RF Capillary Jet - a Tool for Localized Surface Treatment

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Received 9 May 2006, accepted 13 July 2006
Published online 10 February 2007

Key words Atmospheric pressure plasma, plasma cleaning and plasma activation, protective coatings, plasma enhanced CVD, UV emission.

PACS 52.80.Tn, 31.65.Cf, 52.40.Hf, 52.70.Kz

The UV/VUV spectrum of a non-thermal capillary plasma jet operating with Ar at ambient atmosphere and the temperature load of a substrate exposed to the jet have been measured. The VUV radiation is assigned to N, H, and O atomic lines along with an Ar*2 excimer continuum. The absolute radiance (115–200 nm) of the source has been determined. Maximum values of 880 µW/mm²sr are obtained. Substrate temperatures range between 35 °C for low powers and high gas flow conditions and 95 °C for high powers and reduced gas flow. The plasma source (13.56, 27.12 or 40.78 MHz) can be operated in Ar and in N₂. The further addition of a low percentage of silicon containing reactive admixtures has been demonstrated for thin film deposition. Several further applications related to surface modification have been successfully applied.

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1 Introduction

Non-thermal plasmas have been applied in several topics related to surface treatment at elevated pressures up to atmosphere during recent years, e.g. for the treatment of foils to improve printability, for surface cleaning, and protective coatings [1-3].

Among other approaches, capillary plasma jets represent an emerging technique to generate and stabilize non-thermal plasmas at atmospheric pressure in a relatively wide range of geometrical dimensions. In particular, they can be miniaturized to permit a local treatment of non-flat, structured 3D surfaces: e.g. cavities, trenches etc. in the sub mm range.

Other attractive advantages include:
- Relatively deep treatment effect thus allowing variable substrate distances to the point of remote plasma operation,
- Surface treatment in a region which remains essentially free from electrical field,
- Scalable plasma sizes,
- Simple integration into automated processes.

Nowadays, notable efforts towards an optimized plasma tool are made to supply the growing market demand. A handheld device based on a miniaturized jet source described in this paper is shown in figure 1.

Jets are drawn out by an enhanced gas flow, partly in combination with the electric field. The classification of jets distinguishes thermal jets (plasma torches) created out of thermal gas discharges like arcs and non-thermal jets, produced by non-thermal discharge types, among them corona discharge, dielectric barrier discharge, microwave discharge, gliding arcs and mid-frequency or radio frequency (rf) discharge [4-11]. Here, a non-thermal, rf capillary jet is studied.

A key property of this particular plasma jet is the low temperature load of substrates during treatment, allowing the exposure to fragile surfaces such as polymers, paper, or biological material. The accurate temperature range for the source described here had yet to be determined. Hence, we have carried out experiments to correlate the measured substrate heating with outer parameters of the source, namely gas flow, power input, and substrate distance.

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In an earlier paper [12] it was found that significant part of the optical emission of a similar capillary jet (Ar with small admixtures of N\textsubscript{2}, running in ambient air) appears in the UV region. We attributed this emission spectrum to Ar-, Ar\textsuperscript{+}, and N lines and the NO band. Moreover, traces of Si, Si\textsuperscript{+}, and SiH were found, when SiH\textsubscript{4} was added to the flow gas. Radiation within this wavelength range plays an essential role in the activation of surfaces. Therefore, we carried out spectroscopic measurements in the region between 115 nm and 400 nm to identify the major atomic spectral lines and molecular bands. The current study also presents the absolute spectral radiance of the plasma jet in the VUV-region.

The significant enhancement of the surface energy of substrates along with chemical reactivity and UV radiation in the plasma and the afterglow as well, provide a potential for numerous applications e.g. in surface technology and the medical or biological field.

2 Experimental

The basic design of the radio frequency (13.56 MHz, 27.12 MHz or 40.68 MHz) plasma jet has been described in an earlier paper [12]. The first electrode geometry featuring two ring electrodes around a quartz capillary was limited to rare gases (e.g. argon). In order to extend the spectrum of operating gases to molecular gases as e.g. N\textsubscript{2} or air, which reduce the operating costs significantly, we have developed an improved electrode arrangement. This source is characterized by a center rod electrode inside the quartz capillary which is coupled to the power source via matching network and one grounded ring electrode (figure 2). For the purpose of film deposition, coaxially nested tubes providing additional channels have been constructed to keep delicate thin film precursors away from the powered electrode tip thus reducing unwanted precursor degradation and coating of the electrode tip. Thin film deposition experiments were carried out using small admixtures (per mil range) of two silicon organic precursors hexamethyldisiloxane ((CH\textsubscript{3})\textsubscript{3}-Si-O-Si-(CH\textsubscript{3})\textsubscript{3}, HMDSO) and ((C\textsubscript{2}H\textsubscript{5}O)\textsubscript{4}-Si, TEOS) which were added to the respective carrier gas.

Temperature measurements to determine the substrate heating have been performed using an optical temperature measurement (Luxtron, FOT lab kit). Substrate heating in plasmas is driven by different mechanisms, besides, probe geometry and material influence the results, too. The value obtained with the probe utilized here (quartz material, small cylinder, electrically floating) represents the upper limit to which a non-conductive substrate is heated under these particular conditions. Moreover, the measurement of optical signals rather than an electrical signal from a thermocouple circumvents possible distortion by electromagnetic noise from the source. One end of an optical fibre, the temperature probe, was exposed to the source whereas the other end was connected to the detector. Here, luminescent magnesium fluorogermanate, excited with the radiation from a Xe-flash lamp, served as fluorescent material. The decay time of the fluorescence signal is temperature dependent and was used to monitor the actual local temperature. Radial temperature profiles were obtained with the temperature probe pointing perpendicular to the jet, at a distance of 10 mm from the source tip (side on), whereas axial profiles were measured end on with the probe tip directed towards the source at a radially centered position (cf. photo in fig. 4d)
Fig. 2 Capillary jet with nested tubes for additional thin film precursor admixture: (1) Plasma jet, (2) outer grounded ring electrode, (3) inner rf rod electrode, (4) inner quartz capillary, (5) buffer gas channel, (6) precursor channel for carrier gas ($N_2$) with reactive admixture.

Fig. 3 Experimental setup for VUV measurement, (DEU): Deuterium lamp, (AP): Aperture, 0.6 mm, (VA): Valve, (MI): Mirror, $f=1.5$ m, (WI): MgF$_2$ window, (PM): Photomultiplier, (MO): VUV-Monochromator; 0.5 m, 1200g/mm, (HO): Steel housing for the investigated plasma source e.g. lamp (LA).

The setup used for UV/VUV spectroscopy (figure 3) can be employed for measurements of various UV/VUV sources by exchanging the particular source to be examined [13]. Its main components include a 0.5 m VUV-Monochromator, a VUV-Photomultiplier and a vacuum chamber with pressures in the range of $2 \times 10^{-4}$ Pa. The perpendicular part of the radiation from a small circular area of the capillary jet (0.6 mm diameter) is coupled into the chamber via MgF$_2$ windows with a cut off wavelength of 115 nm. The setup is equipped with a deuterium lamp (Cathodeon, V03) calibrated by Physikalisch Technische Bundesanstalt (PTB), which allows to determine the absolute radiance with a spectral bandwidth of 1.6 nm. During the measurement of the radiance the entrance slit of the monochromator was kept at 1.0 mm to ensure this spectral bandwidth of 1.6 nm, whereas also better resolved (0.2 nm bandwidth), uncalibrated spectral measurements were performed with a reduced entrance slit width, for identification.
3 Results and discussion

3.1 Substrate heating

Temperature measurements have been carried out depending on gas flow, power input, and substrate distance. Results of these measurements are presented in figures 4 a-d. The power dependence is given in figure 4a for three different typical values of the argon flow. The temperature probe was located end on at a distance of 10 mm from the source tip (cf. inserted photo in figure 4d), a spot, indicative of a typical position of the substrate during treatment. The data reveal that the temperature reaches highest values (95 °C) at high powers and at small gas flow. The gas flowing through the source cools the substrate and counteracts the heating due to increased applied powers. Thus, the temperature can be reduced to room temperature with higher gas flows while the power is kept at lower values. Figure 4b affirms this behaviour. Here, the gas flow has been varied for three different applied powers with the temperature probe pointing to the same spot as in figure 4a. Temperature profiles have been measured by changing the probe position with respect to the source tip. Examples for axial profiles are shown in figure 4c, where axial probe position denotes the distance to the source tip. The axial temperature profile of the source displays only a moderate slope and decreases towards the afterglow to about 70% of the value directly in front of the source tip. The radial profile (figure 4d) has been obtained with the probe side on (cf. left insert in figure 4d) at an axial distance of 10 mm. A radial position of 0 mm corresponds to the center of the jet, where maximum temperatures are found. The measured profile displays the expected Gaussian form as demonstrated with a Gauss curve which has been fitted to the experimental data in figure 4d and which represents the measurements well. The data demonstrate that even for the static situation, when jet device and substrate are not moved relatively against each other, the substrate remains at moderate temperatures about 60 °C for medium applied powers and gas flows. The temperature load of the substrate can be reduced further by increased gas flow and by higher treatment speed.

Fig. 4 Substrate heating: (a), (b): rf power and gas flow dependence (Ar, end on, 10 mm from source tip), (c), (d): axial and radial temperature profiles (Ar, 25 slm), photo insert: single module during temperature measurement; probe pointing either perpendicular to the source (side on, left) or end on (right).
3.2 UV/VUV emission

The UV spectrum between 200 nm and 400 nm of the device under study here (figure 5) is dominated by various emissions which we attribute to the 2nd positive system of molecular nitrogen \( \text{N}_2 \) (\( \text{C}^3\Pi_u \rightarrow \text{B}^3\Pi_g \)) with the most intense band head at 337 nm. Furthermore bands assigned to the Α-system of \( \text{OH} \) (\( \text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi \), band heads between 285 nm and 308 nm) and to the γ-system of \( \text{NO} \) (\( \text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi \), several band heads between 200 nm and 300 nm) are observed. The part of the NO γ-system above 300 nm is obscured by the intense \( \text{N}_2 \) emission.

![UV spectrum of the Ar-jet in air.](image)

A VUV spectrum in the wavelength region from 115 nm to 180 nm is plotted in figure 6. The plasma source has been directed perpendicularly to the \( \text{MgF}_2 \) window of the setup (fig. 3). This situation is representative for a typical surface treatment where the jet points upright to the surfaces to be treated.

![VUV spectrum of the Ar-jet in air.](image)

Five atomic lines dominate the emissions in the VUV region. We ascribe these lines to atomic hydrogen (Lyman-α, 122 nm), oxygen (\( \text{O} \), 130 nm), and nitrogen (\( \text{N} \), 120 nm, 142 nm, 149 nm, and 174 nm). A broad continuum centered at 126 nm is apparent in the region between 115 nm and 135 nm, which is assigned to the \( \text{Ar}_2^* \) 2nd excimer continuum. These findings are in accordance to previous VUV emission studies of dielectric barrier discharges in \( \text{Ar/N}_2 \) and \( \text{Ar/air} \) mixtures [14] at \( 6.7 \cdot 10^3 \) Pa and \( 4 \cdot 10^4 \) Pa, where a controlled admixture of oxygen to an \( \text{Ar/N}_2 \) mixture led to increased intensities of the \( \text{N} \) lines at 149 nm and 174 nm which are prominent lines in our spectrum, too. At the same time, the authors [14] observed a decrease of the \( \text{Ar}_2^* \) after...
adding O$_2$ and for the higher pressure (4 · $10^4$ Pa), leading to a relative intensity level comparable to our results. Significant differences denote:

(1) Apparently, there is no emission from the Lyman-Birge-Hopfield system of N$_2$ ($a^1\Pi_g \rightarrow X^1\Sigma_g^+$) visible. These bands are characteristic in Ar-N$_2$ mixtures at lower pressures [15] but tend to decrease at increasing N$_2$ concentrations and with higher Ar concentration as the pressure is increased [14]. This is indicative of an efficient collisional quenching of the $a^1\Pi_g$ state of N$_2$ by argon at elevated pressures.

(2) The observation of the hydrogen Lyman-α line (122 nm) which might be either obscured by Ar$_2$ in the other case or less intense in an N$_2$/O$_2$ admixture compared with a discharge running in ambient (water containing) air.

(3) A prevailing emission of the O I resonance line at 130 nm. A concentration of atomic oxygen higher than that for the Ar/N$_2$ discharge where impurities account for the only source of oxygen is expected for the Ar/air discharge. The fact that O I is still dominant at ambient pressure conditions indicates that the jet forms an argon gas channel which prevents the ambient air from affecting the gas mixture to much, thus reducing the quenching of oxygen.

The absolute radiance of the capillary jet has been obtained by relating the measured intensities to the radiance of a calibrated deuterium lamp (insert in figure 7) at the same wavelength. The curves in figure 7 represent spectra obtained end on at different distances of the visible plasma jet tip from the window. The value ‘0’ of the abscissa corresponds to the situation when the tip of the visual plasma jet touches the window surface. A further approach of the plasma source towards the window leads to a flattening of the plasma tip and is indicated by negative values in figure 7 while a larger distance is represented by positive values. (The same notation is valid for figure 8). In general, maximum (end on) VUV intensities were measured with the jet nearest to the window. The intensities diminish with increasing distance (exceptions see figure 8). Figure 7 illustrates that the intensity of the N I line at 149 nm depends stronger on distance and vanishes completely at higher gaps. The integration over the wavelength (115-200 nm) leads to maximum absolute radiance values of 880 µW/mm$^2$sr. This value lies slightly above results obtained earlier for a single micro hollow cathode discharge (MHCD) in xenon at 6 · $10^4$ Pa, where a value of 690 µW/mm$^2$sr was measured [16]. Or, in other words: The perpendicular part of the radiation originating from 1 mm$^2$ of the jet roughly equals the radiation of a MHCD, when a total cross section of the micro hollow cathode in the range of 1 mm$^2$ is assumed.
Measurements of selected line intensities in dependence on the axial distance between source tip and window have been performed. The results are plotted in figure 8 for N$_2$ (337 nm), N I (174 nm) and OH (308 nm). It is evident that both, UV and VUV emission is apparent even a few millimeters outside the glow region. The intensities exhibit, however, a dependence on the distance (figure 7): The OH emission displays a slight increase at higher axial distances due to more effective mixing with water containing air, while for N$_2$ and N I the same mixing with air leads to more efficient quenching and subsequently a decrease in intensity, the trend already observed in figure 7.

Fig. 8 Intensities of selected UV/VUV lines in dependence on the axial distance between source tip and window, obtained with source perpendicular to window (annotation: see text).

4 Applications

The intense UV/VUV radiation of the capillary jet in combination with its chemical reactivity due to thermodynamic non-equilibrium results in a number of interesting technological applications. Several applications related to surface treatment were assessed:

(I) Treatment of foils or other polymer substrates to enhance their printability: The dynamic treatment of BOPP foils mounted on a rotating bobbin led to an increase in surface energy, indicated by a distinct decrease of water contact angles from initially 110° to 70° after 3 treatments with a velocity of 20 m min$^{-1}$ [12].

(II) Increasing wettability of nonwoven material and paper has been demonstrated. Here, the absorption time of water droplets after treatment has been reduced to a factor of 10 [12].

(III) Plasma cleaning of surfaces, i.e. the removal of organic substances like chemical additives from the surface has been shown for tissue material, where the content of lignin could be substantially reduced [17].

(IV) Treatment of foils to promote their adhesion has been attempted.

(V) Protective coatings: The addition of silicon organic compounds to the carrier gas leads to a deposition of a SiO$_2$-like film for applications such as increased scratch resistance of polymeric materials or enhanced barrier properties against gases, polyolefins or water. Exemplary thin film deposition experiments with HMDSO and TEOS led to films (figure 9) which are solid, transparent and homogeneous. The surface energy is increased as compared to the polymeric substrate. Since the coated area is larger than the static footprint of the source, it has to be moved in a controlled way over the substrate. The resulting dynamic deposition rate reaches 150 nm $\cdot$ s$^{-1} \cdot$ cm$^2$. 
(VI) Miniaturization: The miniaturized design ensures local treatment of small trenches i.e. of micro titre plates. Figure 10 demonstrates the access of the jet to inner walls of a similar microstructure performed to enhance the microfluidic properties.

(VII) Treatment of inner surfaces of elongated devices, tubes etc. (figure 11).

(VIII) Decontamination of biomedical surfaces or the reduction of germs has been shown [18].

**Fig. 9** Photograph (scanning electron microscope) of a film edge (5µm thick) on a polymer substrate (film deposition from TEOS). (Online colour: www.cpp-journal.org).

**Fig. 10** Plasma treatment of small cavities inside a micro structured polymer substrate with a miniaturized jet (0.5 mm diameter). (Online colour: www.cpp-journal.org).

**Fig. 11** Plasma treatment of inner walls. (Online colour: www.cpp-journal.org).
5 Conclusion

The UV/VUV spectrum of a non-thermal capillary Ar-jet running in air and the temperature load of a substrate exposed to the jet have been measured. The VUV radiation is assigned to N, H, and O atomic lines along with an Ar$_2^*$ excimer continuum. The absolute radiance (115-200 nm) of the source has been determined. Maximum values of 880 $\mu$W/mm$^2$sr are obtained. Substrate temperatures range between 35 °C for low powers and high gas flow conditions and 95 °C for high powers and reduced gas flow. The plasma source (13.56, 27.12 or 40.78 MHz) can be operated in Ar and in N$_2$. The further addition of a low percentage of silicon containing reactive admixtures has been demonstrated for thin film deposition. Moreover, a multitude of further applications related to surface modification has been successfully applied.

A comparison of the performance of the capillary plasma jet described here against other plasma sources at atmospheric pressure reveals several advantages:

- moderate operating voltages (1.5-2.5 kV$_{pp}$)
- no water cooling required
- low substrate temperature load
- easy up scaling
- scanning the tool leads to homogeneous surface treatment
- remote plasma operation possible
- electrically floating substrates possible
- molecular process gases (e.g. N$_2$, air)
- simplified implementation into lines
- miniaturization
- local treatment

Drawbacks of the source types include:

- The operation of rf plasmas requires elaborate matching of the varying plasma impedance to the 50 $\Omega$ load for the rf generator.
- A proper rf shielding becomes necessary for selected applications and surroundings.

The plasma source modules can either be arranged to arrays, thus allowing the treatment of larger surfaces, or applied to non-flat substrates.

The significant enhancement of the surface energy of substrates along with the high chemical reactivity and intense UV radiation in the plasma and the afterglow as well, provide a potential for numerous applications which are subject to further evaluation.

Acknowledgements The authors thank U. Haeder, P. Holz and U. Lindemann for providing practical assistance (photos, VUV measurements and microscopy).
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