associated with the deposition process. The variation of the plasma parameters when varying the distance between the metal substrate and the tube of the plasma source are discussed and the carbon nanostructures deposited are investigated.

2. Experimental set-up and diagnostics

The plasma reactor (figure 1) consisted of a dielectric (quartz) chamber with cylindrical shape including two metal flanges (top and bottom) and a miniature microwave plasma source [6] attached to the bottom flange. The exciter of plasma surface waves had an outer diameter of 3 mm and a 1-mm thick steel capillary as inner conductor. A thin alumina ceramic tube was used as a discharge tube and as a dielectric in the coaxial exciter. This material is able to resist the high gas temperatures of the plasma.

![Figure 1. Experimental set-up and optical diagnostics system.](image)

The plasma source was powered by a signal from an MPG-4M generator (0 – 100 W at a frequency of 2.45 GHz) through a coaxial line. The forward and reflected powers were measured by a Pasternack PE 2219-30 directional coupler. Precise matching to the MW source and minimum reflected power from the plasma source were achieved by a Maury 1878C triple stub. The plasma source could self-ignite in continuous and pulsed regimes at a specific threshold value of the input power. The pulses were generated at a rate in the range 70 – 700 Hz with a duration of 100 μs to 14 ms. The pulse parameters were recorded by a Tektronix TDS 360 oscilloscope. The gas mixture (Ar/H$_2$/CH$_4$) (187 sccm/10 sccm/3 sccm) was fed in through the capillary, the gas flow ratios being controlled by APEX-AX-MC mass-flow meters.

The substrate was positioned directly above the plasma jet. A moveable holder of the metallic substrate, made of stainless steel tube including a Teflon head and an additional heater, allowed us to vary the distance between the substrate and the plasma jet.

The temperature of the substrate was controlled by the current in the additional heater; however, the temperature was also influenced by the distance to the plasma source and by the microwave pulse parameters (frequency and duration of the microwave signal). Additional voltage (–100 V) was applied to assist the vertical growth of the carbon nanostructures. The direct current induced by the
DC voltage caused a further heating of the substrate. The temperature of the substrate was measured by an electronic system with a thermocouple [6].

The emission spectra from the excited species formed in the active region of the plasma jet were investigated by an HR Ocean Optics spectrometer (figure 2). The light from the plasma column was collected by a lens system (collimator) coupled with an optical fibre; the raw data was processed by a PC.

The gas temperature was obtained from the OH-emission band using LIFBASE software simulations compared with the experimentally acquired band. The electron temperature and density were investigated using the line-ratio method [7, 8].

3. Results
The plasma reactor was designed for deposition of carbon nanostructures on small Ni and Cu metallic plates. Before placing the plates in the reactor, they were cleaned for 5 minutes in 10% hydrofluoric acid bath in order to remove the organics and the oxides. After positioning the plate above the plasma source in the reactor, the substrates were subjected to plasma cleaning and activation in argon-hydrogen plasma at substrate temperatures below 400 °C for half an hour. During this process, the oxygen and the nitrogen should reach minimum concentrations in the reactor chamber. The experiments were carried out with a microwave signal at a rate of 100 Hz and pulse duration in the range 100 μs – 4 ms, which ensured a gradual increase of the substrate temperature and a stable plasma operation. The total gas flow was 200 sccm. The methane flow was set in the range 2 – 5 sccm during the deposition process. The analysis of the spectrum obtained by optical spectroscopy showed the presence of reactive species, as CH, C, and a Swan band, which proved that the decomposition of the methane was effective under these experimental conditions.

The gas temperature in the plasma jet was investigated by OH emission band (305 nm – 315 nm) simulation using the LIFBASE software. Comparing the best fit with the experimental spectrum, the averaged gas temperatures obtained for different distances between the tube and the substrate, namely, 0.2, 0.5 and 1 cm, were 2100 K, 2000 K and 1400 K.

The simultaneous determination of the electron temperature and plasma density by the emission line ratios for low-temperature plasmas in argon gas was described in detail in [7, 8]. It is based on the collisional-radiative model (CRM) of excited particles. The model includes 21 rate balance equations for excited Ar atoms (Ar(1s5-1s1), Ar(2p10-2p1), Ar(2s3d), Ar(3p)), positive Ar²⁺ ions and excited molecules Ar²⁺. Studies on the electron temperature and plasma density dependences on the line-ratios \( I_{727.3}/I_{114.7} \) and \( I_{338.9}/I_{727.3} \) [8] have shown that they are suitable for simultaneous determination of the plasma parameters. The isolines of the above-mentioned line-ratios had different behavior as \( T_e \) and \( n_e \) were varied. The cross-point of the isolines determined the \( T_e \) and \( n_e \). The cross-point method was applied and initial results for different distances between the substrate and the discharge tube are shown in figure 3. The plasma parameters at a distance of 0.2 cm between the tube and substrate were close to the parameters obtained in the plasma column in the discharge tube [8, 9], while at 0.5 cm the electron temperature decreased slightly (1.5 ± 0.2 eV). At longer distances (1 cm), the values of the electron temperature and plasma density (1.4 ± 0.2 eV and 0.3×10¹⁵ cm⁻³) were lower because the volume of the plasma column increases while the microwave energy for sustaining the discharge is constant. Substrates in the deposition process were Ni and Cu plates with an area up to 25 mm². A few Cu substrates were chosen for SEM imaging, which showed the presence of black layers visible by an optical microscope.
Figure 3. \( T_e, n_e \) dependence of the experimental line-intensity ratios \( I_{\lambda 227}/I_{\lambda 14.7} \) and \( I_{\lambda 228}/I_{\lambda 227.3} \) for distance between the end of the discharge tube and the substrate a) 0.2 cm; b) 0.5 cm; c) 1 cm.

Figure 4. Deposited carbon structures: a) layer visible by optical microscopy on a copper substrate and b), c) SEM images of carbon nanostructures at different distances.

These observations showed that the black layers were in circumferences exactly around the surface directly exposed to the plasma jet. This result gives reason to assume that the most suitable conditions of deposition are in the discharge afterglow [10].

The SEM images on figure 4 (b) and 4 (c) exhibit initial forms of carbon nanowalls. The process of deposition needs optimization of the conditions. Similar structures as in figure 4 (c) have been observed in experiments (figure 5 in [11]) in a DC discharge at atmospheric pressure in the 3-min period from the beginning of the deposition process of carbon nanowalls. This is the reason for conducting experiments with varying the distance between the plasma source and substrate in order to
optimize the deposition process with respect to the gas temperature and the density of the reactive species. Increasing the distance between the substrate and the discharge tube resulted in a decrease in the gas temperature. Further investigations by Raman spectroscopy and/or XPS are needed to characterize the deposited nanostructures. Future works will include additional investigations of the plasma parameters and the deposition process.

4. Conclusions
We presented experiments using a plasma reactor with a surface-wave-sustained discharge in an argon/hydrogen/methane gas mixture at atmospheric pressure and additional substrate heating for deposition of carbon nanostructures. By varying the substrate-to-discharge tube distance and analyzing the resulting changes in the plasma parameters, we demonstrated that this reactor is suitable for deposition of carbon nanostructures and that this process occurs mainly in the discharge afterglow.

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References

[1] Wu Y H, Yu T and Shen Z X 2010 J. Appl. Phys. 108 071301
[2] Jiaxin Zheng, Lu Wang, Ruge Quhe, Qihang Liu, Hong Li, Dapeng Yu, Wai-Ning Mei, Junjie Shi, Zhengxiang Gao and Jing Lu 2013 Sci. Rep. 3 1314
[3] Wenjing Yuan and Gaoquan Shi 2013 J. Mater. Chem. A 1 10078
[4] Cai M, Outlaw R, Butler S and Miller S 2012 Carbon 50 5481
[5] Jasek O, Synek P, Zajickova L, Elias M and Kudrle V 2010 J. Electrical Eng. 61 311
[6] Kiss’ovski Zh, Djermanova N, Mitev D and Vachkov V 2014 J. Phys.: Conf. Series 514 012007
[7] Iordanova S and Koleva I 2007 Spectrochimica Acta. B 62 344-56
[8] Kiss’ovski Zh, Ivanov A, Iordanova S and Koleva I 2011 J. Phys. D: Appl. Phys. 44 205203
[9] Kiss’ovski Zh, Kolev M, Ivanov A, Lishev St and Koleva I 2009 J. Phys. D: Appl. Phys. 42 182004
[10] Tatarova E, Henriques J, Luhrs C, Dias A, Philips J and Abrashev A 2013 App. Phys. Lett. 103 134101
[11] Zheng Bo, Kehan Yu, Ganhua Lu, Pengxiang Wang, Shun Mao and Junhong Chen 2011 Carbon 49 1849