Influence of molecular admixtures on filamentation in microwave plasma torch

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Introduction

Microwave (MW) discharges are one of the most flexible plasma devices operating under wide range of experimental conditions which makes them suitable for many practical applications. High frequency nature of MW discharges limits the power transfer by skin effect, leading to a splitting of a single plasma channel into spatially inhomogeneous and possibly temporally unstable plasma filaments at atmospheric pressure [1, 2]. In contrast, most applications require homogeneous, stable and repeatable operating conditions. Detailed study of filament formation and sustaining is therefore of utmost importance for both basic and applied plasma science.

Operation at atmospheric pressure often leads to a presence of small amount of impurities due to adsorbed gases, water vapour, gas leaks of ambient air, or electrode sputtering. Targeted admixing of common molecular gases is therefore a good way to study their influence.

Moreover, in most applications, some admixture (precursor, etching agent, etc.) is added intentionally. In our case of graphene nanosheet synthesis a carbon based precursor is needed. In study by Dato et al. [3] it was shown that MW plasma decomposition of ethanol or dimethyl ether (DME), exhibiting identical stochiometry, have the ideal ratio of C:H:O for controllable graphene synthesis which can be directly influenced by an amount of admixture.

Recently, we have discussed influence of plasma stability on the synthesis of graphene nanosheets in dual-channel MW plasma torch (MPT) discharge [4] and showed that for given combination of plasma power, argon and ethanol flowrate various types of carbon nanostructures could be synthesised.

Therefore, in this work we study the influence of molecular admixtures, relevant for graphene synthesis in atmospheric pressure MW plasma, on stability and properties of initial plasma filament and its properties.

Experimental

We investigated a filamentary regime in MPT plasma, operated mainly in atmospheric pressure argon. Important experimental parameters were the input MW power, argon flowrate and amount (0-2%) of admixture (O_2, H_2, N_2, Ar+EtOH - argon passing trough a bubbler with ethanol, carrying its vapours in ratio 1/100). This regime was studied with an outlook to a graphene synthesis as described in our previous work [4].

The experimental equipment (Fig. 1) consisted of a microwave generator (2.45 GHz, 2 kW max. power), connected to a standard rectangular waveguide and transmitting the MW power through a waveguide-coaxial transition to a hollow nozzle electrode. The main working gas (Ar) was supplied to the plasma through the central channel of this electrode, made of graphite. The electrode was placed inside a reactor chamber, consisting of 20 cm long fused silica tube with 8 cm diameter and terminated by aluminium flange with outlet. The chamber was electromagnetically shielded by metallic mesh enclosure.

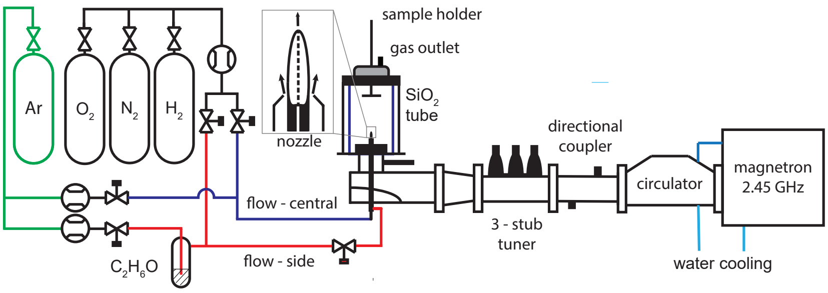

Figure 1: *Experimental set-up.*

Properties of the plasma were investigated using several techniques. Digital imaging was used for geometrical analysis of filaments produced. Optical emission spectroscopy was used for analysis of plasma emissions (AvaSpec 200-1000 nm), detecting population of species present and for calculation of the gas temperature (JY Triax 550). MassiveOES software was used for fitting the experimental spectra. Microwave interferometry (34 GHz) was used for measurement of electron densities.

Results and discussion

Laminar atmospheric MPT forms a uniform, bright, stable argon filament. Its geometry depends linearly on input power until certain threshold level. As absorbed power is limited by a skin effect, higher power causes the splitting of the filament. Molecular admixture has a direct effect [2] in homogenisation of originally filamentary discharge, mostly due to energy loss in rotational and vibrational excitations.

Among dominant species in argon plasmas are argon metastable and resonant states and ions Ar^+, Ar_2^+. According to [5] the dissociative recombination of Ar_2^+ is the main mechanism for discharge contraction in pure argon plasma. Molecular ions Ar_2^+ are formed by a three-body conversion and maintained by a positive density gradient thanks to a inhomogeneous heating. Molecular admixtures can have significant impact on these processes governing contraction of argon filaments as can be seen in Fig.3.

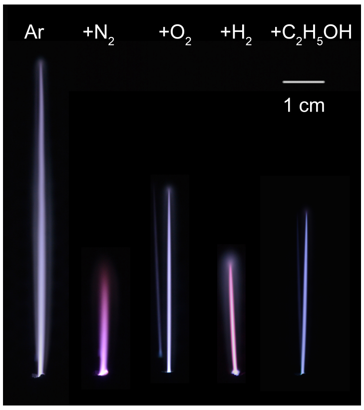

Figure 2: *Photographs of plasma filament with different admixtures. Exp. cond.: 500 sccm Ar, 50 W, 1% admixture.*

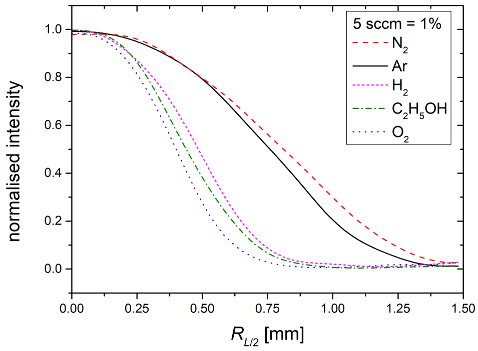

Figure 3: *Influence of the amount of admixture on filament radial profile. Exp. cond.: 500 sccm Ar, 50 W, 1% admixture.*

In the presence of O_2 we can distinguish active species of atoms O(^{3}P, ^{1}D) and metastable molecules $O_2(a^1\Delta_g, {}^1\Sigma_g^+)$. Ar has higher ionisation potential (15.76 eV) than O_2(12.06 eV) and O(13.61 eV), even its lowest P states are higher than dissociation energy of O_2 (5.1 eV). Presence of argon increases n_e and reaction rate for electron impact dissociation of O_2 [6]. We found that adding of 2% of oxygen (which is electronegative) decreases the electron density by 40% from $n_e = 15{\cdot}10^{19}\text{m}^{-3}$. Oxygen admixture significantly reduced diameter (Fig. 3) of the filament and its total volume while having smallest effect on its length (Fig. 2).

In case of nitrogen admixture, its dissociation energy is 9.76 eV. The ionisation potential of N(13.1 eV) and N_2(15.58 eV) is quite high and closer to that of Ar(15.76eV). The excitation of N_2 vibrational levels (2-3.5eV) are main process responsible for electron energy losses and argon metastable states are also quenched in collisions with N_2. This leads to small dimensions of plasma filament. While the Ar-N_2 filament is the shortest, its diffuse character leads to highest apparent volume (see Figs. 2 and 3). Electron density is $n_e = 12(2){\cdot}10^{19}\text{m}^{-3}$.

Dissociation energy of H_2 is 4.48 eV, excitation energy 10.2 eV and ionisation H(13.6 eV) and H_2(15.43 eV). In case of small percentage of hydrogen in discharge we can observe small decrease of n_e $18(2){\cdot}10^{19}\text{m}^{-3}$. Hydrogen Balmer series is observed in emission spectra and OH and NH populations are growing with higher admixture percentage.

Admixture of ethanol has 100× lower percentage than the rest of the molecular gases used. Ethanol molecule contains two of the studied admixtures and its applicability for graphene synthesis is the main reason for this study. Its plasma kinetics is very complex, governed by more than three hundred possible reactions [7]. While ionisation energy is tabulated at 10.48 eV, other ions with energies in 10-22 eV range were observed, too. Its thermal dissociation begins at

1000–1500 K [7], temperatures comparable to those in pure Ar MPT filament. Electron density was $n_e = 15(2)\cdot10^{19}\mathrm{m}^{-3}$. Naturally, we observed hydrogen Balmer series, atomic and molecular carbon, NH, CN, OH and Ar emissions in the measured spectra. Most of the molecular bands tend to grow with higher ethanol percentages except the OH which remains almost constant.

Gas temperatures were assumed equal to rotational ones, estimated by fitting the measured spectra of OH(A-X) by MassiveOES. Results for various admixtures are shown in Fig. 4. Thermal conductivity κ [mW/m·K] of the plasma gas was correlated in [2] with the plasma filament diameter – e.g. rare gases have small values of κ exhibiting plasma contraction. These values at high temperature can significantly differ from those at room temperature (300 K): Ar:17.9, O_2:26.3, N_2:26, H_2:186.9 and EtOH:14.4.

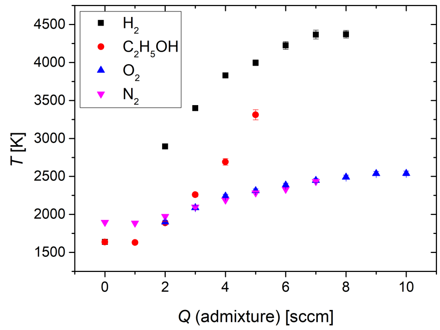

Figure 4: *Influence of the amount of admixture on filament temperature. 500 sccm Ar, 50 W.*

Conclusion

Presence of the small amount of molecular admixtures had significant influence on plasma parameters of stable laminar argon filaments in MPT. Rotational and vibrational excitations of admixtures led to loss of energy and decreased the volume of filament. Radial intensity profiles showed significant contraction for all admixtures except nitrogen which was wide and diffuse, leading to highest apparent volume. Ethanol admixture caused strong gas heating despite its low concentration.

Acknowledgements

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