

Atmospheric pressure plasma jet for treatment of polymers

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ABSTRACT

Purpose: Polymers are commonly used as packing materials as well as for optical and microelectronic applications. For these purposes different requirements like impermeability for different gases, scratching firmness and electrical conductivity are demanded. Since, polymers usually do not exhibit these attributes a surface modification is necessary.

Design/methodology/approach: This paper describes possibilities for coating of polymers with a cold atmospheric pressure plasma jet (APPJ). Due to the rather low temperature of the process the plasma jet is suitable for the treatment of temperature-sensitive materials with melting points below 150°C. For coating of polymers the organic precursor Hexamethyldisiloxane (HMDSO) has been used to deposit silicon oxide layers on surface.

Findings: Spatial distributions of reactive species have been measured by optical emission spectroscopy (OES) in the range between 280 and 1100 nm during the plasma process. The energy influx to the substrate was determined by thermal probe measurements. For the affirmation of the chemical composition of the surface X-ray photon spectroscopy (XPS) has been performed.

Practical implications: It could be confirmed that SiO_x thin film deposition on polymeric substrate using commercially available APPJ with no internal precursor feeding is possible.

Originality/value: The examinations of atmospheric pressure plasma jet for treatment of polymers.

Keywords: Plasma jet; Diagnostic; HMDSO; Atmospheric plasma

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1. Introduction

Atmospheric pressure plasma jets have been established as suitable sources of low-temperature and non-equilibrium atmospheric pressure plasmas [1, 2]. The main distinctive features of this plasma tool is the remote operation (jet is not confined by electrodes) and its scalable dimension which can be adjusted from several cm down to the sub-mm region, thus, allowing local treatment of 3D surfaces, e.g. inner walls, trenches or cavities [2].

Among other applications, the treatment of temperature-sensitive surfaces such as biological material is of interest, in particular the interaction of plasma with living cells, tissues and bacteria, e.g. for cultivation, deactivation or remedial treatment of diseases.

Organosilicons provide a large variety of possible fragments for plasma-polymerization processes because these compounds are generally sufficiently volatile close to room temperature, relatively nontoxic, non-flammable, cheap and commercially available. HMDSO is often preferred as a precursor of plasma

polymerization because of its highly organic character as well as its high vapour pressure [3]. HMDSO plasma-polymerized thin films can be assayed for a large number of applications in several fields such as protective anti-scratch coatings, barrier films for food and pharmaceutical packaging, corrosion protection layers, coatings for biocompatible materials and low-k dielectric layers for microelectronic applications [4, 5].

Plasma deposition from HMDSO mixed with different carrier gases has been extensively studied using low pressure non-thermal plasmas [6, 7]. One of the limitations to use plasma enhanced thin film depositions is the need of vacuum systems. In order to avoid these limitations, an APPJ was developed by the INP and neoplasm GmbH Greifswald.

The present work focused on the formation of HMDSO-based coatings on polyethylene methacrylate (PMMA) substrates using an APPJ with argon in the air mixture and the related diagnostics.

For the characterisation of the plasma jet, respectively, the plasma beam, thermal probe and spectroscopic measurements have been performed.

It is well known that in low pressure plasmas, the surface temperature of the substrate T_s which is strongly affected by plasma-wall-interaction effects elementary surface processes like adsorption, desorption, and diffusion as well as chemical reactions (e.g. chemical sputtering, surface film reaction) [8, 9]. On the other hand, especially in the case of thin film deposition, the structure and morphology as well as the stoichiometry of the film depend strongly on the energetic conditions at the surface [3, 10].

Since atmospheric pressure plasmas (APP) came into the focus of application there is also a need to investigate the energy influx from the plasma towards the substrate. Measuring the energy flux at atmospheric pressure is challenging because the appearance and the dimensions (e.g. they form tiny, filamentary discharge channels or have a small size like micro hollow cathodes) of atmospheric pressure plasmas are different to low pressure plasmas.

2. Experiments

The used capillary APPJ is a commercially available plasma source which is operated by an rf-frequency of 1.7 MHz. This frequency, which cannot be changed, has turned out to be the most suitable one for this device geometry and dimension.

A scheme of the APPJ is shown in Figure 1. The rf-power supply is connected to the centre rod electrode via matching network. The whole system power is about 65 W and the supplied voltage is between 2.5 and 3.5 kV_{pp}. The electrode is surrounded by a ceramic capillary which forms the gas stream and a grounded ring electrode. This electrode stabilizes the operation of the jet. The argon gas pressure is 1.5 bar and the resulting gas flow through the jet is constant 4.8 slm. The used device has no internal precursor feeding. Reactive gases are injected into the plasma jet outside the nozzle through a small gas inlet forming an own precursor atmosphere. The maximum length of the plasma jet is about 14 mm and the diameter is 1 mm like the inner diameter of the capillary. The gas temperature was measured to be in the range from 30 to 95°Celsius [11].

The integral energy flux from the plasma towards the substrate has been measured by a compact thermal probe. A

detailed description of the theory can be found in [12] and the used probe is described in [13].

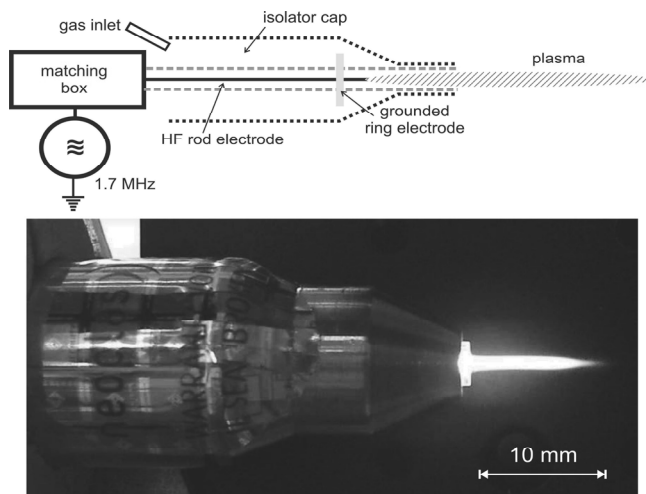


Fig. 1. Sketch (top) and photograph (bottom) of the used APPJ

For the optical diagnostics of the plasma jet a commercial spectrometer (Ocean Optics-HVR 2000+) was used. This apparatus allows studying emission lines in the range 280 - 1100 nm.

3. Results and discussion

3.1. Thermal probe measurements

The energy influx from the plasma jet to the substrate was measured with a thermal probe. A typical measurement curve is shown in Figure 2.

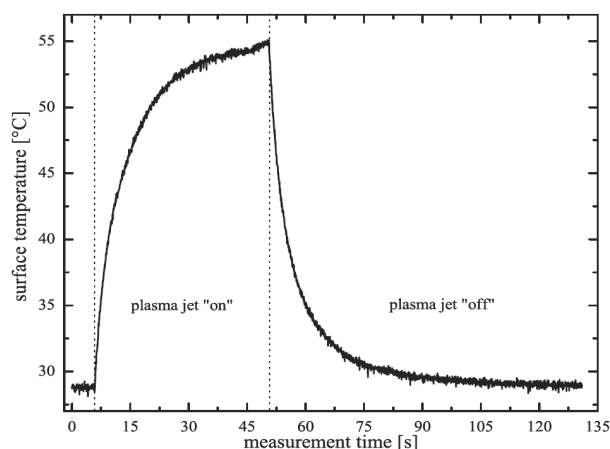


Fig. 2. Measured temperature curve. The plasma jet was switched on at $t=6$ seconds. The surface temperature of the thermal probe increases. After 40 seconds the jet was switched off and the thermal probe cools down

The axial measurements of the total energy influx in dependence on the distance between the orifice of the plasma jet and the thermal probe are shown in Figure 3.

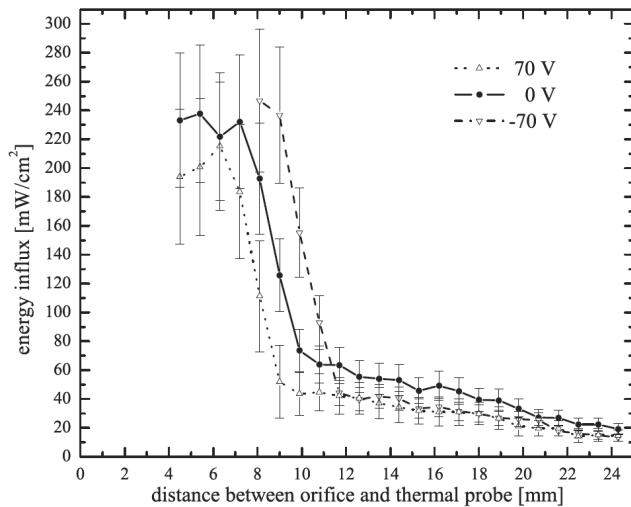


Fig. 3. Total energy influx against the distance between the orifice of the plasma jet and the thermal probe for three different bias voltages of the probe

The measurement starts at a distance of 25 mm from the orifice. About 14 mm behind the orifice the visible plasma beam ends (see Fig.1 bottom) as observed by the naked eye. Up to this position the total energy influx is about 15 mW/cm². When the thermal probe was moved closer to the plasma jet the total energy influx slowly increases and at a distance of 11 mm the mean value for the influx is ca. 50 mW/cm². Depending on the bias voltage, a fast increasing of the energy influx starts between 10 and 12 mm in front of the jet. Still three mm closer to the nozzle the energy influx shows a maximum for each bias voltage. For the negative voltage (-70 V) the highest value is 250 mW/cm², for the positive voltage (+70 V) this maxima is around 210 mW/cm² and for the grounded probe the maximal energy influx is 230 mW/cm². When the thermal probe comes closer to the plasma jet, the energy influx is more or less constant, or shows a little decrease, respectively. At a distance less than 6 mm it was not possible to perform any measurements. The reason was a strong interaction between the plasma and the probe. Here many filaments are created. In addition to the energy influx the current thermal probe was determined at the same time.

The measured currents are plotted in Figure 4. The current for all three bias voltages between 25 and 16 mm is almost not measurable (~0 mA). This observation corresponds to the results for the energy influx.

When the probe comes closer to the plasma jet a different behaviour is observed. The grounded and negative biased probes show an increase of the probe current up to 2 mA. The maximum values are nearly the same but the time to reach this value is shorter for the negatively biased probe. The behaviour of the probe current for a positively biased thermal probe is close to the negatively biased probe but the maximum value is -2 mA. When the bias voltage at the thermal probe is more positive as the

floating potential of the surrounding plasma, more electrons are collected and the resulting current to the probe becomes negative. In contrast, if the bias voltage is more negative, the current to the probe is positive due to collection of the ions. In general, the current to the thermal probe is very low in comparison to other experiments at low pressure with an energy influx in the same order [13]. The reason is clear that the plasma jet is operated at atmospheric pressure. Therefore, we assume that the most part of the measured energy influx has its origin in the UV-radiation of the plasma jet [2]. Charge carriers (electrons and ions) do not play an important role, especially at a distance between the plasma jet and the probe larger when 10 mm. We estimated this part with less than 10% of the total energy influx. If charged species would play a dominant role for the energy influx, a dramatic increase, in the positive probe current for higher negative bias voltages would be observed [13]. This is obviously not the case. Spectroscopic measurements by Foest et al. [2] provided energy influxes due to VUV / UV radiation between 15 and 50 mW/cm² for a comparable plasma jet. The temperature maxima which were reached at the thermal probe was 55°C. The knowledge of the maxima temperature can be helpful for applications of the plasma jet, e.g. modification of temperature sensitive surfaces or biological materials.

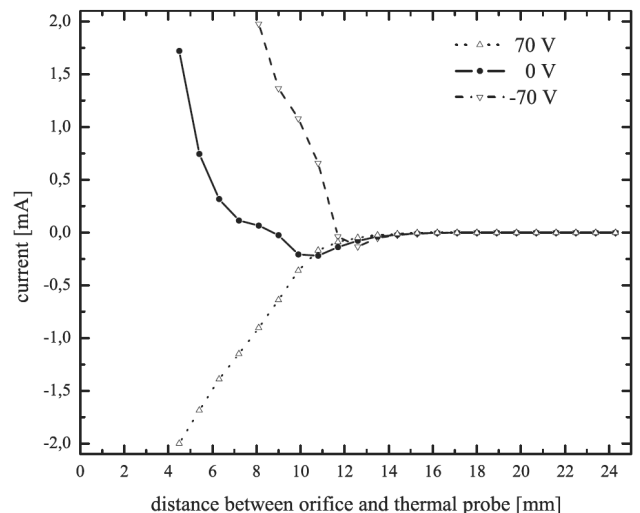


Fig. 4. Measured current to the thermal probe from the plasma against the distance between the orifices of the plasma jet for the same three bias voltages of the probe

3.2. Optical emission spectroscopy

A typical spectrum of the used plasma jet (without HMDSO) is shown in Figure 5.

The main intensive argon lines can be found in the region between 670 and 970 nm. Few argon lines with much lower intensity can be found at 415 and 420 nm. In addition to the argon lines, some lines from nitrogen, oxygen, hydrogen and the hydroxyl group could be identified, e.g. the H α line at 656.28 nm or the hydroxyl group at 308 nm. These lines result in

dissociations and excitation (due to the plasma jet) of the surrounding air which contains nitrogen, oxygen and water. The intensities of the spectral lines show a characteristic distribution along the plasma jet axis.

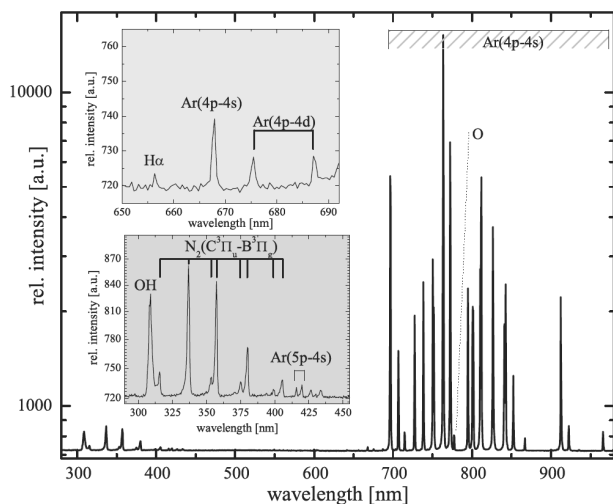


Fig. 5. Spectra overview of the plasma jet with pure argon gas in ambient air

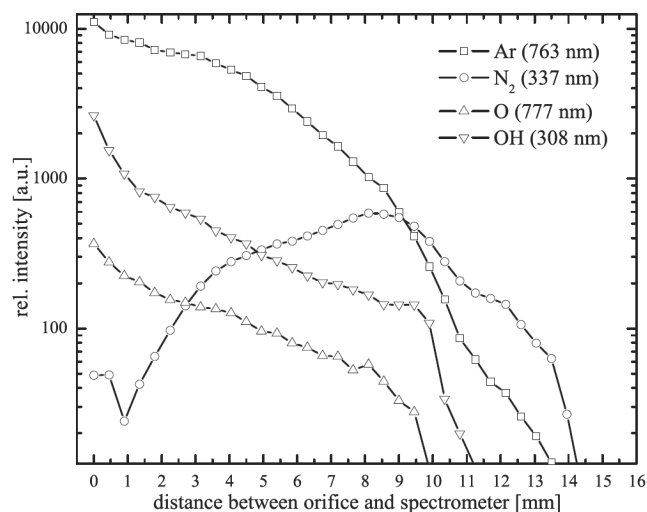


Fig. 6. Relative intensities of selected species, e.g. Ar, O, OH and N₂ in dependence on the distance between the spectrometer and the orifice of the plasma jet

In Figure 6 the most intensive lines for argon, nitrogen, oxygen and the hydroxyl group in dependence on the distance from the plasma jet orifice are shown. In general, two tendencies can be observed: The maximum of argon, oxygen and OH lines is located at the orifice of the plasma jet. With increasing distance to the orifice these signals decrease. The signal of the O and the OH lines vanishes at ca. 11 mm. In comparison with fig.1 a change in the light of the plasma jet is observable at that position. The beam becomes smaller and the colour changes from white into light

blue (not visible in gray scale image). The nitrogen line shows a different behaviour. At the orifice the intensity is in the order of 40 ± 20 counts. The signal increases with increasing distance to the plasma jet and reaches a maximum at 9 mm from the orifice. At this point the signal also decreases as well as the other intensities. The measurable intensity for the argon and nitrogen lines ends at a distance of around 14 mm. This corresponds again with the observation done by the naked eye. The excitation and dissociation of the oxygen and water molecules happens due to the UV-radiation, which is similar to the formation of the ozone. In contrast, the nitrogen molecules are mainly excited due to the collision with the metastable argon atoms. Hence, the nitrogen molecules have to diffuse into the plasma jet. Because of these different mechanisms the different spatial distribution of the line intensities can be explained. The analysis of the argon line intensity confirmed the measurements by Foest et al. [2], where development of an argon channel is described, which hardly interacts with the ambient air.

3.3. Thin film deposition with HMDSO

During the plasma process the HMDSO was split into the $C_3H_5OSi_2^+$ - molecule and a CH_3 group [14]. The molecule can be deposited onto the substrate surface and form thin films of different properties depending on the stoichiometry. During the thin film deposition some unrequested carbon atoms also are included in the films. The reason for this is that the precursor is fragmentarily dissociated. With additional oxygen, ration between silicon and oxygen in the film can be varied and form polymer like (1:1) up to quartz like (1:4) structures.

The XPS-spectra for the treated and untreated PMMA substrate with HMDSO are plotted in Figure 7.

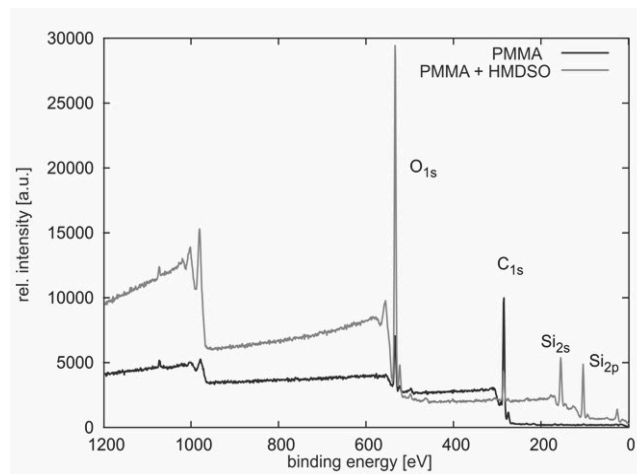


Fig. 7. XPS overview spectra for the untreated (black line) probe and the HMDSO coated PMMA probe (gray line)

The XPS spectra of the coated probe show peaks of Si_{2s} (154.5 eV), Si_{2p} (103.5 eV) states and increase of oxygen (533.5 eV) peaks.

4. Conclusions

Thermal probe measurements verified the possibility to treat temperature sensitive materials with this APPJ. The maximum substrate temperature was measured to be around 55 °Celsius. OES measurements have shown a need for a precursor atmosphere around the jet because of weak interaction of the jet with surrounding atmosphere. It could be confirmed that SiO_x thin film deposition on polymeric substrate using commercially available APPJ with no internal precursor feeding is possible.

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