THE INFLUENCE OF GAS ADMIXTURES ON THE SYNTHESIS OF GRAPHENE NANOSHEETS IN ARGON MICROWAVE PLASMA TORCH DISCHARGE

TOMAN Jozef[1], JAŠEK Ondřej[1], JURMANOVÁ Jana[1]

[1] *Masaryk University, Faculty of Science, Department of Physical Electronics, Brno, Czech Republic, EU*
jtoman@mail.muni.cz

Abstract

In this work possibility of the synthesis of two-dimensional graphene nanosheets in gas phase was studied. We used microwave plasma torch discharge (2.45 GHz, 210 W) operating at atmospheric pressure conditions to synthesize carbon nanosheets with rectangular shape and typical size of hundreds of nanometres. The torch discharge was ignited in argon flowing through the central channel of the nozzle. Liquid ethanol, whose vapours were led to the discharge by carrier gas - argon, was selected as a precursor. The mixture of ethanol vapour, argon and oxygen or hydrogen was introduced to the discharge through outer channel of the nozzle. Decomposition of ethanol vapours, at specific deposition conditions, led to the synthesis of graphene nanosheets. The synthesized material was collected on the silicon substrate placed in the sample holder situated few centimetres above the discharge. The influence of different amount of oxygen or hydrogen in the gas mixture on the properties of synthesised graphene nanosheets was investigated. Such prepared samples were analysed by scanning electron microscopy, Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDX). The discharge was examined using optical emission spectroscopy.

Keywords: Graphene, nanosheets, microwave plasma, torch discharge

1. INTRODUCTION

Recently, there has been increased interest in using plasma techniques for creating graphene-based materials like carbon nanotubes (CNT), nanofibres, graphene, nanoribbons or nanoflakes. The production of graphene-based materials requires specific conditions such as sufficiently high energy of atomic and molecular species supplied to the growth zone and balanced influx of carbon particles. One of the most used techniques to provide suitable conditions for graphene synthesis is chemical vapour deposition (CVD). Numerous achievements were made since 2008, when a growth of large area single- to few-layer graphene at ambient pressure on metallic substrate was demonstrated for the first time [1]. Large-area synthesis of graphene layers was successful on various metallic substrates, using different precursor mixtures and subsequently the graphene films were transferred to various non-metallic substrates. Such prepared stretchable graphene films exhibit outstanding optical, electrical and mechanical properties which enable numerous applications [2, 3]. However, this technique requires a very high temperature ranging from 1000°C to 1300°C and transfer of deposited films onto non-metallic substrates.

Alternatively, plasma-enhanced chemical vapour deposition (PECVD) has been developed to synthesize graphene on a relatively large scale. The unique chemically active plasma environment provides suitable conditions for creating high yields of clean and highly ordered graphene sheets with well controlled structural qualities. Many applications exploit the ability of plasmas to break down complex molecules considering that plasma systems provide simultaneously high temperatures and a highly reactive environment.

First attempts to investigate synthesis of graphene-based materials in the presence of plasma sources were carried out in low pressure plasma environments. A technique using microwave (MW) PECVD for the synthesis of vertically aligned, high quality, crystalline, freestanding few-layer graphene (FLG), just 4 to 6 atomic layers thick and up to several micrometres wide. Various substrates were used and a mixture of CH_4/H_2 was used as a precursor in the synthesis of FLG for various growth times ranging from 1 to 3000 s [4]. A radio-frequency expanding plasma beam in combination with magnetron sputtering for catalyst deposition was used for

graphene film growth. A detailed study of plasma-chemical processes in an $Ar/H_2/C_2H_2$ plasma environment was carried out and connected with the synthesis of carbon nanowalls of different quality [5]. A DC high current divergent anode-channel plasma torch can also be used for the growth of graphene-like materials by decomposition of propane-butane and methane in a thermal plasma jet [6].

Alternative approaches, which deal with atmospheric-pressure plasma environments, were also studied, using different plasma sources and precursors. Free-standing ultrahigh-quality graphene has been created without the use of substrates for the first time through gas-phase microwave synthesis in a single step method. An aerosols consisting of argon gas and liquid ethanol droplets were delivered directly into argon plasma generated using an atmospheric-pressure microwave plasma torch [7]. Also, different hydrocarbon precursors were used with the same method and synthesis of graphene was reported using dimethyl ether (DME) as a precursor. Based on these findings, ethanol and DME could have the ideal ratio of C, H and O atoms for graphene synthesis [8]. A synthesis of few layer graphene with small amount of defects was reported using microwave atmospheric pressure plasma driven by surface waves. To synthesize graphene sheets, evaporated ethanol molecules carried through argon plasma together with specific deposition conditions had to be achieved [9].

In this work, we have studied synthesis of graphene nanosheets using argon microwave plasma torch discharge at atmospheric pressure conditions and the influence of hydrogen or oxygen admixtures on the structure of prepared graphene material.

2. EXPERIMENTAL

The experimental equipment consisted of a microwave (MW) generator, working at a frequency of 2.45 GHz, 2 kW maximum power, with a standard rectangular waveguide, transmitting the MW power through a coaxial line to a hollow nozzle electrode. Ferrite circulator protected the generator from the reflected power by re-routing it to the water load. Matching of the plasma load to the line impedance was achieved by a 3-stub tuner. The gases are supplied to the discharge chamber through the nozzle which has two gas channels. The inner channel, in the nozzle axis, is used for introduction of working gas - argon and subsequent ignition of plasma. The outer channel is used for introduction of carrying gas with precursor vapours into the plasma environment. Reactor chamber consists of a quartz tube, 8cm in diameter, which is 15 cm long. Both ends are fixed to stainless steel caps by elastic silicon bands. A schematic view of the experimental set-up with a detailed view of the nozzle configuration is shown in **Figure 1**. More details about the experimental set-up, discharge characteristics and deposition of other carbon nanostructures can be found in previous publications [10, 11].

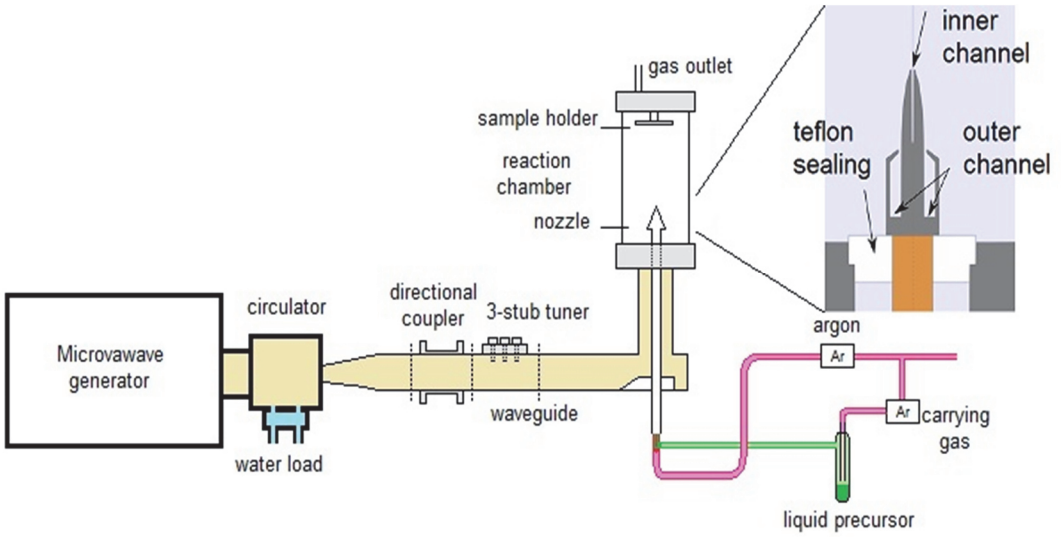

Figure 1 Experimental setup for synthesis of graphene flakes by decomposition of ethanol precursor in microwave plasma torch discharge with a detailed view of the nozzle [12]

Samples were characterized by Raman spectroscopy. Raman spectroscopy was carried out using HORIBA LabRAM HR Evolution system with 532 nm laser, using 100 x objective and 25 % ND filter in the range from 1000 to 3200 cm^{-1}. Samples were imaged with Tescan scanning electron microscope (SEM) MIRA3 with Schottky field emission electron gun equipped with secondary electron (SE) and back-scattered electron (BSE) detectors as well as Oxford Instruments EDX analyser.

3. RESULTS AND DISCUSSION

3.1. Synthesis of graphene nanosheets by decomposition of ethanol vapours

The deposited material properties changed with the variation of deposition conditions. During the experiments, following experimental parameters were changed: the microwave power P, the flow of working gas - argon - through inner channel Ar_c and the flow of carrying argon with ethanol vapours Ar_b. As a result, we were able to adjust the deposition process to such an extent, that the produced flakes consisted of 2 graphene layers (GV1). **Table 1** sums up deposition conditions of experiments discussed in this article. **Figure 2** shows Raman spectra of the experiment GV1 and a SEM image of GV2. The SEM image shows, that the deposited material consists of layered structures, approximately 500 nm in diameter. Raman spectroscopy, as a versatile tool for graphene material analysis suggests, that prepared graphene flakes consist of 2 to 4 graphene layers [13].

Table 1 Experiments discussed in the article

Sample	Ar_c [sccm]	Ar_b [sccm]	H_2 [sccm]	O_2 [sccm]	I_{2D}/I_G	FWHM 2D [cm^{-1}]
GV1	500	700	-	-	1.80	56.8
GV2	420	400	-	-	1.39	60.8
GV3	500	700	-	-	0.91	66.9
GV4	500	700	-	10	1.13	64.5
GV5	500	700	-	50	1.13	64.5
GV6	500	700	10	-	0.40	66.0
GV7	500	700	25	-	0.33	69.6
GV8	500	700	100	-	-	-

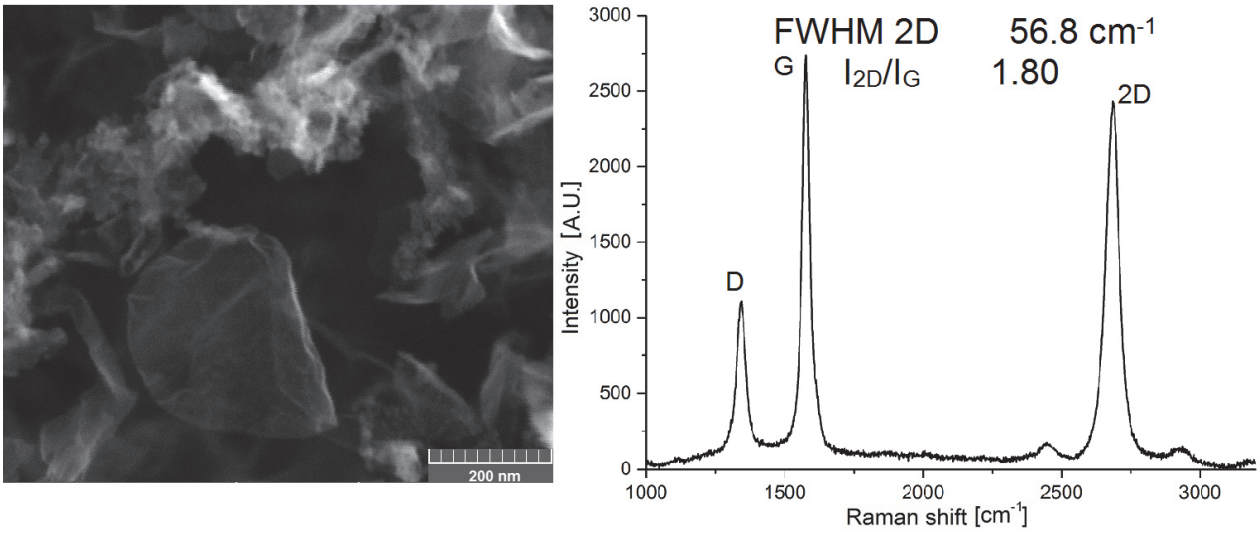

Figure 2 (A) SEM image of prepared graphene flakes (GV2); (B) Raman spectroscopy of GV1

3.2. Precursor consisting of ethanol vapours with gas admixtures

Another six experiments were carried out and the influence of gas admixtures was investigated. The difference between these six experiments was only in the amount of hydrogen or oxygen introduced into plasma environment during the deposition process. **Figure 3a** compares Raman spectroscopy of material prepared during the experiments GV3, GV4 and GV5. In the range of 0 sccm to 50 sccm of oxygen admixture, we did not observe a significant change in shape of Raman spectra. Different situation occurred when molecular hydrogen was introduced to plasma discharge. **Figure 3b** shows Raman spectra of three experiments, where different amount of hydrogen in the range of 10 sccm to 100 sccm was admixed with ethanol vapours carried by argon. It is clear, that the quality of graphene gradually decreases with increasing amount of molecular hydrogen. To compare with previous work dealing with graphene synthesis in MW plasma [14], a positive influence of smaller amount (1 sccm) of hydrogen on the material quality was reported. On the other hand, presence of aditional hydrogen resulted in formation of hydrocarbon species and decreased amount of graphene material.

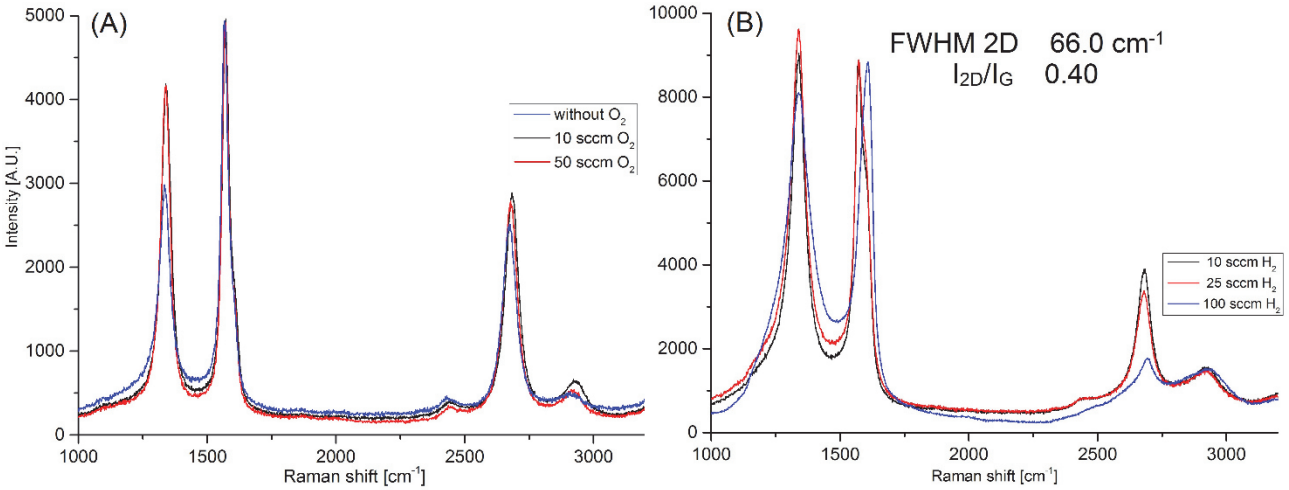

Figure 3 Raman spectroscopy of prepared graphene material in presence of: (A) oxygen admixture or any admixture; (B) hydrogen admixture

4. CONCLUSION

We successfully synthesised graphene flakes in microwave plasma torch at atmospheric pressure conditions. Prepared structures consist of 2 to 4 layers of graphene and the flake size is approximately 500 nm in diameter. With increasing amount of hydrogen (from 10 sccm to 100 sccm) admixed with the precursor vapours we observed a decreasing quality of prepared graphene material. On the other hand, Raman spectroscopy showed that oxygen, in the range of 10 sccm to 50 sccm has no significant impact on the quality of prepared material. Due to the layered structure and high surface area of prepared material, applications in the field of sensors are of increased interest for our future research.

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