Effects of air entrainment on surface modification by an atmospheric pressure argon microplasma jet

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Abstract: Polymer surface modification by an atmospheric pressure argon microplasma jet was analyzed by measuring locally resolved radial profiles of the water contact angle and profiles of chemical surface properties using X-ray photoelectron spectroscopy (XPS). Special emphasis was given to the effects of air entrainment. Two different plasma chemical regimes evolve due to these effects which most pronounced can be seen in the profiles of nitrogen based surface chemical functionalities.

Keywords: surface functionalization, microplasma jet, air entrainment.

1. Introduction

Miniaturized low-power atmospheric plasma jets can be operated in discharge parameter ranges which are inaccessible for many other plasma sources.¹² Their characteristic size, electron density, electron temperature and neutral gas temperature are such that special applications become possible in the fields of e.g. analytical chemistry, surface modification and thin film deposition. Most promising are applications which require localized access to surfaces of heat-sensitive complex three-dimensional objects. Clearly, in those cases long extended free standing jets are best useful. Also, contact with surrounding humid air will be customary. These conditions strongly facilitate entrainment of air into the jets. However, for technical or application reasons the jets are operated using the working gas argon, typically. That circumstance poses a problem since plasma chemistry will be influenced by the presence of oxygen, nitrogen, and also humidity of air. Surface modifications due to reactive oxygen species such as atomic oxygen, hydroxyl radicals and ozone must be expected, leading to surface oxidation, erosion by oxidation or creation of oxygen functional groups. Thus, for successful use of micro-plasma jets detailed knowledge of the consequences of air entrainment is mandatory.

In this paper, results are presented of an experimental investigation of respective effects of oxygen admixture, air entrainment and nitric oxide generation on the local variation of chemical surface functionalisation. Supposed a radial symmetry of the jet is given, axial and radial variations of entrainment must be considered. Whilst effects of axial variations can be moderated by keeping a constant and relatively short distance between jet nozzle and substrate, effects of radial variations must be known in detail. During most applications the jets are scanned. In such cases radial variations will directly determine and possibly limit obtainable lateral treatment homogeneity. This was the reason to focus the present investigation on radial variations. In a first step, experiments were performed to get information on local effect of the jet in general and to select optimum conditions for further detailed investigations. Basically, this was done by measurements of local distributions of water contact angle distributions in dependence on treatment time and substrate position. Additionally, analysis of the radial variation of the optical emission spectrum of the surface-contacting plasma jet was performed. Then, for the selected conditions locally and energetically highly resolved X-ray photoelectron spectroscopy (XPS) was applied to study obtained surface modifications in detail. Additional admixture of air was used to further characterize influence of air entrainment and nitric oxide generation.

2. Experimental

In Figure 1 the experimental setup for the rf driven (27.12 MHz) miniaturized APPJ is schematically shown.[1]

Fig. 1: Schematic plot of the capillary jet and a photo of the jet in action.

The jet consists of a centre rod electrode inside a quartz capillary (with an inner diameter of 1 mm and an outer diameter of 4 mm) which is coupled to the power source.
via a matching network and a grounded ring electrode. For the here presented investigations the jet was operated with argon at a flow rate of 5 slm and small admixtures of N₂, O₂, or air, respectively.

The polymers modified in this study were Polystyrene (1 mm thickness) and Polycarbonate foil (250 µm thickness). The water contact angle measurements were performed with the help of a semiautomatic GBX Digigrop contact angle meter and by the sessile drop method. The chemical changes on the polymer surface were studied by X-ray photoelectron spectroscopy using an Axis Ultra (Kratos, Manchester, UK). XPS spectra had been generally recorded for 1s electrons from C, O, N, F, and 2p Si using a conventional hemispherical analyzer, a monochromatic Al Kα source at 1486.6 eV with 150 W X-ray powers in a standard configuration. The peak fitting procedure was carried out with the help of CasaXPS software version 2.2 (Casa Software Ltd., Teignmouth, UK). Gauss-Lorentz (30 % Lorentz) distribution, Tougaard-baseline, and a fixed FWHM between 1.1 and 1.5 eV were used. All values are given in atomic-% and ratios thereof. The N 1s peak was fitted with peaks of functional groups for which the peak positions were given by Wilken and co-workers [3].

Optical emission spectroscopy was carried out using a Princeton Instruments Pi-Max Digital ICCD Camera in combination with an Acton Spectra Pro 2500i monochromator/spectrograph (0.5 m).

3. Results and Discussion

In the first step of investigations plasma induced surface functionalization effects were studied by contact angle measurements. From this, knowledge of the temporal evolution of treatment effects could be obtained. Figure 2 shows the profiles of contact angles at 1 s and 300 s treatment time. These results were taken for a nozzle-substrate distance of 5 mm. In that case, the tip of the light-emitting active zone of the jet touches the substrate and spreads to a disc-like shape with about ten millimetre diameter. The width of the steep contact angle profile after 1s coincides with this dimension. Hence, it can be assumed that this modification results from the active plasma. A small remainder of this effect is still visible after 300s treatment. But obviously, also the radial, not radiating downstream of the plasma has lesser but still activating effect. Interestingly, this effect can not produce the low contact angles observed in the centre of the footprint. This is another hint on different plasma chemistries in the two regions. Generally, the temporal behaviour reminds to the typical time course of plasma assisted surface activation where a first steep decrease of contact angles is observed which then slowly tends to saturate.

![Profiles of water contact angles along a line across the centre of the chemical imprint of the microplasma jet on polycarbonate substrates.](image)

As a main difference between the two regions the much higher air entrainment to the radial flowing afterglow is assumed. A confirmation of this effect could be found analysing profiles of the optical emission across the jet. In figure 3 the profile of the 777 nm oxygen (\\(^{3}\)S\\(_{1}\) - \(^{3}\)P transition) to 772 nm argon line ratio in the vicinity of the nozzle is given. This profile was obtained by end on observation of the jet in axial direction, viewing through the transparent substrate for a nozzle-substrate distance of 5 mm. The profile exhibits a flat region in the centre and steeply increasing wings at both sides. The apparent width of the flat region compares to the width of the substrate-touching disc-like active plasma region. Referring to the principles of actinometry this optical line ratio might be meaningful for the concentration of oxygen atoms in the discharge, at least regarding the tendency from point to point. So it comes clear that there is a steep increase of atomic oxygen at the beginning of the radial afterglow. This can be expected. Assuming flow dominated transport, a counterbalance of radial transport of active species out of the active region and of air entrainment can lead to a maximum of atomic oxygen in a ring-shaped region surrounding the active zone. However, more downstream, the active species and atomic oxygen soon will be consumed, i.e. a radial decay of atomic oxygen density in the gas phase must occur.

In air-containing rare gas plasmas, initiation of surface reactions most likely will proceed via abstraction of hydrogen from polymers by atomic oxygen or hydroxyl radicals. This is due to the high rate constants of these reactions in comparison to other reactions e.g. with atomic hydrogen or ozone. Different alkyl radicals will be produced which start to react with atomic oxygen, molecular oxygen or ozone to form alkoxy or peroxy radicals. These radicals in turn continue to react. Some of the radicals have very long life times. Therefore, reactions
with molecular oxygen can continue after completion of processing and contact to air. Therefore, oxygen uptake is not a perfect marker for detailed study of air entrainment. In contrast, nitrogen uptake might be more useful since molecular nitrogen is not reactive.

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Fig. 3: Profiles of the O/Ar line ratio of the optical emission (777 nm O, 772 nm Ar) along a line across the centre of the microplasma jet

Indeed, there are also visible effects of nitrogen entrainment in the plasma. In figure 4 a uv-vis-emission spectrum of the central active part of an argon jet with 1% air admixture is given. As a result of admixture the argon emission is reduced, the OH-emission is strongly suppressed and the N\textsubscript{2} and NO-emissions are strongly enhanced. This indicates a transition from argon dominated to nitrogen and oxygen dominated electronic and chemical discharge regimes and suggests the use of nitrogen species as indicators for different plasma chemistry in the central and radial downstream regions as well as for air entrainment induced effects in general.

Fig. 4: UV-VIS-spectra of the jet for argon plus a small air admixture (below); argon flow 5 slm

By a study of a similar jet using quantitative determination of NO\cite{4} it was shown, that at low admixtures the NO emission is a measure for NO content in the plasma gas phase. But generally, the amount of NO is so small that it does not compete with oxygen. Interestingly, also for pure argon as carrier gas some NO and OH emissions are present. NO emission was reduced by a factor of about 50 compared to the maximum. These results suggested looking for nitrogen functional groups on the surfaces. With respect to the special selective reactivity of NO towards alkyl radicals certain groups of this type might allow deeper insight to the effects of air entrainment such as surface radical generation by gas phase oxygen or hydroxyl radicals.

In fact XPS analysis of the N 1s peak showed that all existing nitrogen containing chemical surface bindings are nitric oxide related. Highly resolved peak fits revealed oxymes (C=\text{N-OH}) which are characteristic for the incidence of secondary alkyl radicals, nitroso groups (C-N=O) which are characteristic for the incidence of tertiary alkyl radicals and nitrate groups (C-O-NO\textsubscript{2}) which may be considered as products of reactions of nitroso groups with NO\cite{3}.

Figure 5 shows the profiles of the nitric oxide related bindings for pure argon and a short nozzle-substrate distance. In the central region oxyme and nitroso groups generation seem comparable while no nitrate groups can be observed. Possibly, high energetic plasma in the centre of the jet favours alkyl radical generation while only relatively few oxygen based species are present to facilitate abreactions. The situation quickly changes with increasing distance to the centre. Within the disc-like impinging active jet region the generation of nitroso groups is highest, indicating less energetic conditions. In the region where maximum atomic oxygen production can be assumed (see above), appreciable nitrate production occurs. That could be reaction a product of surface nitroso groups with NO. However, higher oxygen admixtures also will increase consumption of NO by gas phase reactions generating e.g. NO\textsubscript{2}. Thus, effects of this entrainment must be more complex. At the present level of approach one can only speculate about relevant effects. Taking into account that this is a downstream situation it is a good assumption to consider gas phase chemistry initiated by long-lived active neutrals which were produced in the centre part of the jet, especially by excited nitrogen N\textsubscript{2}* and atomic nitrogen.

Nevertheless, again it becomes clear that there are considerable differences in gas phase and surface chemistry between the central part, the surface contact region and the radial downstream region of the jet. The general effects of air entrainment do not much depend on the degree of entrainment. This is shown by the results of figure 6. There, a small amount of air is added directly to the gas supply. The only effects are, that production of oxymes in the centre and production of nitrates in the oxygen region are increased.
Fig. 5: Radial profile of the nitrogen bindings on the surface of polystyrene substrates, determined from peak fitting of highly resolved scanning XPS measurements; pure argon; treatment time 20 s.

Fig. 6: Radial profile of the nitrogen bindings on the surface of polystyrene substrates, determined from peak fitting of highly resolved scanning XPS measurements; 5 slm argon plus 26 sccm air admixture.

4. Summary

In this study the effects of entrainment of ambient humid air into an atmospheric pressure microplasma jet have been characterized by water contact angle measurements and X-ray photoelectron spectroscopy of the treated polymer surfaces as well as by optical emission spectroscopy of the jet. The contact angle measurements give evidence to assume multiple different plasma chemistries governing the functionalization. The Ar/O ratio attained from OES measurements shows in the centre a flat profile with a low oxygen amount increasing steeply to the sides. Accordingly, the disc-like region of the impinging active part of the plasma jet may be distinguished from a radial afterglow region, the beginning of which is characterized by a considerably higher value of the atomic oxygen concentration. As the oxygen uptake of the surface is not a good marker for studying local structure of the jets effects, because of multiple reaction paths with the surface, and due to an indication in the OES-spectra for a transition from argon dominated to nitrogen and oxygen dominated electronic and chemical discharge regimes, nitrogen species were used as indicators for different plasma chemistry. XPS analysis of the treated surface, especially the N 1s signal, exhibited a distinct structure of different nitric oxide related surface bindings. This showed that the air entrainment into a jet run with pure argon even in the central region is not negligible and that there are considerable differences in gas phase and surface chemistry between the central and the radial downstream region as radial distribution of different alkyl-radical markers differ considerably.

5. References