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Plasma reactor for deposition of carbon nanowalls at atmospheric pressure

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Abstract. In this study a novel plasma reactor for deposition of carbon nanowalls at atmospheric pressure is constructed and characterized. A low power microwave discharge is used as a plasma source and working gas of $Ar/H_2/CH_4$ gas mixture. The substrate is heated by plasma flame and its temperature is in the range 600-700 C. The chemical composition of the plasma and the gas mixture effect on the concentration of the various particles in the plasma is investigated by optical emission spectroscopy. The emission spectrum of the plasma jet in $Ar/H_2/CH_4$ mixture shows the presence of carbon (Swan band) and an intensive line of CH (388 nm), which are necessary species for deposition of carbon nanostructures. Additional voltage in the range from -20 V to -100 V is applied in order to ensure the vertical growth of graphene walls. Results of deposited carbon nanostructures on metal substrate are shown.

1. Introduction

Graphene and carbon nanostructures of several graphene layers draw attention with numerous applications in microelectronics [1], for sensors [2] and super capacitors [3]. In recent years research has been focused on deposition of vertically oriented graphene (carbon nanowalls) due to its specific morphology - intersecting vertical walls with sharp edges and enormous ratio of surface area to the volume. Plasma-enhanced chemical vapor deposition (PECVD) is a key technology for the preparation of carbon nanowalls. Variety of gas discharges (DC, RF and microwave) are used for deposition of nanowalls, but they operate in a vacuum chamber at low pressure, which leads to long periods of deposition. In recent years carbon nanowalls are successfully obtained in a normal glow discharge at atmospheric pressure by plasma enhanced chemical vapor deposition [4] in $Ar/H_2/CH_4$ gas mixture by addition of H_2O. The mirror-polished stainless steel anode plate is used as a substrate for deposition. Microwave plasmas are widely used for synthesis of graphene [5 and 6] and carbon nanostructures [7]. Microwave discharges are characterized with high density plasma and relatively high gas temperature, which cause quick decomposition of hydrocarbon gas and production of many reactive species.

In this study a novel plasma reactor for deposition of carbon nanostructures is presented. A low power microwave discharge is used to create plasma at atmospheric pressure in a gas mixtures of $Ar/H_2/CH_4$. The chemical composition of the plasma flame is investigated by optical emission spectroscopy and results show that the plasma in the reactor is suitable for deposition of carbon


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nanowalls at atmospheric pressure. Obtained plasma parameters and measurements of substrate temperature demonstrate the possibility for heating of substrate to temperatures above 600 C.

2. Experimental set-up and diagnostics

A plasma reactor is presented in figure 1. It consists of dielectric (quartz) chamber with cylindrical shape with two metal flanges (top and bottom). The miniature microwave plasma source is fed with a signal from MPG – 4M generator (0-100W; 2.45 GHz) through a coaxial line. The exciter of plasma surface waves has an outer diameter of 2 mm and 1mm thick steel capillary as inner conductor. The forward and reflected powers are measured with Pasternack PE 2219-30 directional coupler. In order to withstand the high gas temperature a thin alumina ceramic tube is used as discharge tube and as a dielectric in the coaxial exciter.

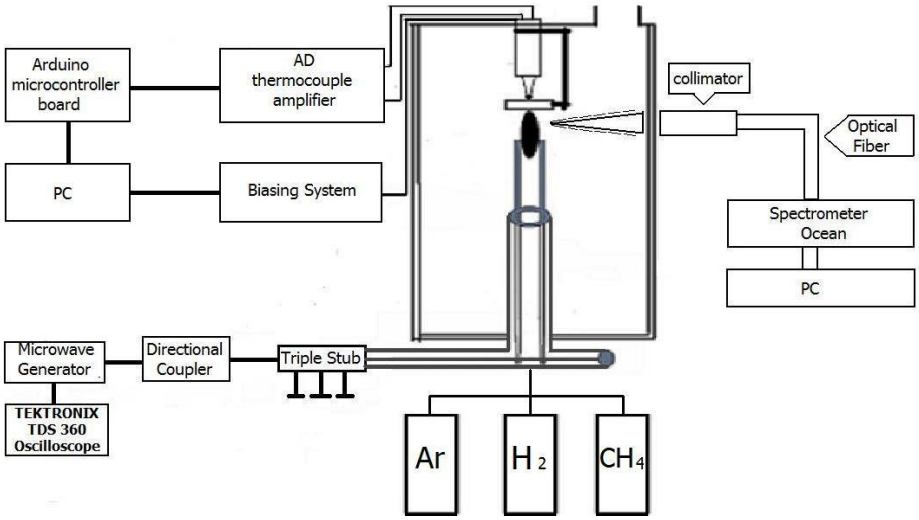


Figure 1. Experimental set-up and diagnostics

The tuning of the source at 2.45 GHz is carried out by a Maury 1878C triple stub. Indication for precise matching is the minimum of reflected power. The plasma source can self-ignite in continuous and pulse regimes at a specific threshold value of the input power. Pulses have frequency in the range of 70-700 Hz with duration of 100 μs to 14 ms. Pulse parameters are recorded with Tektronix TDS 360 oscilloscope. A gas mixture ($Ar/H_2/CH_4$) let through the capillary and gas flow ratios are controlled by APEX-AX-MC mass-flow meters. The holder of the metallic substrate for deposition is made of stainless steel tube, that includes teflon head. Heating of the substrate is controlled mainly by pulse frequency, duration and distance between the plasma source and the substrate [8]. To reach the required substrate temperature for certain compositions of nanostructures a mini heater is also used. Additional voltage in the range -20 V to -100 V is applied to the substrate to decrease the time needed for surface cleaning and to assists the vertical growth of graphene walls. The direct current due to this voltage causes further heating of the substrate. The temperature of the substrate is measured by an electronic system with a thermocouple [8].

The species formed in the active region of the plasma jet in a pulse regime are investigated with HR Ocean Optics spectrometer. The light from the plasma column positioned between the discharge tube end and metallic substrate is collected by a lens system (collimator) coupled with an optical fibre and the raw data is processed with a PC.

3. Results

The plasma reactor is constructed for deposition of carbon nanostructures on small metallic plates (1.5 mm x 1.5 mm). Ni and Cu plates are subjected to a chemical cleaning by ethanol followed by

10% hydrofluoric acid bath. After positioning the plate above the plasma source in the reactor, it is subjected to plasma cleaning in argon-hydrogen plasma at substrate temperatures below 400 C for a half hour. Experiments are carried out at frequency 100 Hz, microwave signal and pulse duration in the range 100 μs - 4 ms, which ensures gradual increase of the substrate temperature and stable plasma operation. The gas temperature, obtained via simulation of OH (306-310nm) band, reaches 2000 K at the tube end. In the process of understanding the deposition of carbon nanostructures, optical spectroscopic measurements were performed of two different gas mixtures - an Ar /H_2 (240 sccm/10 sccm) and Ar/H_2/CH_4 (239 sccm/10 sccm /1 sccm). The chemical decomposition of methane in the plasma and the influence on the appearance of the various reactive species of the gas volume ratios in the mixture are investigated using the emission spectra of the plasma jet.

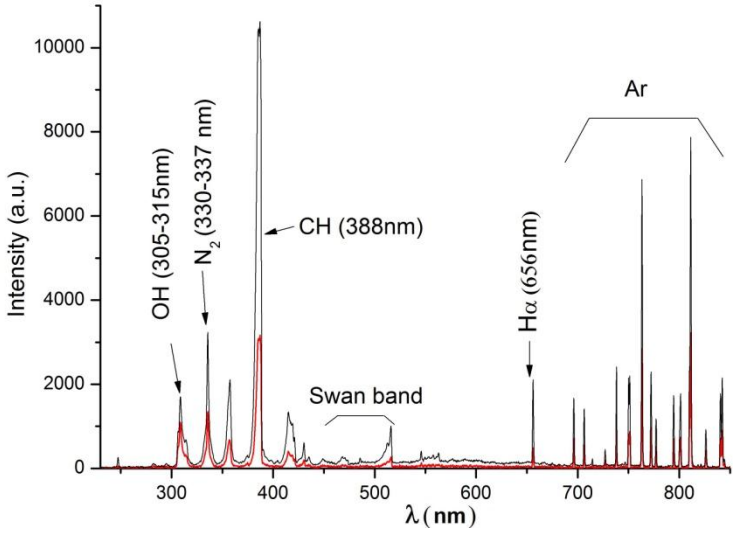


Figure 2. Emission spectra of plasma flame in Ar/H_2 (red) and Ar/H_2/CH_4 (black) gas mixtures

Argon spectral lines are recorded at the wavelength range from 690 to 900 nm under different experimental conditions explored in the study. An example of spectrogram in the first gas mixture (Ar/H_2) is shown in figure 2 (red line). Atomic argon lines in the red/near-infrared region are clearly dominating the spectra due to the contribution of the radiative transitions between the excited levels of the $3p^5 4s$ and $3p^5 4p$ configurations. Strong H_α line and OH band are also observed in the spectrum, while the intensity of N_2 band decreases with the pretreatment time.

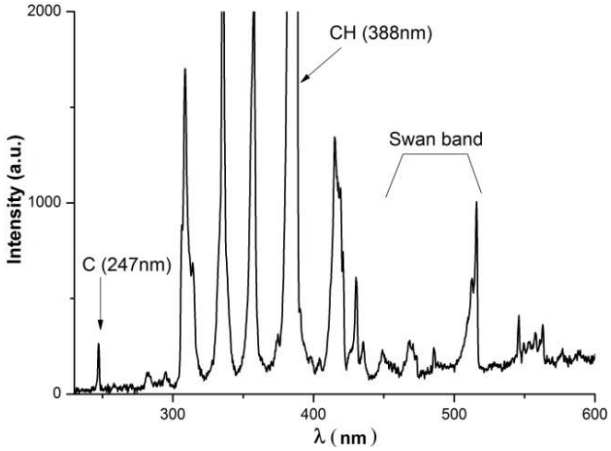


Figure 3. Spectrum of Ar/H_2/CH_4 plasma

At substrate temperature above 600 C in the $Ar/H_2/CH_4$ plasma a recorded spectrogram (figure 2) is used for identification of excited species. Due to decomposition of methane additional lines are observed (Figure 3). Spectrum shows presence of atomic carbon line at 247.8 nm, C_2 band system (Swan band) and an intensive CH (388nm) line. The presence of these species is a prerequisite for carbon nanostructures deposition.

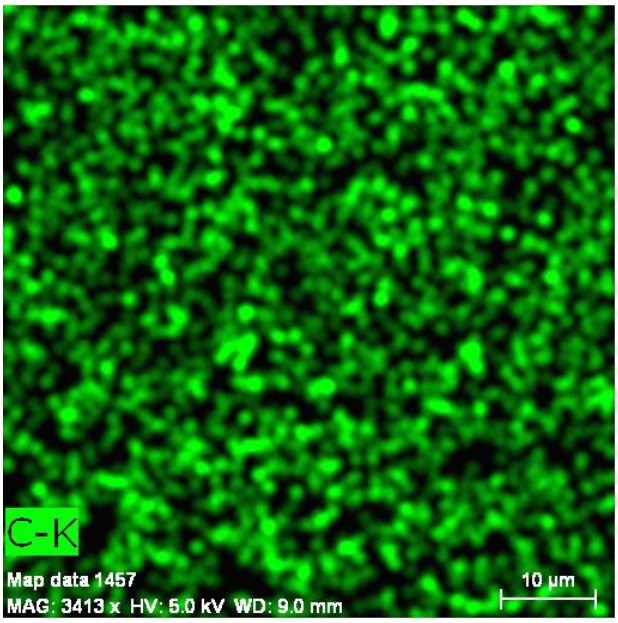


Figure 4. SEM image of deposited carbon on nickel substrate.

The comparison of spectra, registered in plasma jet in Ar/H_2 and $Ar/H_2/CH_4$ gas mixtures, confirms the effectiveness of the microwave discharge of the methane decomposition and the creation of numerous reactive species with high concentrations. The SEM image of carbon on Ni surface is presented in figure 4. It shows first step of growth of carbon nanostructures at substrate temperature of 650 C. Further investigations will include deposition at higher substrate temperatures and optimization of the deposition process.

4. Conclusion

Plasma reactor with microwave source works with argon, hydrogen and methane gas mixture at atmospheric pressure including an additional substrate heating. The registration of key reactive species (C, CH, Swan band) by optical spectroscopy and the achieved temperatures (650 C) prove the potential of the plasma reactor to produce specific carbon nanostructures.

Acknowledgements

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References

[1] Jiaxin Zheng, Lu Wang, Ruge Quhe, Qihang Liu, Hong Li, Dapeng Yu, Wai-Ning Mei, Junjie Shi, Zhengxiang Gao Jing Lu, *Scientific Reports* **3**, 1314 (2013)
[2] Wenjing Yuan and Gaoquan Shi, *J. Mater. Chem.* A,**1**, 10078 (2013)
[3] Cai M, Outlaw R, Butler S, Miller S, *Carbon*, **50**, 5481 (2012)

[4] Bo Zh, Yu K, Lu G, Wang P, Mao S, Chen J, *Carbon*, **49**, 1849 (2011)
[5] Tatarova E, Henriques J, Luhrs C, Dias A, Philips J, Abrashev A, *App. Phys. Lett.* **103**, 134101 (2013)
[6] Tatarova E, Dias A, Henriques J, Botelho do Rego AM, Ferraria AM, Abrashev MV, Luhrs CC, Phillips J, Dias FM and Ferreira CM, *J. Phys. D: Appl. Phys*. **47** 85501 (2014).
[7] Jasek O, Synek P, Zajickova L, Elias M, Kudrle V, *J Electrical Eng*. **61**, 311(2010)
[8] Kiss'ovski Zh, Djermanova N, Mitev D and Vachkov V. *J.of Physics: Conf. Series* **514**, 012007 (2014)