Spectral study of argon-methane mixture plasma jet generated by a DC plasmatron

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Abstract. We present the results of studying optical emission spectra of Ar:CH4 plasma produced on a DC plasmatron for graphene synthesis. We have identified the basic set of spectral lines and bands in the obtained spectra and shown that H lines and C2 bands appear due to direct excitation by an electron strike of corresponding neutral particles. C2 molecular bands were also identified in the spectra with intensity considerably lower compared to previous studies where He: C2H2 mixture was used as plasma-forming gas.

1. Introduction
Synthesis of carbon nanomaterials is performed using microwave, high-frequency, glow and electric arc discharges in a mixture of an inert gas and a hydrocarbon [1-8], methane in particular [3-5]. Optical spectroscopy methods are widely used to obtain data on plasma composition and concentration of its components, primarily active particles, which act as “condensation nuclei” of synthesized nanoproducts [3, 8]. The aim of this work was to study the spectral parameters of Ar:CH4 plasma jets generated by a DC plasmatron [9] for methane pyrolysis at atmospheric and reduced pressure. The plasmatron is more powerful by an order of magnitude than the ones used in other studies [3].

Optical emission spectra were registered at the following parameters of the stabilized electric arc: current 300 A, voltage drop 50-100 V, arc length 15-20 mm, initial flow rate ratio (Ar): C2H2 (CH4) ≈ 3.5 g/s:0.05÷0.37 g/s. The highly ionized plasma created in the plasmatron with a volumetric atomic ratio (Ar):C:H ≈ 0.6÷0.8:0.2÷0.1:0.2÷0.1 provided graphene synthesis environment in the plasma reactor chamber.

Optical emission spectra were registered using a three-channel optical fiber spectrometer AvaSpec 2048 with spectral resolution about 0.2 nm in 220–1100 nm wavelength range. A collecting lens was used to create a sharp image of the plasma jet section at the selected longitudinal coordinate and radius in the input end plane of the fiber. The fiber could be moved along and across the axis of the plasma jet exiting the plasmatron channel with an output diameter of 10 mm, which made it possible to record the plasma emission spectra at different distances from the plasma torch nozzle exit and jet radii.

2. Determination of electron temperature and concentration
We have identified numerous spectral lines and bands: ArI, Hα and Hβ of Balmer series, a few of CI, Cu (due to insignificant erosion of the plasmatron channel) and Swan bands of C2 in the studied wavelength range from 220 to 1100 nm. Typical observed spectra are shown in figure 1 and figure 2.

The analysis of relative intensities of the registrated spectral lines makes it possible to determine the electron temperature $T_e$ in the studied plasma by using the Boltzmann exponent method [10].
Figure 3 illustrates the use of this method for ArI spectral lines. The electron temperature $T_e$ obtained from the slope of the line that approximates the experimental points is 9500 K. Reduced populations $n_k/g_k$ of the emitting levels shown in figure 3 by circles were determined using more than ten ArI lines (see figure 2) with excitation energies $E_k$ from 13.09 to 14.85 eV. This ensured that electron temperature was determined with error $\delta T_e \approx (T_e / \Delta E_k)$, less than 10%.
Figure 4 shows the water-cooled diagnostics section of the setup with observation windows shown by gray fill used to observe the plasma jet. Since plasma moves from top to bottom and observation slits are located perpendicular to the flow, it enables recording the distribution of radiation intensity along the jet radius on two longitudinal coordinates. Six points where electron temperatures had been determined are located in the centers and edges of observation windows.

The well-resolved contours of the Balmer H\(\alpha\) and H\(\beta\) lines, and the availability of accurate values of their Stark broadening coefficients [11] provide reliable values of electron concentration \(n_e\). The values of \(n_e\) in the studied coordinates were obtained from the half-widths of the H\(\beta\) line are presented in Table 1.

![Graph showing electron temperature determination](image)

**Figure 3.** Electron temperature determined by using the Boltzmann exponent method to ArI spectral lines. Found temperature is \(T_e = 9500\) K.

![Diagram of water-cooled diagnostics section](image)

**Figure 4.** Scheme of the water-cooled diagnostics section (a) and electron temperatures \(T_e\) determined at various points of its observation windows (b).
Table 1. Electron concentrations $n_e$.  
| Concentration of electrons across the width at half-height of the Hβ line, $10^{16}$ cm$^{-3}$ |
|---|---|---|---|---|---|
| Center | Left | Right | Center, 2 cm from the nozzle | Left, 2 cm from the nozzle | Right, 2 cm from the nozzle |
| 3.2 | 2.1 | 2.5 | 2.0 | 1.7 | 1.8 |

3. Molecular spectrum analysis

To estimate vibrational and rotational temperatures of C$_2$ molecule in Ar-CH$_4$ mixture we applied the best match method for measured spectra and spectra modeled in Specair software. The values of vibrational $T_v$ and rotational $T_R$ temperatures in four peripheral regions in which the temperature allows the molecules formation, are presented in Table 2.

Table 2. Vibrational and rotational temperatures of C$_2$.

| Rotational temperature $T_R$, K | Left | Left, 2 cm from the nozzle | Right | Right, 2 cm from the nozzle |
|---|---|---|---|---|
| 3000 | 2800 | 4700 | 2900 |
| Vibrational temperature $T_v$, K | Left | Left, 2 cm from the nozzle | Right | Right, 2 cm from the nozzle |
| 3000 | 2500 | 4700 | 2900 |

An important research objective is estimation of generation efficiency of so-called condensation nuclei - C$_2$ radicals. The population of C$_2$ electron-vibrational energy levels in plasma jet relaxation region can be measured from the frequency-integrated spectral intensities of the observed electronic-vibrational-rotational Swan bands corresponding to the electronic transition $d^3\Pi_g \rightarrow a^3\Pi_u$ and containing sequences $\Delta\nu = \nu' - \nu'' = +2,+1,0,-1,-2$. The positions of the edges of the corresponding bands are shown in figure 1. The integral intensity of molecular radiation is expressed by the universal relationship [11]:

$$I_{\nu'\nu''} = \hbar \langle \nu \rangle A_{\nu'\nu''} N_{\nu'\nu''}$$  \hspace{1cm} (1)

Here $A_{\nu'\nu''}$ is Einstein’s coefficient for electron-vibrational transition $n' \rightarrow n''$ (index $n$ refers to electron term), $\langle \nu \rangle$ is the averaged over the vibrational band frequency of transition, $N_{\nu'\nu''}$ is the concentration of the emitting molecules on the electron-vibrational level $\nu'\nu''$. Under local thermodynamic equilibrium conditions (its presence will be shown further by comparing calculated and measured values of electron concentration and temperature), the relation between given concentration $N_{\nu'\nu''}$ and total concentration of molecules of given type $N$ is [12]:

$$N_{\nu'\nu''} = N g_{\nu'\nu''} \exp \left( -\frac{E_{\nu'} + E_{\nu''} + E_j}{kT} \right) \equiv N g_{\nu'\nu''} \exp \left( -\frac{E_e}{kT} \right),$$  \hspace{1cm} (2)

where $g_{\nu'\nu''}$ is the statistical weight of the emitting energy level, $Q$ is statistical sum for the molecule.

We shall estimate the efficiency of C$_2$ molecules formation in the recombination region of the plasma by comparing the radiation intensities of the bands (0-0, edge at 516.5 nm) and (0-1, edge at 563.6 nm) with the intensity of the Hβ band located between them. For lateral spectra registration the measured intensity $J_\lambda$ of an optically thin plasma is the local emissivity $\varepsilon_\lambda(r)$ integrated along the observation line (commonly the diameter):

$$J_\lambda = \int_{-R}^{R} \varepsilon_\lambda(r)dr \sim \int_{-R}^{R} n_e(r)dr \sim n_{e}\text{eff}L_{\text{eff}}$$  \hspace{1cm} (3)
where local emissivity $\varepsilon_\lambda (r)$ is determined by both distribution of the emitters $n^*(r)$ along the observation line and spatial extent of emitters of given type $L_{\text{eff}}$. For the studied object—a highly ionized plasma in a water-cooled channel, we compare the radiational flux of hydrogen band with excitation energy 12.75 eV emitted by the hottest axial region of the plasma with 10000 K temperature to the radiational flux of C$_2$ Swan bands. Swan bands are emitted by plasma regions with temperature 3000–5000 K which is indicated by their measured vibrational and rotational temperature.

When applying the relative intensities method to determine local temperatures, it is required to compare the local emissivities $\varepsilon_\lambda (r)$ [W/(cm$^3$nm)] of the studied emitters rather than integral emissivities $I_\lambda$ [W/(cm$^2$nm)] which are integrated over space with inhomogeneous emission parameters. The calculations in [3] for equilibrium populations of emitting states of CI (940.6 nm) and H1 (H$\beta$) performed using Saha-Boltzmann approximation have shown that for the considered atomized mixtures of inert gases in high-current DC plasma at axial temperatures up to 14000 K the intensities of atomic and ion lines in inert gases, hydrogen and carbon with excitation energies over 9 eV monotonously decrease with radius. Application of this approximation is justified by the measured values of temperature over 10000 K and electron concentration over $10^{16}$ cm$^{-3}$ (see below). Therefore, the relation between the Swan bands and H$\beta$ line registered in traverse observation, can be written as following, taking (1–3) into account:

$$2^{\nu'} \left[ \begin{array}{c} v \nu' \cr * \cr \end{array} \right] \text{C}_2 (0,0) \text{exp.} \left( \begin{array}{c} -12.75 eV \\ T_e \end{array} \right) = \left( \begin{array}{c} -2.48 eV \\ T_e \end{array} \right) \frac{16 A_{\nu'}}{Q} \frac{S_{\text{0,0}} + S_{\text{0,1}}}{S_{\text{H}\beta}} \frac{g_{\nu' \nu}}{A_{\nu'}} \frac{\langle \nu \rangle}{\langle \nu \rangle} \frac{A_{\nu'}}{Q} \frac{c_2 \cdot A_{\nu'}^{\text{exp.}}(T) \cdot \exp \left( \begin{array}{c} -12.75 eV \\ T_e \end{array} \right)}{\exp \left( \begin{array}{c} -2.48 eV \\ T_e \end{array} \right)} \frac{\langle \nu \rangle}{\langle \nu \rangle}$$

(4)

Here $S_{\text{0,0}} + S_{\text{0,1}}$ is the area, in arbitrary units, under the intensity curve of C$_2$ bands corresponding to the sequences $\Delta \nu = 0$ (490 ÷ 516.5 nm) and $\Delta \nu = -1$ (525 ÷ 563.6 nm), $S_{\text{H}\beta}$ is the area under H$\beta$ line contour in the same units, $\langle \nu \rangle$ is average frequency of the considered Swan bands (0-0) and (0-1) for the C$_2$ molecule which almost matches the transition frequency $\nu_{\text{H}\beta}$ for H$\beta$ line in the denominator. We used Boltzmann law and equation (2) to switch from concentrations of emitting particles to concentrations of ground states of [C$_2$] radical and [H] atom at temperatures of predominant luminescence of compared emitters. The statistical weight of the emitting level of the radical $d^3\Pi_g$ is $g_{\nu' \nu} = 6$, the statistical sum of molecule $Q$ takes into account the ground state X$^1\Sigma$ and the first excited state a$^3\Pi_u$; further taking into account the energy of the excited term and $T=4000$K we have $Q=5.4$. Now we shall utilize (4) to obtain an equation for the relation between the concentration of C$_2$ molecules in the region of their emission (jet periphery with temperature 3000–5000 K) to the concentration of atomic hydrogen in the axial region with the measured temperature of 10000±1000 K:

$$\frac{[\text{C}_2]}{[\text{H}]} = \left( \frac{S_{\text{0,0}} + S_{\text{0,1}}}{S_{\text{H}\beta}} \right) \frac{16 A_{\nu'}}{A_{\nu'}^{\text{exp.}}} \frac{g_{\nu' \nu}}{Q} \exp \left( \begin{array}{c} -12.75 eV \\ T_e \end{array} \right) \frac{\langle \nu \rangle}{\langle \nu \rangle}$$

(5)

We can determine concentration ratio of C$_2$ radicals and H atoms in ground states in regions of their maximum radiation by using the data on radiation constants [13, 14] and data on experiments with Ar-CH$_4$ and He-C$_2$H$_2$ [3] mixtures and using the relation (5). The values of Ar-CH$_4$ plasma density calculated under the assumption of Saha-Boltzmann equilibrium and complete atomization of the hydrocarbon for the zone of predominant emission of the H$\beta$ line (near-axial region with a temperature of ~10000 K) and in the near-wall region (~4000 K), where the emission of the Swan bands is
concentrated, are given in Table 3. Since the length of these zones has not been experimentally established, the assessment of C2 fraction performed earlier is a lower-bound estimate, since the comparison is performed using chord measurements according to (3), and the radial temperature profile is characterized by large gradients near the cooled wall, giving \(L_{\text{eff}}^C2 \leq L_{\text{eff}}^{\text{H}}\). 

For Ar-CH4 mixture: arc current 290 A, power 22.8 kW, argon flow 3.5 g/s, carbohydrate flow 0.1 g/s, pressure 341 Torr, molar ratio of plasma mixture components at plasmatron input Ar:C:H \(\approx 0.74:0.05:0.21\) with axial parameters \(T_e=10000\ K, n_e\approx 2.0 \times 10^{16}\ cm^{-3}\).

The measured relation \(\frac{S_{0.0} + S_{0.1}}{S_{\text{H}}^\text{exp.}}\) has an approximate value of 0.5, then according to (5)
\[C2(T = 4000 K) \approx 0.5[H(T = 10000 K)] \cdot 10^{-3} \approx 3.5 \times 10^{13} cm^{-3},\] giving the efficiency of carbon atom association into C2 molecules
\[\frac{C2(T = 4000 K)}{C2(T = 10000 K)} = \frac{3.5 \times 10^{13}}{4.5 \times 10^{16}} = 7.8 \times 10^{-4} \approx 0.008\% ,\] which is a negligibly small value compared with the He:C2H2 mixture [3], for which this efficiency, according to a similar estimate, is about 20%.

### Table 3. Mixture component concentrations.

| Component | Ar | Ar+ | C | C+ | H | H+ | ne |
|-----------|----|-----|---|----|---|----|---|
| \(T=10000\ K\) | 24.7 | <10^-4 | 1.0 | 1.5 | 6.5 | 0.2 | 2.0 |
| \(N, 10^{16}\ cm^{-3}\) | | | | | | | |
| \(T=4000\ K\) | 61.7 | - | 4.5 | - | 17.5 | - | - |

4. Result discussion

The electron concentration measured from the Hβ and Hγ line widths, which varies in the observed jet region in the range \(n_e = (1.7–3.2) \times 10^{16}\ cm^{-3}\), corresponds to ionization equilibrium in Ar:CH4 plasma mixtures with an electron temperature close to \(T_e\) value measured from ArI spectral lines.

Plasma nonisothermality is insignificant in the axial region (\(T_e(r = 0) \equiv 10000\ K \sim T_a\)) due to high efficiency of elastic losses in electron collisions with light atoms and hydrogen ions, which account for about 20% of the mixture (\(\delta e^{\text{elH}} = 2m_e/MH_1 = 2/1836\)). It is also unlikely to be manifested in the the region of predominant radiation of C2 radicals (near-wall region, \(r = r^*\)) due to additional inelastic energy losses by electrons in collisions with molecules H2, C2 and others. In this region, \(T_e\) is close to the measured rotational temperature \(T_v\): \(T_e(r = r^*) \approx T_v(r^*) \approx T_a(r^*) \approx 3000 \div 5000K\).

High specific power of the utilized plasmatron \(W = IE \approx 10^4\ W/cm\) facilitates dissociation of hydrocarbons and partial ionization of carbon and hydrogen atoms in the energy input area. However, maintaining the optimal plasma cooling rate for the formation of nanostructures in the reactor zone next to plasmatron exit requires careful selection of carrier gas, hydrocarbon sort and molar composition of the mixture. For example, helium, being a light inert gas with high thermal conductivity and enthalpy, is capable of providing the best environment for C2 synthesis as a carrier gas [5]: without participating in ionization processes (carbon atoms are ionized, providing the required plasma conductivity), helium, due to a large molar fraction and high heat content, limits the cooling rate of the plasma. This is also facilitated by the processes of three-particle electron-ion recombination and recombinacion of carbon and hydrogen atoms in the jet.

Comparison of C2 molecule Swan bands intensities in He-CH4 and Ar-CH4 mixtures at the outlet of the plasmatron indicates that C2 concentration for the first of the mixtures is several times higher [3]. At the same time, the absolute values of the C2 concentration in He-C2H2 are significant and can reach 20% of the total number of carbon particles in the jet region with the temperature of 3000–5000K. A possible reason for such a significant difference in conversion efficiency of CH4 and C2H2 to C2 is the incomplete atomization of hydrocarbons during their passage through the energy input region in the plasmatron. The tangential swirl of the plasma flow in the inlet near-cathode region (which was
introduced to prolong the life of the cathode and the water-cooled walls of the plasmatron) contributes to the "slippage" of a significant fraction of hydrocarbons without their complete dissociation in the near-wall region. In the case of C2H2, this leads to the formation of C2 and C2H particles which are desirable for the generation of nanoproducts. When methane is used, the "condensation nuclei" (C2 radicals) are absent among the products of incomplete dissociation (C, CH3, CH2…).

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