Optical emission spectrocopy of the barrier torch discharge

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Barrier torch discharge at atmospheric pressure is a relatively new plasma deposition system capable of working at atmospheric pressure in the open air. Barrier torch discharge is used for deposition of ZnO and TiO_2 layers. In this paper we present the qualitative analysis of the emission spectra of the barrier torch discharge during deposition. The first results of spectroscopic measurements of Balmer H_β line width aimed at estimating the electron density in plasma jet at atmospheric pressure are presented as well. Electron concentration was estimated at special conditions (DC plasma jet with Ar as working gas).

1. Introduction

Interest in the atmospheric plasma systems increases from year to year. These systems do not need expensive vacuum chambers, are not limited by the volume of these chambers, do not use vacuum pumps. The deposition rate in these systems may be higher than those in the vacuum systems [1, 2]. Low temperature dielectric-barrier discharges [3 - 7] are very often applied for PECVD (Plasma Enhanced Chemical Vapour Deposition) of polymer and other kinds of thin films [8 - 10]. We applied single RF plasma jet system for deposition of ZnO and TiO_2 oxide thin films on quartz glass, Ni, polymer and silicon substrates. At atmospheric pressure is the analysis of the properties, which occur in the discharge, more complicated than at reduced pressure. We will present here that electron concentration in the atmospheric plasma jet system can be estimated by spectroscopic measurements.

2. Experiment

Schematic diagram of the single barrier torch plasma jet system can be seen in Figure 1. The system works at the atmospheric pressure; it is just encased in acrylic glass box, which is provided by a pipe leading the used working gases out of the building. Precursors (Ti-thd or Zn-acetylacetonate) can be treated at the atmospheric pressure, and their toxicity is moderately low. The mixture of He+N_2 was used to transfer precursor to the plasma zone.

The distance between nozzle outlet and the substrate was 4-13 mm. Due to the high RF field at the edge of the powered electrode the RF barrier-torch discharge is generated in the mixture of He+N_2 gases. Vapours of precursors were fed directly into the nozzle powered by RF electrode. The stable precursor temperature resulted in stable precursor flow rate (stable He-N_2-precursor flow rate) even if we could not directly measure the precursor flow rate. The flow rates were measured and regulated by susceptible digital flowmeter MKS 247 Instrument. Quartz glass, silicon, Ni, polymer and glass were used as substrates. The temperature on the surface of the substrate during deposition by barrier torch discharge was around 250 ^oC. Coating of the larger area was provided by motor-driven x-y movement of the grounded Al substrate holder with a water-cooling system. The ceramic tube with internal diameter 1.5 mm is surrounded by the stainless steel RF powered electrode. This tube was cooled by cooling water system as well. Plasma system excited by RF source worked in pulse modulated mode. This modulation allowed exciting of the high density plasma in the active part of the duty cycle and simultaneously keeping the neutral gas in the plasma jet near the substrate reasonably cold thus protecting polymer substrate from thermal damages. The repetition frequency was 20-40 Hz.

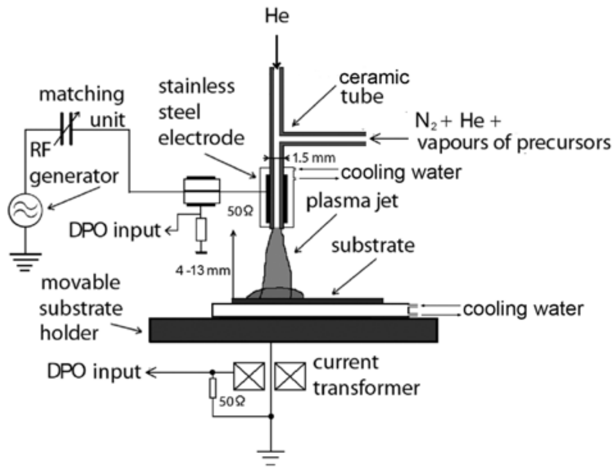

Figure 1. Schematic diagram of the single barrier torch working at atmospheric pressure.

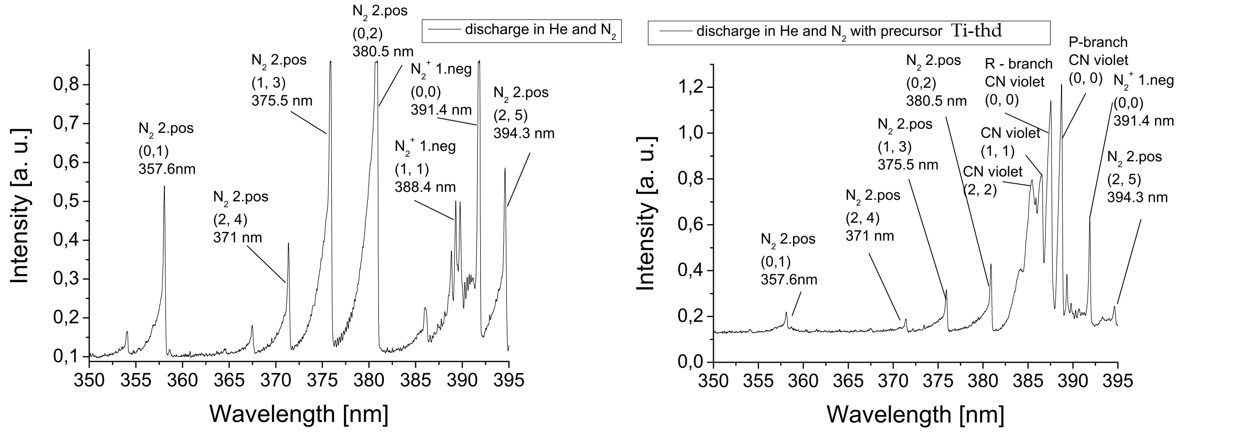

Figure 2. Emission spectra of the barrier torch discharge in He and N_2 mixture. Left panel - without precursor, right panel - with precursor Ti-thd. Wavelength range 350-395 nm.

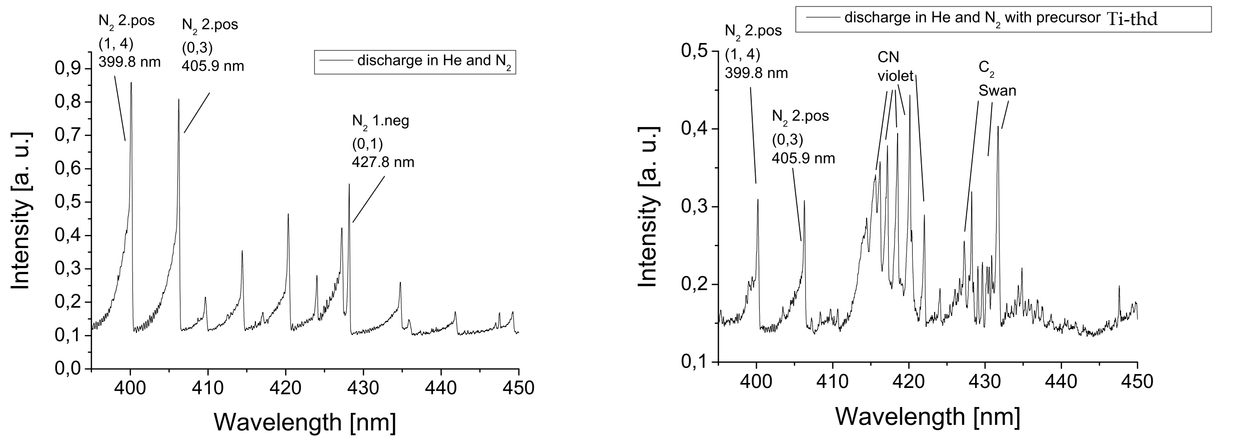

Figure 3. Emission spectra of the barrier torch discharge in He and N_2 mixture. Left panel - without precursor, right panel - with precursor Ti-thd. Wavelength range 395-450 nm.

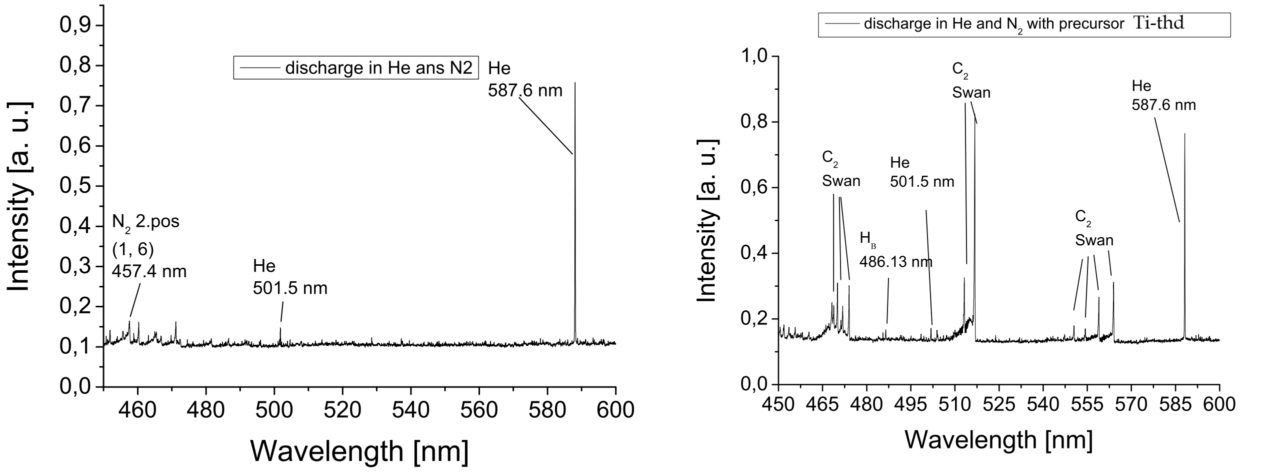

Figure 4. Emission spectra of the barrier torch discharge in He and N_2 mixture. Left panel - without precursor, right panel - with precursor Ti-thd. Wavelength range 450-600 nm.

Length of the active part of the cycle was 5 ms when (duty cycle 1:9 at 20Hz). The RF power (600W) was applied on the electrode connected with the 13.56 MHz RF power generator via the matching unit (capacitive coupling).

3.1. Qualitative analysis of the emission spectra

Using the arrangement depicted in Figure 5 with He and N_2 as working gases we observed emission spectra from barrier torch discharge at similar conditions to deposition ones. All spectra were recorded perpendicularly to the plasma channel.

Typical spectrum emitted by the plasma channel without precursor with He and N_2 as working gases is shown in left panels of Figures 2-4. In these

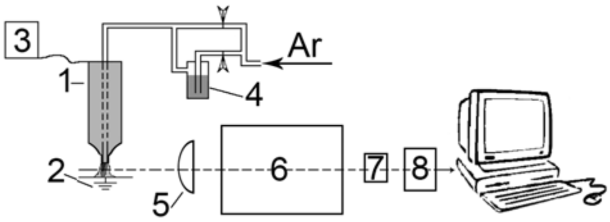

Figure 5. Schematic diagram of the spectroscopic measurements of the electron concentration in the plasma jet at atmospheric pressure: (1) metal nozzle, (2) grounded electrode, (3) power generator, (4) humidifier, (5) lens system, (6) spectrograph, (7) photomultiplier, (8) amplifier.

spectra, we observe the N_2 second positive system ($C^3\Pi_u$ - $B^3\Pi_g$) and N_2^+ first negative system ($B^3\Pi_g$ - $A^3\Sigma_u^+$). The He I lines (501.57 nm and 587.56 nm) can be observed as well.

Right panels of Figures 2-4 show emission spectra of the barrier torch discharge in working gases He and N_2 with precursor Ti-thd. N_2 (second positive system), N_2^+ (first negative system) and He spectral lines can be observed as well. However, new spectral lines appeared in the spectrum.

CN - molecular lines emission

In the emission spectra from barrier torch discharge CN violet system ($B^2\Sigma^+$-$X^2\Sigma^+$) is observed. The violet system of CN is strongly excited by carbon arcs in air, by the reaction of active nitrogen with variety of organic vapours, and by combustion processes [11]. The violet systems are also prominent in emission in the spectra of comets and in absorption in the spectra of R - and N - type stars.

C_2 - molecular lines emission

The C_2 molecules possess seven known triplet and six known singlet electronic states giving rise to nine band system, which lies across the vacuum ultraviolet, the visible and the infrared spectral regions [12]. In Figure 4 (right) we see the strongest and most easily excited of these band systems; the Swan system that lies between 420 - 770 nm [13]. Following re-assessment and systematization of the energy level scheme and nomenclature for the C_2 molecule [12], we assign the notation ($d^3\Pi_g$-$a^3\Pi_u$) for the Swan system instead of the previously used notations ($A^3\Pi_g$-$X^3\Pi_u$) and ($A^3\Pi_g$-$X^{`3}\Pi_u$).

3.2. Measurement of electron concentration with help of H_β line Stark broadening

We present the first results of the electron density estimation at atmospheric pressure in Ar direct current plasma jet.

The electron concentration is estimated from the H_β line Stark broadening. For the n_e calculation we adopted the simple relation between $\Delta\lambda^{Stark}(H_\beta)$ and n_e exploited already by Jasiński et al. in [14]:

$$n_e = 10^{16}\,[\Delta\lambda^{Stark}(H_\beta)]^{1.55},$$

where $\Delta\lambda^{Stark}(H_\beta)$ is in nm and n_e in cm^{-3}.

In our case the profile of an emission line can be affected by two broadening mechanisms: Stark (collisional) and instrumental.

In Figure 5 there are depicted the main parts of the experimental setup used. These are power generator (3), Ar gas supply, humidifier (4), lens system (5), spectrograph (6) and PC computer.

In the preliminary experiments described here, we have powered the discharge by a DC source using the power range 125-200 W. Small amount of water vapour is admixed to the Ar working gas by means of humidifier. Ar gas mass flow rate is Q_{Ar}=700sccm=1.2 Pa m^3 s^{-1} and that of mixture of $Ar+H_2O$ $Q_{(Ar+H2O\}}$=300 sccm=0.5 Pa m^3 s^{-1}. It is the optimal flow rate $Ar+H_2O$, in case of using the lower one the ratio signal-noise in spectrum of barrier torch discharge is very small, in case of higher flow rate the discharge does not burn. Metal nozzle (1) with inner diameter 1.4 mm and outlet diameter 6 mm were used as electrodes. Distance between the metal nozzle and the grounded electrode (2) varied in the range 3-6 mm. To measure the H_β spectral profile, the light emitted by plasma jet is focused onto entrance slit of the spectrograph (SPM2, 1200 grooves/mm) by means of a lens system (5). The width of the entrance slit of the spectrograph was 10 μm. The H_β spectral line is fitted by Voigt profile. To eliminate the instrumental broadening we used the profile of Hg spectral line (435.8 nm) as an instrumental function. This spectral line is fitted by Gauss profile. The measured H_β line profile is fitted by the Lorentz, Gauss and Voigt profiles in Figure 6. The best fit is apparently the Voigt profile: convolution of Lorentz and Gauss profiles. By

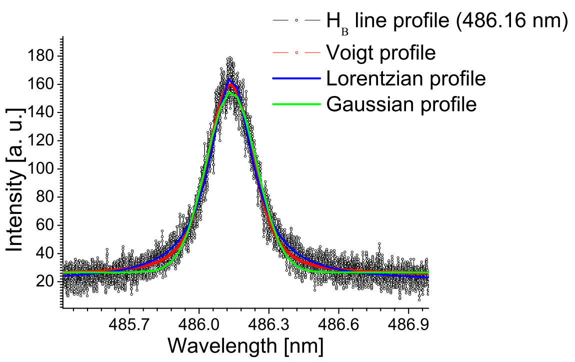

Figure 6. Experimental H_β line profile (486.13 nm) and its approximation by the Voigt, Gauss and Lorentz profiles.

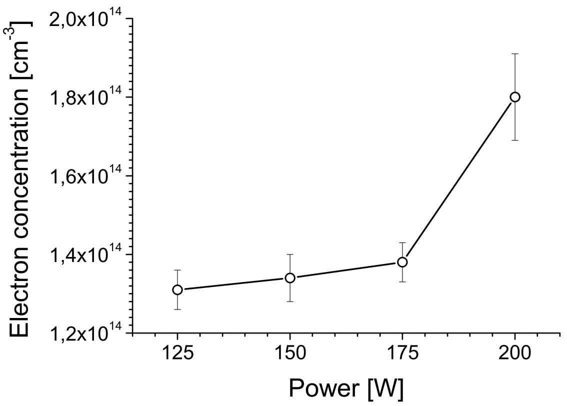

Figure 7. Dependence of the electron concentration in Ar plasma jet at atmospheric pressure on the power supplied into the plasma.

eliminating the instrumental broadening using de-convolution we can get the Lorentz profile of the line and from that estimate the Stark broadening and consequently the electron concentration n_e.

The measurements were reproducible within approximately 6% error limit. The measured electron densities ranged above 10^{14} cm^{-3}. The plasma density increased with increasing of the supplied power, see Figure 7.

Attempts to apply this method for a barrier-torch discharge in He did not give us satisfactory results so far. The most probable reason lies in smaller electrons density in He in comparison to Ar at similar deposited power [15] and consequently in too low H_β line width. The electron concentration calculated from the data of impedance measurement in barrier-torch plasma jet in He was 2×10^{13} cm^{-3} [16] and it is generally assumed that the sensitivity limit of the electron density estimation based on H_β line Stark broadening lies at n_e around 10^{13} cm^{-3}.

4. Conclusion

The electron concentration estimated with help of spectroscopic measurement is in a range of 10^{14} cm^{-3}.

Emission spectra of the barrier torch discharche allowed us to identify N_2, CN, C_2 molecular lines and Ti, H, He atomic lines.

Acknowledgments

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