Optical emission spectroscopy of a recently-developed atmospheric pressure microwave argon plasma jet

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Abstract: A new microwave plasma jet operated in argon and open to ambient air intended for thin film deposition by PECVD was developed and studied by OES. This source is characterized by a peculiar spatial structure in which off-axis filaments in the discharge tube converge towards a single on-axis point near the exit, followed by a diffuse plasma plume. OES measurements show a strong influence of the ambient air in the discharge, resulting in a maximum at the convergence point of the rotational temperature deduced from OH emission. Analysis of Ar emission lines combined with a collisional radiative model for Ar 4p states further reveals a peak in electron temperature along with a significant decrease of the number density of metastable atoms beyond the convergence point.

1.Introduction

Atmospheric-pressure plasmas are being increasingly studied as a tool for various material processing applications such as surface modification [1] and nanomaterials synthesis [2]. The main advantages of such plasmas over their low-pressure counterparts are the absence of expansive vacuum equipment and the high densities of active species allowing fast treatments over large area substrates. Among the various sources available, jet configurations represent interesting building blocks for the in-line processing requirements of specific industries (for example, glass and textile processing).

In most studies, plasma jets at atmospheric-pressure are sustained by pulsed electrical fields or by high-frequency electromagnetic fields (in particular RF). In this work, a surface-wave plasma jet operated in nominally pure Ar and open to ambient air was developed for deposition of functional, nanostructured coatings on glass substrates by PECVD. Surface-wave plasmas can be sustained over a wide range of conditions (frequencies between 1MHz and 40GHz, tube dimensions, input power, gas flows, etc.). This allows a rather unique control of the plasma properties, and thus of the physical and chemical properties of the coatings required for the desired technological application.

In a previous study, surface-wave plasmas in the microwave regime operated in argon with small amounts of hexamethyldisiloxane (HMDSO) precursor was found to produce silicon oxycarbide nano-powders directly on the discharge tube walls [3]. This behaviour was attributed to the high degree of precursor fragmentation across the whole discharge length due to the high number densities of charged particles (~10^{14} cm^{-3}). To adapt this source to thin film deposition on substrates placed outside the microwave plasma column, a new configuration was developed and characterized by spatially-resolved optical emission spectroscopy (OES) to determine the electron temperature, the neutral gas temperature (from the rotational temperature) as well as the number density of metastable atoms.

2.Experimental setup

The atmospheric-pressure plasma jet investigated was sustained using a 2kW Sairem microwave generator operating at 2.45GHz. The microwave power was delivered and coupled to a 6 mm ID (8 mm OD) fused silica discharge tube using a surfaguide. A circulator was placed between the magnetron head and the surfaguide to direct unwanted reflections to a water-cooled load. A bidirectional coupler paired to a bolometer was used to measure the incident and reflected powers (and thus to determine the absorbed power). The argon gas flow was controlled by a mass flow controller and directed downward in the tube in a custom-made vortex, which ensures a good mixing of species during PECVD.

Furthermore, a thick brass piece was placed directly above the surfaguide to reduce the plasma-precursor interaction time and thus to limit nano-powders formation on the discharge tube walls. Indeed, this grounded piece prevents surface wave propagation above the surfaguide, such that the plasma length is shortened by half. In addition, only a 1cm portion of the discharge tube exceeded downward of the surfaguide. As a consequence, the portion of the plasma in the tube was split into 3 stable filaments, as opposed to an on-axis plasma for the same absorbed power when the tube exceeds the surfaguide by tens of centimeters. By doing this, interactions of plasma-generated fragments and powders with the walls only occurs over ~2cm (1cm downward + 1cm inside the surfaguide) before interaction with ambient air.

3.Experimental results

As mentioned above, injection of precursors in microwave plasma columns sustained by electromagnetic surface waves are known to produce powders on the discharge tube walls due to the very high fragmentation levels [3]. To prevent such limitations, the tube length downward of the surfaguide was significantly reduced. In such conditions, because of the reduced length, the three off-axis filaments close to the wave launcher converge into a single on-axis point outside the tube region in ambient air, as reported in [4]. This peculiar jet behaviour is illustrated in Fig. 1. Below the converging point, a more diffuse discharge can be seen. As expected, the brightness and length of this afterglow region increase with the absorbed power. The length also increases with the gas flow rate (not shown).

Fig. 1: Picture of the jet behaviour with association of filaments and afterglow generation.

Spatially-resolved optical emission spectroscopy measurements were performed outside the tube region. The resulting spectra for the first few millimeters are shown in Fig. 2 over the 370 to 440 nm wavelength range.

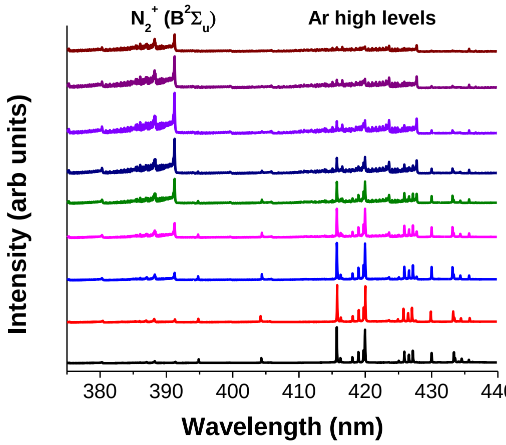

Fig. 2: Axial emission spectra of the plasma in the ambient air section (position 0 is the end of the discharge tube).

As expected, Ar I emission lines from high levels are visible between 415 and 435 nm. Emission intensities from these states decrease as the discharge progresses outside the glass tube. On the other hand, while the nitrogen signature between 380 and 395nm is almost invisible at the tube exit (0 mm), it becomes more intense beyond this point, with a maximum intensity at 6mm. This indicates that the nominally pure argon discharge in the tube becomes mixed with ambient air near the outlet.

Fig. 3 shows more clearly the axial evolution of the N_2^+(B) band head emission intensity at 391nm and the easily visible 4p-to-4s argon transition at 763nm. Also shown is the OH rotational temperature spatial profile obtained from the contruction of a Boltzmann plot (OH(A-X) emission between 307nm and 314nm was recorded using a high-resolution monochromator). While the Ar emission intensity monotonously decreases after the end of the discharge tube, the N_2^+ emission intensity sharply rises close to the converging point, suggesting a more significant interaction with ambient air in this region. As a result, the neutral gas temperature (assumed to be linked to the rotational temperature of OH) shows a maximum; a feature that can probably be explained by neutral gas heating due to dissociation of N_2 [5].

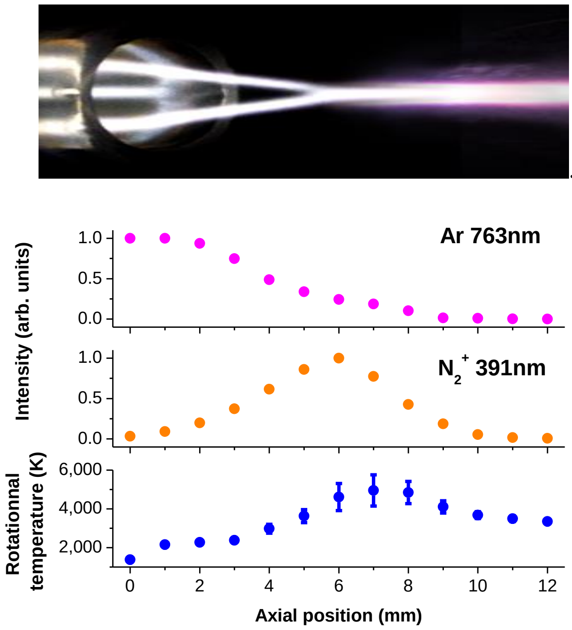

Fig. 3: Ar and N_2^+ emission intensities and rotational temperature along the nominally pure Ar plasma open to ambient air

These results were also compared to those deduced from the analysis of the Ar 4p-to-4s emission lines between 700nm and 850nm. Emission intensities were compared to the predictions of a recently-developed collisional-radiative model for atmospheric-pressure Ar plasmas using the average electron energy (or electron temperature assuming a Maxwellian electron distribution function) and the number density of Ar 4s atoms (assuming equal populations for Ar $1s_2$, $1s_3$, $1s_4$ and $1s_5$ states) as the only adjustable parameters. The results for the electron temperature and the number density of Ar 4s atoms are presented in Fig. 4.

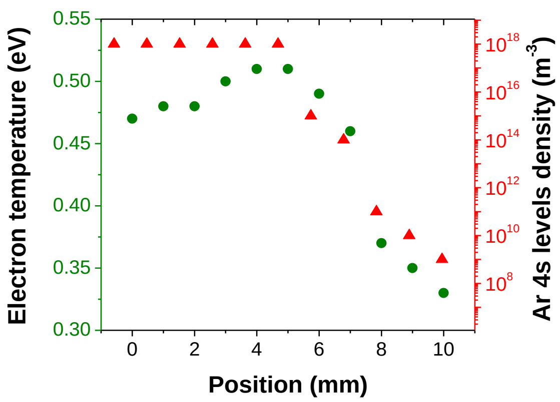

Fig. 4: Axial electron temperature and Ar 4s levels density profiles in the ambient air section

Electron temperature near the end of the tube is around 0.5eV, which is close to the values inside long and spatially-homogenous (non-filamentary) microwave plasma columns sustained by surface waves obtained by many methods (excitation temperature, analysis of the continuum emission, and modeling of 4p emission lines).

By comparing the data displayed in Figs. 3 and 4, it can also be seen that the electron temperature follows the same trend as the rotational temperature, with a maximum and comparable values around 5mm. Also, it is worth noticing that at the exit of the tube, the electron temperature is higher than the rotational one, as expected from non-equilibrium discharges. However, past the convergence point, the electrons tend to "thermalize" with neutral species, suggesting that the medium approaches equilibrium.

As for the Ar 4s levels, their population drastically drops beyond the convergence point; a feature that can certainly be ascribed to their interaction with ambient air, in particular $N_2(X)$ species characterized by high quenching rates. Before the convergence point, the Ar 4s populations remain more or less constant due to the opposite effects of the rise in creation rates due to the higher electron temperatures and the rise in the loss rates by quenching with $N_2(X)$. These number densities will be compared to those obtained by optical absorption spectroscopy. Experiments are in progress.

5. Acknowledgments

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6. References

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