A novel plasma jet with RF and HF coupled electrodes

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Abstract: In order to achieve low processing temperature and efficient coatings deposition for manufacturing applications, a novel torch has been developed that couples in a double DBD design high frequency (HF ~17 kHz) and radio frequency (RF ~27 MHz) excitations. The design allows to obtain a stable RF plasma also in reactive processes and with the possibility to control on the treated substrates ions flux and surface charging, avoiding the micro-discharges. The plasma has been electrically and optically characterized by emission spectroscopy.

Keywords: atmospheric plasma, frequencies coupling, argon.

1. Introduction

The applications fields of atmospheric plasma jets are always widening from the medical applications to food industry or electronics. The manufacturing applications are increasingly seeking for the best compromise between low temperature and high plasma density. These requirements are needed to treat sensitive substrates from bioresorbable polymers to organic materials, to textiles or macromolecular structures. However, the low temperature is not the only requirement, indeed, the atmospheric plasma devices are no more limited to standard activation or hydrophobic and hydrophilic applications but are demanded to achieve functional properties such as: nanostructured morphologies, surface conductivity, creation of binding sites such as epoxy groups, multilayers for properties combinations, antimicrobial or catalytic features. Such requests are the novel frontiers for atmospheric pressure plasma jets (APPJ) which involve the use of liquid as precursors or nanoparticles dispersions or complex chemicals. There is an increased need of low fragmentation of the precursors and of the control of chemical and physical evolution of the forming nanoparticles or films. The only way to control all these parameters is related to the possibility to achieve at atmospheric pressure homogeneous conditions, avoiding localized heating or high electric fields gradients such as those due to streamers. This issue is usually solved by the use of helium or depending on the applications by nanopulsing or using remote conditions.

Here, as a novel technical solution, we present a patented plasma jet where the coupling of RF and HF electrodes offers cold, stable and efficient conditions. The plasma is operated with argon as main process gas and it keeps its efficiency even with relatively high oxygen or precursors concentrations (< 2%). The coupling offers the possibility to guide the plasma created by the RF excitation directly to the substrates, avoiding the formation of micro-discharges. Electrical and optical plasma jet characterization will be presented. Temperature measurements will highlight its low temperature processing, close to room temperature.

2. Experimental

For the characterization of the effect of coupling the RF and HF electrodes we used a prototype based on the Nadir Stylus Plasma (Nadir srl) [1]. The device is a DBD plasma jet where no electrodes are in direct contact with plasma. This configuration with electrodes hidden from plasma avoids their potential erosion and therefore ensures clean processes. The electrodes are positioned externally and coaxially to an alumina tube through which argon is fluxed, and plasma is ignited. Two other ducts are present: an inner duct for precursors inlet in the vapor or aerosol phase and an outer duct to control the atmosphere at the outlet of the torch, where air or nitrogen are generally used. The main feature that characterizes the device is the use of a double couple of electrodes: a first upstream couple powered with a high voltage supply in the kilohertz regime (HF, ~ 17 kHz) and a downstream couple in radio frequency (RF) at about 27 MHz (Fig. 1)

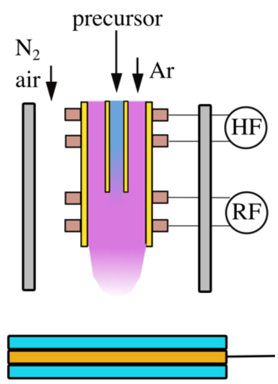

Fig. 1 Scheme of the prototype APPJ used in this work based on the Stylus Plasma Noble (Nadir srl)

The electrical characterization was performed recording voltage and currents on insulating and conductive substrates positioned below the plasma jet. The currents are measured on a copper substrate connected to ground by a resistance of 4.7 kΩ.

The optical emission spectroscopy was performed using a PI-Acton spectrometer of 500 mm focal length, equipped with a 1800 gr mm^{-1} grating and coupled to a PI-Pixis camera with 1340 × 400 square pixels of 13 µm. The spectral emission was analyzed in the range from 300 nm to 850 nm in the area close to the sample surface (≈ 2 mm from the substrate).

3. Results and discussion

To have an intuitive picture of the plasma considered in this work we started with a rough estimate of the overall thermal load of the Nadir Stylus Plasma commercial device, evaluated by the heating of a copper mass used in place of the samples in static conditions. The thermal power turned out to be within 70 and 600 mW respectively for a forward RF power of 11 and 40W and an HF power of 4.5 and 7 W. The power transmission efficiency to the plasma for the RF power supply was estimated to be around the 20%. A fast check of the potential low operating temperature of the torch was obtained just by observing the jet with a thermographic camera (Fig. 2). It can be easily observed that the processing temperature is well below 50°C. The low temperature of the processes is also confirmed by the possibility to treat PCL films reported in a previous paper [2].

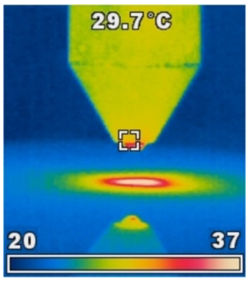

Fig. 2. Image obtained with a thermographic camera of the plasma device applied on a plastic substrate in stationary conditions (after 5 minutes) and 15Wof RF forward power and HF 6W.

For the electrical and optical measurements, a prototype device was used instead of the commercial one in order to have access to the electrodes in an easier way to perform the measurement. The prototype has lower RF power transmission efficiency than the commercial device.

The electrical behavior of the APPJ was monitored by voltage and current measurements on conductive substrates positioned below the plume (Fig. 3). It can be highlighted that the micro-discharges due to the HF excitation are limited by the RF; at low values of RF power, even lower than the applied HF power, the micro-discharges current decreases by at least one order of magnitude. The effect is the same for both polarities. At the same time, when both generators were used, the displacement currents at both frequencies can be observed on a copper substrate. The amplitude of the current oscillation at the 27 MHz depended only on the RF power. Similarly, that at 17 kHz depended on the HF power. However, the plasma is really coupling the two excitations since, as found by a Fourier transform analysis, not only the higher order harmonics of the two frequencies are present but also their crossed combinations. Moreover, the HF could be detected also on the RF electrodes, and it was filtered by the matching preventing the RF power supply damaging. The presence of the displacement currents on the substrate highlights its continuous capacitive connection with the electrode. Thus, a diffused even if not uniform plasma was always present between the electrodes and the substrate. As the plasma was switched off, no capacitive coupling could be observed any longer.

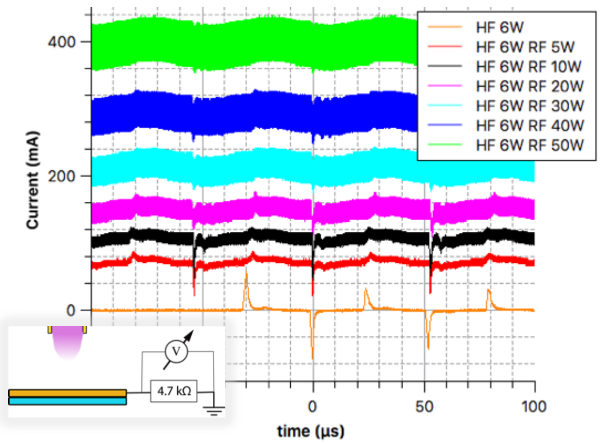

Fig. 3. Current measurements on the substrate comparing the only HF and the coupled HF+RF configurations.

When a sodalime microscope slide was positioned over the metallic substrate, in the HF-only configuration a strong reduction of the negative streamers to the substrate was clearly visible. This effect is probably due to the surface charging of the dielectric. When the RF power supply was switched on, both effects were observed as found with the metallic substrate: the displacement currents were again clearly visible for both exciting frequencies and the HF micro-discharges current reduction was again recorded. However, a glow also appeared on the surface of the dielectric due to the surface charging and plasma propagation on the insulator surface. In the RF-only configuration, no plasma surface propagation was observed on the microscope slide surface. The possibility to overlap the HF component to the RF plasma seems to allow a control of the surface charging. In order to verify this hypothesis, we measured directly the voltage of the metallic substrate insulating below the dielectric with a high voltage probe. When the metallic substrate was coupled to ground with an impendence of the order of about 10 pF, and both HF and RF supplies were working, voltages of the order of few kV could be reached. In contrast, when the only the RF supply was used only a few tens of V could be measured. The combination of the RF and HF seems therefore to allow to avoid inhomogeneities due to high current micro-discharges or strong electric gradients, and at the same time to control of the ions/surface interaction.

In order to illustrate this effect with a macroscopic phenomenon we used for the insulation of the metal substrate a sodalime slide that was previously ion exchanged with silver ions on the side exposed to the APPJ. On the surface of the sodalime slide a patterned coating of TiO_2 was deposited by sputtering, masking the surface with a transmission electron microscopy copper grid. The grid that was only laid on the surface creating by shadowing a bumped modulation of the titania coating thickness; the maximum coating thickness was about 1 μm. The surface was then exposed to the APPJ using both generator and the titania layer was partially removed using a water solution of EDTA and hydrogen peroxide. Observing the surface by SEM with the secondary electron detector (Fig. 4a), the TiO_2 partially removed layer appears darker over the glass surface where only few scratches and few surface inhomogeneities can be detected, maybe due also to the coating removal. As the backscattered electrons detector was used the image of the masking grid revealed itself from the glass surface (Fig. 4b). The backscattered electrons (BSE) are sensitive to the mass, therefore the darker areas in the glass are related to a lower silver content; the BSE investigates a depth of only a few hundreds of nanometers. This unveiling of the mask pattern is due to the displacement of the silver ions deeper in the glass where the titania layer was thinner, therefore in correspondence of the grid. The silver ion diffusion is induced by the electric field in the glass and by the ion surface charging, then the deposited masking layer has the only role to change the distance between the surface charges and the silver ions.

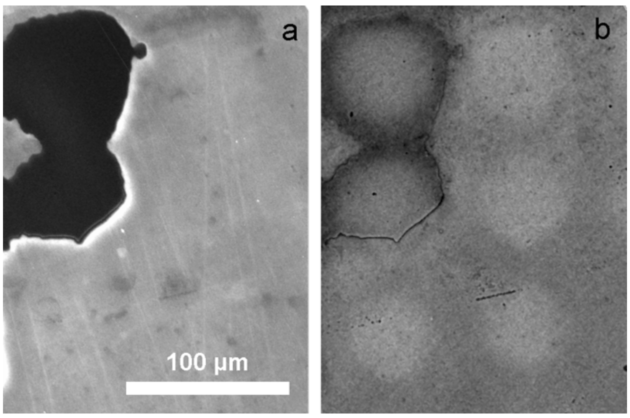

Fig. 4. SEM images with secondary electrons detector (a) and with backscattered electrons (b) of the silver ion exchanged sodalime microscope slide, after the TiO_2 mask deposition, APPJ treatment using HF and RF power supplies and the partial removal of the mask.

When the RF-only excitation was used in the APPJ no ions displacement could be induced in the glass.

Optical emission spectroscopy (OES) measurements close to the substrate surface were carried out on the plasma plume to correlate the plasma parameters with the electrical measurements. The main objective was to highlight the effects of the coupling to plasma densities or temperatures changes. The RF forward power of the APPJ was set at 60W while the HF at 6W. Although the APPJ was driven in Ar as process gas, however the hydrogen and OH emission lines could be detected also inside the discharge tube due to the desorption of water from the dielectric walls. On the other hand, nitrogen molecules vibrations could be detected only after interaction of the jet with the surrounding confinement atmosphere. In Fig. 5 are shown the spectra relative to OH and N_2 bands recorded close to the sample surface in the different configurations. The results on the nitrogen vibrations show that the RF-only configuration achieves the highest warming of the surrounding gas reaching vibrational temperatures of about 350 ± 20 K. However, the different coupling and propagation of the plasma on the substrate may change also the gas fluxes and can change the zones where higher is the energy exchange between the plasma plume and the surrounding environment. Therefore, the temperature differences among the configurations are not significative, but they confirm in any case the low processing temperature of the APPJ under consideration. On the other hand, the OH bands (Fig. 5a) are related to the water present in the process gas. Therefore, their rotational temperature derived by the OES can be correlated to the plasma zone. Also in this case, the temperature is highest for the RF-only configuration at 590 ± 40 K, but close to the 510 ± 30 K of HF+RF one.

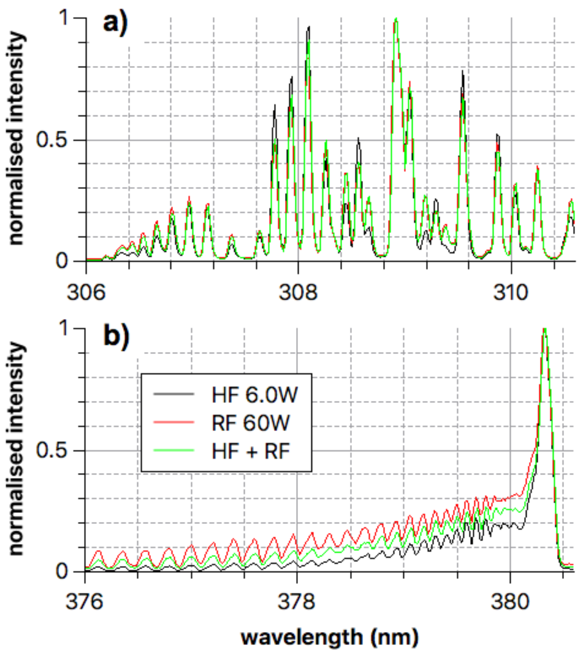

Fig. 5. OES of a) the rotational OH band and b) the vibrational band of the nitrogen second positive system ($C^3\Pi \rightarrow B^3\Pi$) measured close to the substrate.

Electron density and temperature determinations by OES are strongly dependent on the models used. We tried therefore a comparison among the values obtained with several of them. We used the hydrogen lines and their comparison and the ratio among Ar lines [3-6]. The values obtained for the electron density were all of the order of magnitude of 10^{20}-10^{21} m^{-3} and a preliminary analysis suggests an increase of about one order of magnitude of plasma density close to the substrate when both HF and RF are used.

4. Conclusions

A novel APPJ was developed with the ability to achieve relatively low processing temperature and at the same time high plasma densities of the order of 10^{20}-10^{21} m^{-3}. The APPJ introduces the coupling of two different excitation frequencies HF (~ 17 kHz) and RF (27 MHz), which allows to obtain a stable diffused plasma and at the same time to control the ions flux to the substrate surfaces. This phenomenon has been characterized by electrical measurements and by showing the effects of surface charging on silica glass doped with silver ions. The silver ions have high mobility in the glass, therefore they move as a function of the electric field created on the surface itself. Preliminary optical characterization confirms the low temperature of the processing, and the ability to guide the ions to the sample surface.

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6. References

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