Atmospheric pressure plasma deposition of poly(ethylene oxide)-like antifouling coatings from methacrylate precursors

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³Molecular Plasma Group, Rue du Commerce 20, Technoport Hall 4B, L3895 Foetz **Abstract:** Aerosol-assisted plasma-deposition with an open-air atmospheric pressure plasma torch is a cost-effective and scalable process. We investigated the deposition of poly(ethylene oxide)-like antifouling coatings from four precursors with two methacrylate end groups and variable ethylene oxide repeat units. Both the antifouling properties and the stability of the films in water are linked to the chemical composition and deposition mechanism.

Keywords: Atmospheric pressure plasma, Antifouling, Aerosol-assisted plasma deposition

1. Introduction

The sensitivity and lifetime of biosensors and lab-on-chip devices is often hampered by the unwanted binding of proteins and cells to the device surface, also called biofouling. The sensitivity and device lifetime of biosensors is often decreased by biofouling, due to formation of an impermeable layer for the analyte (1). For biomedical devices such as implants it is important that the surface is biocompatible to prevent inflammation and encapsulation of the device (2). A common strategy to prevent fouling is the use of poly(ethylene oxide) (PEO) layers, which are considered as the "gold standard" for antifouling layers (3). Several approaches for surface modification with PEO exist, including the use of selfassembled monolayers (4-6), grafted polymer brushes (7-10), UV-polymerization (11, 12) and plasma deposition (13, 14).

The potential for scaling to mass production has raised increasing interest in cold atmospheric pressure plasma torches. Typical precursors used for plasma deposition of PEO (14) such as tri(ethylene glycol) dimethyl ether and tetra(ethylene glycol) dimethyl ether have a low vapor pressure (0.02 Torr, and <0.01 Torr at 20 °C respectively) which makes them impractical to use for vapor phase deposition at atmospheric pressure. Aerosol-assisted plasma deposition alleviates the need for volatile precursors, broadening the range of potential precursors (15). Unsaturated bonds such as C=C bonds are preferentially activated in a plasma, preserving the functional part of the precursor (16, 17). A typical reaction mechanism is activation of the precursor by reactive species in the plasma, followed by radical chain growth polymerization (16). In conventional radical chain growth polymerization, methacrylate precursors polymerize easily, therefore they are an interesting choice as precursor. It is unknown how methacrylate precursors polymerize in an open-air atmospheric pressure plasma.

In this paper, we investigated the atmospheric pressure plasma deposition of PEO from ethylene glycol dimethacrylate (EGDMA) (boiling point 508 K), di(ethylene glycol) dimethacrylate (2EGDMA) (boiling point 578 K), tri(ethylene glycol) dimethacrylate (3EGDMA) (boiling point 621 K) and poly(ethylene glycol) dimethacrylate with 9 PEG units (9EGDMA) (boiling point not given, but higher than 621 K) with an open-air atmospheric pressure plasma torch. These precursors have a high boiling point and cannot be used for vapor phase deposition. Therefore, we use aerosol-assisted precursor injection: an atomizer creates precursor droplets in a carrier gas, which are injected in the plasma afterglow in a concentric nozzle, open to the atmosphere. The stability of the films in water was investigated for different precursor gas flows, and the composition was analysed with Fourier Transform InfraRed (FTIR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS). In addition, the antifouling properties of the films were measured and linked to the composition.

Material and Methods



Figure 1: schematic of the a) plasma deposition tool used for the experiments b) atomizer for aerosol generation

<u>Materials</u>

Ethylene glycol dimethacrylate, di(ethylene glycol) dimethacrylate, tri(ethylene glycol) dimethacrylate, poly(ethylene glycol) dimethacrylate M_n 550 g/mol, acetic acid, toluene and anti-mouse IgG antibody from goat labelled with an Atto647N fluorescent dye were purchased from Sigma Aldrich, 3-[methoxy(polyethyleneoxy)6-9] propyltrimethoxysilane was purchased from Gelest.

Substrates

P-type silicon wafers with (100) crystal orientation were purchased from MEMC Electronic Materials. The substrates were cleaned by sonication in acetone and IPA. Immediately before deposition, the substrates received an additional 15 min UV/O₃ clean (UVO-cleaner, Jelight Company Inc.) to remove any airborne organic contamination. Silicon coupons with a 100 nm thermal oxide were used for antifouling measurements to prevent quenching of the fluorophores.

Plasma deposition

All plasma depositions were performed using the PlasmaSpot® (Molecular Plasma Group (MPG), Luxembourg) dielectric barrier discharge (DBD) plasma jet (18). This R&D system enables the generation of atmospheric pressure cold (near ambient temperature) plasmas. It consists of two concentric tubular electrodes (Figure 1a) the external one is covered with a dielectric layer and is connected to the power source, while the inner one is grounded. The PlasmaSpot® powered electrode was fed with a high-voltage up to 15 kV peak-to-peak, at a frequency in the 30-40 kHz range. The nominal power output was 90 W for all experiments. A fixed flow rate of 80 standard liters per minute (slm) argon (Alphagaz, Airliquide) was fed to the system acting as discharge gas. Plasma deposition was performed across the entire sample surface using a moving stage with a 16 mm/s line speed and a track width of 2 mm, and all films were deposited with 2 passes of the plasma torch. To shield the reaction area from air, a 3D-printed ring-shaped nozzle was attached to the PlasmaSpot®. In this nozzle the plasma is combined with the precursor. The nozzle to substrate distance was fixed at 2 mm. The precursor is supplied to the plasma in the form of an aerosol, generated by an MPG atomizer (Figure 1b). The exact working principle of the atomizer is described elsewhere (18). The orifice size was 0.4 mm. The precursor gas flow was varied between 0.75 and 0.95 slm for all precursors.

Film characterization

100 µm spot was used.

FTIR was performed in transmission mode using a Nicolet 6700 system from Thermofisher. 60 scans per sample were performed from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The background was corrected by subtracting the spectrum of a blank silicon coupon, obtained right before TQ-analyst the measurements. software from Thermofisher was used to obtain the area of the bands. The stability of the films in water was determined by comparing the integrated band containing the CH, CH₂, CH₃ stretch before and after soaking 10 minutes in deionized water. XPS measurements in Angle Integrated mode were done using a QUANTES instrument from Physical Electronics. The measurements were performed using а monochromatized photon beam (Al Ka:hv= 1486.6 eV), the pass energy was 69 eV and the step size 0.125 eV. A



Figure 2: Transmission FTIR spectra of plasma deposited films from EGDMA, 2EGDMA, 3EGDMA and 9EGDMA at a low and a high precursor gas flow (0.75 and 0.95 slm respectively), together with the spectrum of

the unreacted precursor.



Figure 3: Percentage of the films remaining after a 10 minutes soak in deionized water, as a function of the C=C band area normalized by the CH_{1, 2, 3} band area in the transmission FTIR spectra. Grey circles indicate the films further analysed with XPS and antifouling measurements. Empty, half full and full symbols represent films

deposited at 0.75, 0.85 and 0.95 slm respectively. The lines are a guide for the eye.

Results and discussion

First, we investigate the impact of the precursor gas flow on the film composition. We compare the transmission FTIR spectra for films deposited from EGDMA, 2EGDMA, 3EGDMA and 9EGDMA for a high and a low precursor gas flow setting with the spectrum of the unreacted precursor (Figure 2). The FTIR spectra indicate that the C=C bonds are activated by the plasma: compared to the spectra of the liquid precursors, the intensity of the C=C stretching band at 1635 cm⁻¹ is overall lower in the spectra of the corresponding plasma deposited films. This is further reinforced when the precursor gas flow is lower, and can be explained by a higher energy-per-molecule ratio for low precursor gas flows. This is accompanied by a shift in position of the C=O stretching band from 1720 cm⁻¹ for the precursor to 1750 cm⁻¹ for the deposited films, indicating loss of conjugation with the C=C bond, and decreased intensity of the =CH2 rocking band. The band at 1130 cm⁻¹ in the precursor spectrum, representing stretching vibration of the ether bonds, is still present in the spectra of the deposited films, and a clear band associated with CH2 stretching is observed for all conditions. This suggests that the ethylene oxide units are at least partly maintained in the deposited films.

Table 1: Fitting of the C1s peak in the high resolution XPS spectrum. From low to high binding energy representing 4 peaks containing mainly C-C and C-H bonds, C-O bonds, C=O or O-C-O bonds and O-C=O bonds. XPS spectra obtained from films deposited at 0.75 slm precursor gas flow, after 10 minutes soaking in water. Numbers represent percentage of total amount of carbon.

Numbers between brackets represent the theoretical percentage in the precursor.

	C-C, CH	С-О-С, С-ОН	C=O, O-C-O	0-C=0
EGDMA	41(60)	32 (20)	8	20 (20)
2EGDMA	36 (50)	40 (33)	7	17 (17)
3EGDMA	34 (43)	44 (43)	7	15 (14)
9EGDMA	23 (23)	59 (69)	6	12 (8)
PEG-SAM	17	79	4	0

Next, we investigate the impact of the composition on the stability of the polymer films in deionized water. The stability is determined as the percentage of the band containing CH, CH_2 and CH_3 stretching in the FTIR spectrum remaining after soaking for 10 minutes in water. The stability of the films in water increases strongly upon increased reaction of the C=C bonds, namely films with lower final C=C content after deposition show the highest stability and this for 2EGDMA, 3EGDMA and 9EGDMA as shown in Figure 3.

As described above, the films with different C=C content were obtained by variation of the precursor gas flow. For EGDMA, the majority of C=C bonds is activated, when compared with the precursor for all tested precursor gas flows (C=C/CH_{1,2,3} ~0.02 in the film vs 0.41 for the precursor) and therefore no large variation in the stability is observed.

The films deposited from 2EGDMA contain more unreacted C=C bonds compared to films deposited from EGDMA, although for both precursors the same range of precursor gas flows was used. Presumably, this can be explained by the boiling point of the precursors: EGDMA has a lower boiling point compared to 2EGDMA (508 K vs 578K), which could lead to more droplet evaporation during transport to the substrate, and subsequently more removal of precursor with the plasma gas flow to the exhaust. Films deposited from 3EGDMA and 9EGDMA on the other hand, have a lower C=C content compared to 2EGDMA, following the trend in the precursor (C=C/CH_{1,2,3} ~ 0.13 and 0.035 for the 3EGDMA and PEGDMA).





Important for poly(ethylene oxide)-like antifouling films is a high C-O-C bond percentage, which can be observed in the high resolution XPS C1s spectrum (19). The percentage C-O-C or C-OH bonds detected increases with the number of ethylene oxide repeats in the precursor, from 32% for EGDMA to 59% for 9EGDMA (Table 1). This shows that the films are PEO-like, and 9EGDMA almost reaches the 60% often claimed in literature to be necessary for antifouling (20). The C-O content of the films deposited from EGDMA, 2EGDMA and 3EGDMA is higher than the theoretical content in the precursor, indicating the formation of additional C-OH bonds, in agreement with the FT-IR spectra.

The O-C=O bonds, present in the precursor as an ester function are fully retained in all deposited films. There is a reduction in C-C and C-H bonds with respect to the precursor (except for 9EGDMA) which can potentially be explained by oxygen binding to an activated C-C radical, leading to C=O, C-OH or C-O-C formation, which is further suggested by formation of 7-8% C=O bonds and an increase in O-content in the coatings (data not shown), common for plasma deposited films which are exposed to air during and after deposition (16).

Finally, we investigate the antifouling properties of the plasma deposited PEO films. A polv(ethylene oxide)-like antifouling coating should prevent the non-specific binding of proteins from a solution to the surface (3). We test this by measuring the binding of a fluorescently labelled protein, anti-mouse IgG. The antifouling performance of the plasma deposited PEO film is compared with two reference samples: a poly(ethylene glycol) self-assembled monolayer (PEG-SAM) as a positive control with high C-O content (low fouling) (21), and an uncoated SiOx substrate as a negative control (high fouling). Films deposited from 2EGDMA and EGDMA do not significantly reduce the fouling with respect to an uncoated silicon oxide coupon (Figure 4). Films deposited from 3EGDMA however show significantly reduced fouling. Finally, films deposited from 9EGDMA show very low fouling comparable to the positive control PEG-SAM. The degree of fouling is in agreement with the C-O content from XPS: a high degree of fouling corresponds to a low C-O content (32% for EGDMA), a low degree of fouling can be expected for a high C-O content (59% for 9EGDMA).

Conclusion and outlook

Antifouling coatings remain of high interest for biomedical applications. We investigated the deposition of PEO-like antifouling films from methacrylate precursors with an open-air atmospheric pressure plasma jet. The composition and stability of the films can be controlled by the precursor gas flow. Decreasing the precursor gas flow increases the C=C bond conversion and increases the film stability in water, showing that the polymerization mainly occurs via the C=C bond. The composition, and antifouling properties of the films can be tuned by proper precursor selection: films deposited from the 9EGDMA precursor yield better antifouling properties compared to films deposited from EGDMA, which can be explained by the higher C-O-C content (59% versus 33%) and lower content of C-C and O-C=O bonds. There is a trade of in precursor selection: the methacrylate groups are beneficial for the stability in water but reduce the antifouling properties of the films due to the incorporation of C-C, C=O and O-C=O functionalities. The aerosol injection of the precursor allows us to explore precursors with many ethylene oxide repeats, (9 repeats for 9EGDMA), and thus increase the C-O content and improve the antifouling properties of the films. For future work, precursors with vinyl end groups might be interesting to further increase the C-O content of the coatings, even for precursors with only a few ethylene oxide repeating units. The results of this work show the potential of aerosol-assisted deposition, allowing to convert a broad range of precursors into a polymerized film, with the desired composition and functionality.

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