Atmospheric pressure plasma treatments inside meander-like cavities

Antje Quade, Katja Fricke, Klaus-Dieter Weltmann

Leibniz Institute for Plasma Science and Technology (INP Greifswald e.V.),
Felix-Hausdorff-Straße 2, 17489 Greifswald, Germany

Non-equilibrium atmospheric pressure plasma is used in a variety of applications related to surface treatment [1]. Most of all materials, intended for biomedical application, which must provide specific surface properties (e.g. enhanced wettability, biocompatibility) are exposed to plasma to improve for instance the efficiency of medical devices or the acceptance of implants. Atmospheric pressure plasma jets have reached an increasing importance in many plasma processing applications which is based on their ability to provide enhanced gas phase chemistry without operating at elevated gas temperatures [2]. Furthermore, an important feature of plasma jets is their capability to penetrate into small structures, such like cavities, gaps, crevices, and tubes which enables the treatment of complex geometries (e.g. scaffolds). For this purpose, a three-dimensional (3D) polycarbonate module was used to demonstrate the capability of jet plasmas, driven at atmospheric pressure, to penetrate into small cavities.

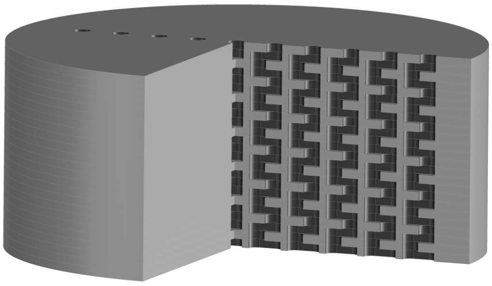

Figure 1:
Schematic drawing of the 3D module with meander-like cavities in a stack of perforated PC-layers.

The 3D module (Fig. 1) consists of perforated PC slices (∅ 24 mm) creating a porous 3D corpus. The slices themselves were laser-cut and the number of slices and the entire geometry is variable according to requirements. The holes of adjacent slices are interconnected in a vertical direction. The vertical pore sequence results in a meander-like single channel configuration throughout the 3D construct. Each slice was 0.5 mm in height, and a stack of 24 slices generates pore channels of an overall longitude of around 1.2 cm. A more detailed description of this newly generated 3D module and its application for cell culture investigations were published by

Bergemann *et al.* [3]. Due to the requirements for osteoblast ingrowth the pore sizes were chosen to be 500 µm in diameter [4].

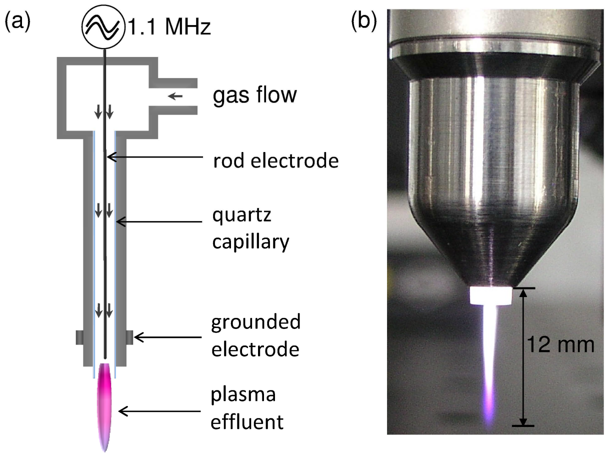

Figure 2: a) Schematic setup of the plasma jet (kINPen09®), b) photograph of the plasma effluent with a length of 12 mm using 5 slm argon gas.

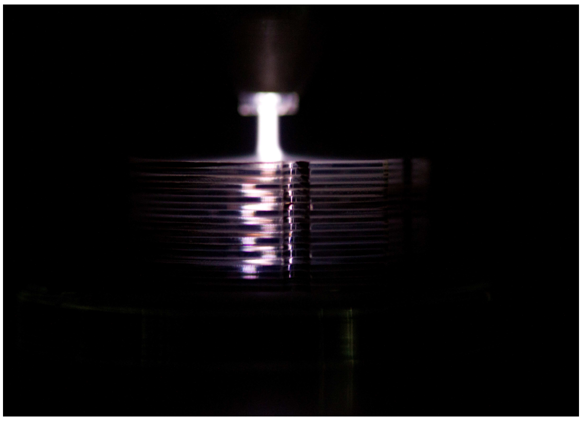

Figure 3: Plasma treatment through meander-like cavity in a stack of 24 PC-slices.

The atmospheric pressure plasma jet (kINPen09®) used in this study is shown in Figure 2. It consists of a hand-held unit for the generation of the plasma jet at atmospheric pressure, a DC power supply and a gas supply unit. In the continuous working mode, used here, a high frequency voltage is coupled to the pin-type electrode. The plasma is generated from the top of the centred electrode and expands to the surrounding air outside the nozzle [5]. As feed gases 5 slm argon (labelled as “Ar-jet”) or 5 slm argon mixed with 0.05 slm molecular oxygen (labelled as “Ar/O_2-jet”) were applied. The plasma treatment through the meander-like cavity (see Fig. 3) was carried out locally at a distance of 2 mm to the nozzle outlet. To study the penetration capability of the atmospheric pressure plasmas, the height of the stack was varied. For the experiments a short plasma treatment time of 30 s and a long-time plasma treatment of 300 s were chosen.

For the examination of the plasma-induced depth effect X-ray photoelectron spectroscopy (XPS) was applied. The surface analysis was performed on the surface of a non-perforated end-layer (made of polycarbonate (PC)), which was layered under the stack. The changes in elemental surface composition were analyzed using an AXIS Ultra DLD electron spectrometer (Kratos Analytical, Manchester, U.K.). The spectra were recorded as a line scan á 0.5 mm with a spot size of ~250 µm at the surface of the end-layer. The O/C ratios of the polycarbonate surfaces exposed to Ar and Ar/O_2 plasma for 30 s and 300 s, respectively, using a stack height of 2 mm (comprised of 4 layers) are depicted in Fig. 4.

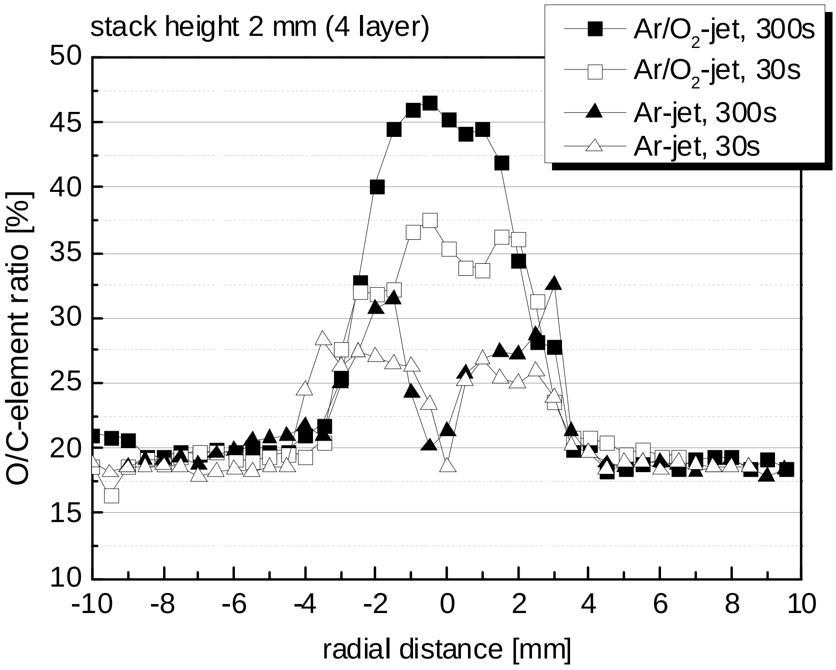

Figure 4: XPS-O/C-elemental ratio at the PC-end-layer after plasma jet treatment through meander-like cavity with a height of 2 mm in dependence on time and operating gases.

As shown in Fig. 4, a functionalization, marked by an increased O/C ratio, of the PC-end-layer via a meander-like channel in a 4-layer stack can be observed. In dependence on treatment time and operating gases the O/C-element ratio varies. For 30 s Ar/O_2-jet treatment the O/C ratio was increased up to 20%, whereas after 30 s Ar-jet plasma treatment even less O-incorporation was noticed (lower O/C ratio). The highest amount of oxygen (O/C ratio of ~47%) was detected after a treatment time of 300 s by using the Ar/O_2-jet. Without oxygen admixture the O/C ratio was increased up to ~30% after long-time plasma treatment. This relatively high O/C ratio obtained by Ar-jet plasma is based on plasma-activated oxygen of the ambient air as well as post plasma oxidation.

Furthermore, along the O/C-curve shapes of the Ar-jet treated samples a distinct decrease of the O/C ratio directly on-axis of the jet can be seen. At this point no additional O-incorporation was detected. A possible explanation might be the low influence of oxygen of the surrounding air in the meander-like cavity due to the high Ar gas flow, which probably generates and operates in its own localized Ar atmosphere.

Since plasma-generated species can lose its reactivity over long distances, the impact of the different process gases on a stack comprised of 24 layers was investigated which is shown in Fig. 5.

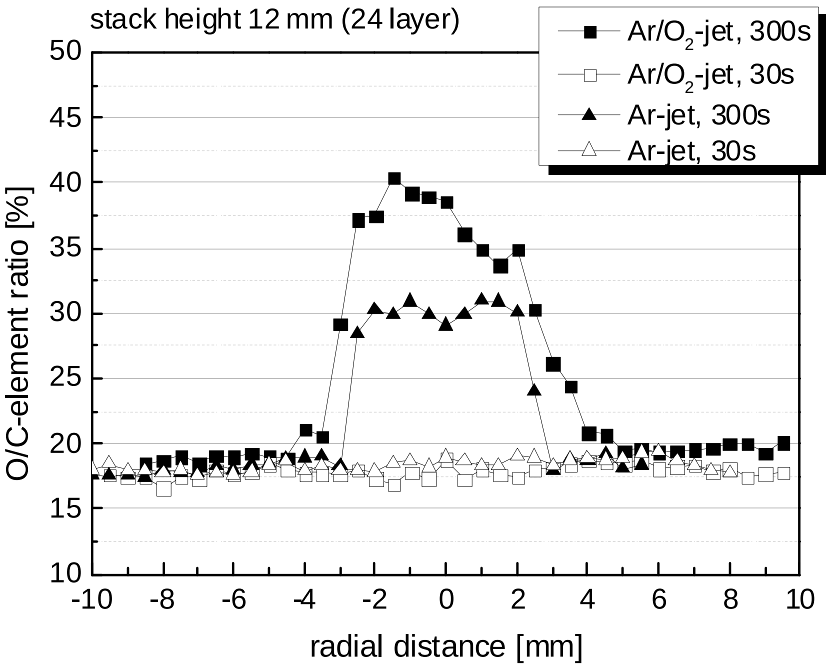

Figure 5:
XPS-O/C-elemental ratio at the PC-end-layer after plasma jet treatment through meander-like cavity with a height of 12 mm in dependence on time and operating gases.

Through a 12 mm long meander-like cavity a significant increase of the O/C ratio at the surface of the end-layer was detected, even though, the O-incorporation depends mainly on the time of the plasma jet treatment (see Fig. 5). A remarkable increase of the O/C ratio of 40% was observed after 300 s Ar/O_2 plasma. Whereas after the short Ar/O_2 plasma treatment of 30 s no oxygen functionalization was detected at the end-layer. In terms of Ar plasma, the O/C ratio was increased to a value of 30% after the long time treatment of 300 s. In accordance to Ar/O_2 plasma, the short time plasma treatment had no influence on the elemental composition of the end-layer.

Summarizing, the ability of an atmospheric pressure plasma jet to create oxygen-functionalities in small cavities in complex 3D geometries was demonstrated. The investigations about the dependence of the functionalization on the applied process gas and treatment time revealed that long-time treatments and Ar/O_2 gas mixtures provide the highest O/C ratio. Furthermore, it was shown, that the surface functionalization can be achieved at high distances.

References

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