Influence of admixtures on atmospheric pressure microwave plasma torch used for graphene nanosheets synthesis

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The influence of molecular admixtures on processes in microwave plasma torch operating in atmospheric pressure argon was investigated. The goal was to to optimise working gas composition during graphene nanosheets plasma deposition from ethanol as precursor. The admixtures affected the process of filamentation, plasma temperature and properties of the deposited material.

1. Introduction

Atmospheric pressure microwave plasma torch is versatile device which can operate under wide range of experimental conditions. It was successfully used for various applications, such as advanced material synthesis, VOC decomposition, plasma surface treatment or as a source for analytic spectrochemistry.

Its operation at atmospheric pressure induces plasma channel contraction and filamentation. This spatial inhomogeneity, while advantageous from the point of view of power density, can negatively affect the intended application. It is known that presence of various admixtures can strongly influence the filament formation and behaviour.

In this contribution such influence is investigated with the goal of optimizing the plasma deposition of graphene nanosheets.

2. Experimental

The plasma torch was excited by 2.45 GHz magnetron (Muegge) with power variable in 10-300 W range. Microwave waveguide line was quite standard, i.e. magnetron head, circulator, reflectometer and matching. It ended with a waveguide-to-rigid coaxial transition, able to operate at substantially higher power levels than flexible coaxial cable.

Its central conductor (6 mm diameter) was hollow which enabled passing of multiple gas lines inside. It ended in exchangeable carbon or stainless steel nozzle with dual flow configuration. The central (axial) channel (0.8 mm diameter) was used for argon (300-1000 sccm). While the intended admixtures can be introduced directly to the central channel it was advantageous to use a secondary channel (annulus with outer radius 8.4 mm and inner radius 7.7 mm), as this configuration increases a stability of operation.

For graphene synthesis, ethanol admixture was used. It was vaporised in bubbler by the carrying argon gas (10 - 700 sccm). The flow of the carrying gas controlled the amount of ethanol in 0-10 sccm range. Other admixtures (O_2, H_2, N_2) were also used, either alone or in combination with the ethanol.

Plasma reactor consisted of fused silica tube (80 mm diameter, 200 mm long) terminated by duralumin flange. Deposited material was Gas collected from the reactor walls and/or the flange. Samples were analysed using Raman spectroscopy and scanning electron microscopy (SEM).

Optical emission spectroscopy was carried out using Jobin Yvon Triax 550 spectrometer. Rotational OH temperature was calculated by *MassiveOES* software [1]. High resolution digital imaging used consumer digital camera Nikon D5200 with Nikkor 200 mm lens.

3. Results and discussion

Microwave plasma torch as many other atmospheric pressure discharges exhibits a tendency to strong radial contraction of the plasma, forming a relatively thin and dense plasma channel. For detailed discussion of underlying phenomena, see e.g. [2].

When a small amount of hydrogen is introduced to the outer channel, the filamentary character of the plasma is maintained (see Fig.1) while its appearance changes. Molecular admixture, due to its low lying excitation levels effectively removes the energy from electrons and so the plasma channel length decreases. Reddish colour is easily attributed to H_α emissions.

One may observe also changes in radial emission profile, as the discharge becomes more diffusive near the tip.

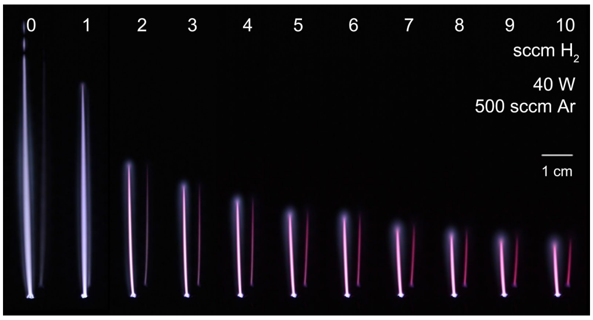

Fig. 1. Influence of hydrogen admixture on appearance of the plasma filament. The filament is reflected by the silica wall, forming false second filament to the right.

The presence of molecular admixture strongly affects the energy transfer from electrons to a movement of atoms/molecules. In pure Ar, the electronic excitations do not couple well with the translations, making the plasma rather cold. With admixtures, the plasma becomes much hotter. From Fig.2, where OH rotational temperatures are plotted, it is seen, that the effect is not same for all admixtures. Effect of hydrogen is strongest, while nitrogen and oxygen behave nearly same. The curve for ethanol does not exhibit a saturation in the observed range.

Gas admixtures influence a balance between C/H/O. It was reported by [3] that ethanol and dimethyl ether (DME) have the same C/H/O ratio and can be used as a precursor for graphene synthesis. In our investigation, if several sccm of O_2 were added to 2 sccm of ethanol only gas products were formed during the synthesis. In the case of H_2 admixture a yellow polymer-like amorphous layer was formed. This result is in contradiction with results achieved by Tsyganov et al.[4], where addition of 1 sccm of H_2 into surface wave discharge led to increased graphene nanosheets quality.

When the ethanol flow rate was increased to 10 sccm and flow rates of oxygen and hydrogen were varied from 10 to 50 sccm, the amount of defects in the graphene nanosheets structure was increasing with amount of admixture gas as shown by SEM and Raman spectroscopy.

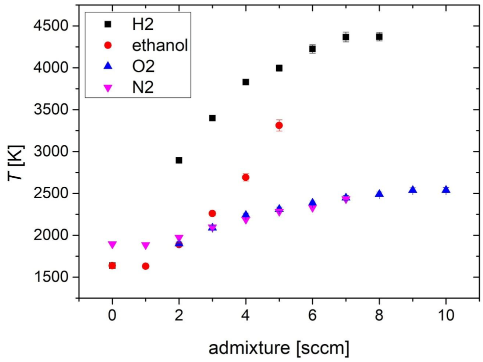

Fig. 2. Evolution of plasma temperature (from OH rotation) with increasing admixture.

4. Conclusion

We investigated influence of reactive gas admixture on the stability and filament formation in the dual-channel microwave plasma torch discharge. The addition of hydrogen containing gases, H_2 and ethanol, led to substantial increase of discharge temperature and in case of higher flow rates of ethanol to the formation of defective graphene nanosheets.

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References

1. J. Voráč et al., Plasma Sourc. Sci. Tech. 26(2) (2017) 025010.
2. Yu. B. Golubovskii et al., Plasma Sourc. Sci. Tech 20 (5) (2011) 053002
3. A. Dato, M. Frenklach, New Journal of Physics 12(12) (2010) 125013.
4. D. Tsyganov et al., Plasma Sourc. Sci. Tech. 25 (1) (2016) 015013.