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μPlasma Printing of amine-containing polymer films using APTMS (3-aminopropyl trimethoxysilane)

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Abstract

In this M.Sc. thesis work, the plasma polymerization of amine containing 3-aminopropyl trimethoxysilane (APTMS) by a µPlasmaPrint system is investigated on a fluorocarbon polymer substrate (FEP). The µPlasmaPrint system utilizes a (multi) pin-to-plate dielectric barrier discharge at atmospheric pressure. The deposition of APTMS, which is injected into the plasma region by means of nitrogen carrier gas, is performed in a flow rate controlled polymerization regime, which results in a film thickness of 8 nm per µPlasmaPrint repeat (PR). The number of print repeats was varied from 1 – 20 PR.

The APTMS monomer is polymerized by the formation of siloxane bonds, via the dissociation of its methyl groups by hydrolysis- and condensation reactions. For 1 PR it is found that the aminopropyl chain is predominantly retained, providing an amine concentration of ∼ 9 at.% (according to the XPS peak deconvolution). The high surface concentration of amine functionalities resulted in a (static) water contact angle of 10 ± 5º, accompanied by a relatively high (polar) surface energy. Oxidation during and/or immediately after deposition reduces the films functionality when the number of print repeats is increased. After 20 PR, the amine concentration in the top 10 nm of the film is reduced to ∼ 5 at.% and the water contact angle is increased to 45 ± 3º. After comparison with experiments where the APTMS deposition is carried out on glass substrates, it is suggested that for the FEP substrate, the incorporation of CF groups in the APTMS film impedes the oxidation of thin APTMS films (1 – 3 PR). After deposition, the presence of amine functionalities is also reduced, both due to post-deposition oxidation and due to hydrophobic recovery.

Furthermore, the ability of the amine functionalities to promote immobilization reactions is demonstrated by means of two examples: an electroless plating process is performed and fluorescamine molecules are anchored to the amine functional groups. The measured fluorescent intensity of the amine-bonded fluorescamine is found to be consistent with the amine concentration, which is derived by XPS.
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Chapter 1

Introduction: Amine functionalities on polymer surfaces

Plasma treatment is known to be an efficient technique to clean, activate or coat the surface of a great variety of substrates, for example to improve the wetting, adhesion or bio-compatibility of polymers.[1, 2, 3] When plasma processes are developed at atmospheric pressure, for example by means of a dielectric barrier discharge (DBD), cost efficient surface modification is enabled. Plasma treatment of polymers has been, and still is, an extensive area of research and application, because it allows to affect the chemical inertness, or low surface energy, of polymer substrates. Also the compatibility with roll-to-roll manufacturing is an advantage in the case of the use of polymer webs.[4]

By modifying the surface of the polymers, specific functional groups, e.g. amine ($NH_2$) functionalities, can be anchored at the surface to allow covalent binding with other molecules and/or an improvement of wettability.[5] Potential applications of plasma surface treatments in general, and of amine functionalities specifically, are summarized in Figure 1.1.

The reactivity of amine functionalities allows covalent polymer-polymer or polymer-metal coupling[6], which has applications in both printed electronics and bio-molecule immobilization.[7, 8] The improvement of adhesion to aluminum is, for example, reported by Arefi-Khonsari et al.[9] They show evidence of $Al-N-C$ bonds at the interface between the substrate and the deposited aluminum film and show an increased adhesion when the surface is pre-treated by an ammonia-fed plasma. On the other hand, also palladium can be specifically bonded to amine functionalities. Subsequently, palladium can be used for reductive deposition of copper or nickel.[10] In this way, electroless and patterned metallization can be performed, e.g. for the production of large area flexible electronics.[11, 12]

For biological applications, on the other hand, amine functionalities can be used for bio-molecule immobilization in biosensor applications or to support the attachment and growth of human cells.[8, 13, 14] Next to that, tuning the physical and chemical properties of a surface allows driving specific responses in biological systems. In this way, novel insights can be provided into how proteins, cells and tissues interact with materials.[15, 16] Also the covalent immobilization of biologically active molecules is often governed by amine functionalities. As can be observed in Figure 1.2, amine functionalities can form carbamide bonds when reacting with carboxylic acids. Carboxylic functionalities - as well as amine functionalities - are often present in bio-molecules like proteins, antibodies and DNA. Amine functionalities are also able to covalently bond to aldehyde groups.[17] Stable amine-aldehyde bonds are formed through $C = N$ bonds. Aldehyde groups are not present in bio-molecules, but may be present in linker molecules, e.g. glutaraldehyde.[13] In the case of biosensors, antibodies are covalently linked into microfluidic channels. These antibodies are able to immobilize antigens, e.g. present in blood samples, to specifically detect potential diseases.[18]
Figure 1.1: Potential applications of amine functionalized surfaces (edited from [19]). The wettability of the surface can be manipulated to obtain hydrophilic (or hydrophobic) channels[20], local metal deposition can be promoted (by electroless plating of nickel, [7]) and biological cells (fibronectin/streptavidin, [18, 21]) or antibodies can be coupled for the fabrication of low-budget diagnostic chips. [7]

**Amine grafting techniques**

The incorporation of amine functionalities at a polymer surface is usually carried out by wet chemistry approaches or by plasma induced surface modification/polymer deposition.

The wet chemical formation of self-assembled monolayers (SAMs) from amine containing monomers is a common approach. In SAM formation, carefully selected monomers are dissolved in an adequate solvent and are subsequently exposed to the surface of the polymer substrate to modify. By intermolecular forces, the monomers are able to organize themselves, leaving their functional groups available for further molecule immobilization.[22, 23] A disadvantage of wet-chemical film growth methods, however, is that solvents may remain in the bulk, potentially affecting the post-processing steps.[2] The use of solvents is also undesirable because of chemical and environmental safety issues.[5]

Next to wet chemistry approaches, several plasma processes are proposed for the incorporation of amine functionalities. Amino functionalities can be grafted on a polymer surface by an ammonia ($NH_3$) plasma treatment.[6, 17, 24] The $NH_3$ gas is usually mixed with nitrogen or hydrogen, but also combinations of $N_2$ and $H_2$ are used without $NH_3$ addition (forming gas).[2, 3] In all cases, the formation of reactive surface sites and their subsequent reaction with plasma radicals such as $NH$ and $NH_2$, is essential for grafting of amine functionalities, both at low-pressure ($3 – 100$ Pa, [2]) and atmospheric pressure.[1] Furthermore, it is found that milder plasma conditions are more efficient in the grafting of amines, due to the absence or reduced effect of ion bombardment and the more dominant presence of long-lived active species.[6] Utilization of atmospheric pressure glow discharges[25] and their afterglow[3, 6] are therefore successfully researched.

A disadvantage of the use of plasma gas mixtures for surface functionalization, i.e. $NH_3$, $N_2$ and/or $H_2$, is that the functionalized surfaces are prone to structural re-orientation. The re-orientation of
functional groups is also defined as hydrophobic recovery of the surface due to the re-arrangement of amine containing polymer chains towards the sub-surface of the substrate.[1, 25, 26] This phenomenon may be limited by promoting the crosslinking of the polymer chains. Crosslinking of functionalized surfaces is usually achieved by providing a mild and controlled ion bombardment during the plasma treatment (e.g. by means of He addition to the gas mixture).

Another option to introduce amine functionalities is the deposition of a thin film by plasma polymerization of an amine containing monomer. Plasma polymerization of vaporized monomers may result in a more crosslinked plasma polymer network which is less susceptible for hydrophobic recovery and loss of functionality. In plasma polymerization, a discharge is ignited to provide energy to a monomer precursor to be activated or (partially) fragmented.[27] The monomer fragments are subsequently able to form new bonds and polymerize at the surface. Plasma polymerization of amine containing monomers can be performed using a great variety of monomers. Most of the polymerization processes are performed using alkylamine monomers like allylamine (AA, [28]), heptylamine (HA, [29]) or diaminocyclohexane (DACH, [30]). Amine containing organosilicon monomers are also investigated: precursors like 3-aminopropyl triethoxysilane (APTES, [31]) and 3-aminopropyl trimethoxysilane (APTMS,[32]) undergo plasma polymerization.

\[\text{\textcopyright PlasmaPrint patterning}\]

In this research project, a \textcopyright PlasmaPrint system is used for a plasma polymerization process. The \textcopyright PlasmaPrint setup is developed by InnoPhysics and allows plasma treatment of dielectric films and plasma deposition in a dielectric barrier discharge (DBD) setup. The substrate itself serves as dielectric, while it is supported by a high-voltage plate electrode. Grounded needle electrodes can be actuated above the substrate to turn the plasma on and off. The exact working principles of the \textcopyright PlasmaPrint setup, together with its plasma properties, are described in Sect.2.1.

The \textcopyright PlasmaPrint system enables area selective functionalization of a polymer, deposition of thin films by plasma polymerization as well as etching processes. The type of plasma treatment can be changed, depending on the gas composition. The plasma processes occur at atmospheric pressure, which makes vacuum equipment unnecessary. The biggest advantage of the \textcopyright PlasmaPrint setup, however, is the use of the needle-to-plate geometry, which allows dot-wise patterning of the plasma treatment over the surface of the substrate. Other patterning techniques often require a large number of process steps, expensive vacuum equipment and/or the necessity to handle environmentally undesired chemicals.[12, 33] Also the use of a mask is usually inevitable, e.g. by photolithography or plasma-chemical etching. When the pattern is frequently changed, changing masks may be time consuming and expensive. With the \textcopyright PlasmaPrint setup, a pattern can be digitally programmed and easily changed, which results in a very flexible and relatively cheap on demand plasma patterning system.

Potential applications of the deposition of amine functionalities were already discussed and shown in Figure 1.1. Patterned plasma treatments can be used in microfluidics, printed electronics or lab-on-a-chip devices and biosensors.[12, 21, 34]
**Research goals and outline**

As described, by the actuation of a grounded needle above a high voltage plate electrode, the µPlasmaPrint system allows the (patterned) grafting of specific functionalities at polymer surfaces by plasma polymerization of vaporized monomers or by surface functionalization with non-depositing gases. Such a patterned treatment can be repeated to increase the effect of such a treatment or to increase the film thickness of a deposited film. Multiple repetitions of such a 'print' treatment will be addressed as the number of print repeats (PR).

In order to investigate the incorporation of amine functionalities by the plasma polymerization of amine containing organosilicon monomers, in this research project, the µPlasmaPrint system is adopted to deposit APTMS (3-aminopropyl trimethoxysilane) films on a fluorinated ethylene propylene co-polymer (FEP) substrate. The investigation of the plasma polymerization of APTMS is addressed by means of the following research questions:

1. What is the chemical structure of the deposited APTMS films?
   - What is the stoichiometry of the plasma polymerized APTMS films? Which chemical bonds of the APTMS molecule are dissociated and which bonds are present in the deposited film? Which chemical bonds are formed with the polymer substrate in the early stages of APTMS polymerization?

2. What is the influence of the number of µPlasmaPrint repeats (PR) on the structure of the deposited film?
   - How does the concentration of amine functionalities change with an increase in print repeats? Do the deposited films age and if yes, how does ageing occur? Can the choice of the substrate influence the ageing process?

3. Are the deposited amine functionalities able to participate in further immobilization reactions?
   - Is it possible to immobilize fluorescamine on the aminated surface? Are all amine available for further immobilization reactions? How deep do fluorescamine molecules diffuse into the deposited film? Is it possible to quantify the amine surface concentration? Is it possible to perform an electroless plating process, starting from the amine functionalities?

In order to investigated the plasma polymerization of APTMS, the basic principles of plasma generation by the µPlasmaPrint setup and the established plasma properties are discussed in Chapter 2. In this chapter also the theoretical background of plasma polymerization is discussed. The working principle of the µPlasmaPrint setup itself and the deposition parameters are discussed in Chapter 3. The deposited APTMS films are analyzed by several surface-sensitive diagnostic tools, which are also described in Chapter 3. Answers to the above-reported research questions are provided in Chapter 4. Chapter 5 contains a summary of this M.Sc. thesis work.
Chapter 2

Theoretical background

The µPlasmaPrint technique, as developed by InnoPhysics, is a digital printing technique, in which individual needles are actuated to move up and down in order to generate short micro-discharges. If the grounded needle electrodes are lowered towards a high voltage electrode, it is possible to generate a gas discharge. This principle is shown in Figure 2.1: if a needle is in the ‘up’ position, the plasma will be off, while if the needle is ‘down’, the plasma will be switched on. The properties of the generated plasma are discussed in Sect. 2.1.

By using this concept in combination with a digital print system, a substrate can be plasma processed in a dot-wise manner, based on a predefined digital pattern. The type of atmospheric pressure plasma processing (surface modification, deposition or etching) is determined by the gas mixture supplied to the inter-electrode gap. For this project 3-aminopropyl trimethoxysilane (APTMS) is plasma polymerized. The basic principles of plasma polymerization in general, and for the APTMS precursor in particular, are discussed in Sect. 2.2.

The plasma polymerization of APTMS leads to the development of amine functionalities in the deposited films. Amine-containing surfaces can be used to improve wettability, surface adhesion and/or (bio-) molecule immobilization, as discussed in Chapter 1.

2.1 µPlasmaPrint principles

The µPlasmaPrint system consists of multiple needle electrodes which are actuated towards a high voltage substrate, as shown in Figure 2.1. This concept utilizes Paschen’s law to switch the plasma on and off. When the plasma is on, a micro-discharge is generated. In order to reduce the dissipated power in the discharge a dielectric is placed in between the electrodes. The dielectric also prevents the substrate from being damaged. By the placement of the dielectric a dielectric barrier discharge (DBD) is established. This is also shown in Figure 2.1.

Paschen’s law, the formation of micro-discharges in a DBD setup and the plasma properties in a DBD setup are discussed in this section.

Paschen’s Law

The basic condition for establishing a gas discharge between two parallel plates is given by Paschen’s law.[35] According to Paschen’s law, shown in Figure 2.2, a minimum potential difference should be applied between two electrodes in order to ignite a discharge.[35] The minimum potential difference for a specific gas or gas mixture, only depends on the pressure of the system and the distance between the electrodes. So, if the pressure is constant, the breakdown voltage ($V_{\text{breakdown}}$) is directly related to
Figure 2.1: Principle of the µPlasmaPrint technique. When a needle is ‘down’, a discharge can be ignited for surface modification.

The distance between the two electrodes. The breakdown voltage is the minimum voltage which should be applied to one of the electrodes to ignite a gas discharge, while the other electrode is grounded.

Figure 2.2: Paschen’s law for nitrogen gas.[35] By the reduction of the distance between the electrodes at constant applied voltage (dark blue arrow), a discharge can be ignited. The breakdown voltage ($V_{\text{breakdown}}$) is the minimum voltage which should be applied to one of the electrodes to ignite a gas discharge, while the other electrode is grounded. $V_{\text{breakdown}}$ is determined for the µPlasmaPrint setup (light blue,[36]), which deviates from Paschen’s law due to the pin-to-plate geometry and the dielectric substrate present.

The principle of Paschen’s law is utilized by the µPlasmaPrint system: a plasma is ignited by decreasing the distance between a grounded needle electrode and a high-voltage plate electrode at a constant voltage, i.e. by moving the needle electrode towards the plate electrode. Due to the decrease in distance, the electric field between the electrodes increases. The increased electric field enhances the acceleration of free electrons, which increases the cross section of ionization processes during electron-atom collisions and the subsequent ignition of a discharge.

In Figure 2.2, also measurements are included of Paschen’s law for the µPlasmaPrint setup.[36] The breakdown voltage is higher compared to Paschen’s law, due to the presence of a dielectric, which
results in a decrease of the potential difference in the plasma gap. On the other hand, the breakdown voltage is slightly decreased due to the pin-to-plate geometry of the setup. Since the electric field lines in the µPlasmaPrint setup are bended, the density of field lines, i.e. the electric field, is increased close to the needle electrode, enhancing breakdown in the µPlasmaPrint setup. Overall, however, the voltage which should be applied to ignite a plasma by the actuation of the needle electrode, is higher than suggested from Paschen's law, as can be derived from Figure 2.2. The ignition of a discharge by the reduction of the distance between the electrodes at constant voltage is also shown in Figure 2.2 (dark blue arrow).

The distance between the needle electrode and the surface as a function of time is shown in Figure 2.3. It is also visualized when the plasma is "on". The duration of one motion cycle of a needle is less than a millisecond during which the plasma is ignited for $100 - 500 \mu s$. This plasma pulse time depends on the minimum and maximum distance between the electrodes, the applied voltage (and frequency), as well as the gas composition.

![Figure 2.3](image)

Figure 2.3: Time-dependent movement of a needle electrode above the plate electrode. If the needle is close enough, a discharge is ignited. If the needle is pulled back again, the plasma can no longer be sustained.

**Discharge ignition in a DBD**

The high pressure side of Paschen’s law (the right side in Figure 2.2) is limited by the collisional mean free path of the electrons: the electrons should be accelerated sufficiently within their average mean free path to be able to have an ionizing collision.[37] If electrons are accelerated sufficiently, small discharges can be generated with a large surface-to-volume ratio. Charged particles recombine quickly outside the active plasma space; furthermore excited species are de-excited through radiation emission and collisions.[38] A micro-plasma is obtained, due to the compensation of the relatively high diffusion losses at the plasma edges with respect to the enhanced plasma generation due to the high pressure and the short mean free path. The very short mean free path at atmospheric pressure results in plasma generation with high electron densities ($n_e \geq 10^{13} \text{ cm}^{-3}$, [39]). The diffusion effect at the relatively large plasma edges, together with very non-uniform electric field in the radial direction, result in a micro plasma of $\sim 50 - 100 \mu m$ radius.[40, 41]
At atmospheric pressure, electrical breakdown in a parallel plate setup is usually governed by multiple micro-discharges. A micro-discharge is ignited by an electron avalanche as illustrated in Figure 2.4: electrons are accelerated by the applied electric field, allowing them to have ionizing collisions with neutral species. If the electrons gain enough energy to ionize the neutral particle, an ion is generated, together with an extra electron. Both electrons can again be accelerated in order to induce another ionizing collision. The exponential growth of the electron density ($n_e$) when accelerated over a certain distance ($z$) in the discharge gap is given by the Townsend coefficient ($\alpha$) in Eq. 2.1. The electron density in the discharge gap before plasma ignition, e.g. due to excitation by irradiation, is given by $n_{e,0}$.[41]

$$n_e = n_{e,0} \exp (\alpha \cdot z) \quad (2.1)$$

If the electron avalanche is big enough, a cathode directed streamer discharge is initiated. Because the electrons in the streamer formation are much faster than ions, the electrons always run at the 'head' of avalanche leaving the ions behind, creating a dipole,[41] which results in an enhancement of the local electric field at the streamer head, as can be observed in Figure 2.4. Streamer formation at the 'head' of the avalanche is, therefore, faster than the drift velocity of the electrons.[40] When the avalanche head reaches the anode, the electrons sink into the electrode leaving the ions filling the discharge gap. A streamer grows due to the formation of secondary avalanches, which converge towards the main avalanche.[41, 42] Secondary avalanches may be formed by ionization by photons, which are emitted due to recombination of electron-ion pairs. This is also shown in Figure 2.4.

![Figure 2.4: Start of a streamer discharge. Electrons are accelerated from the cathode to the anode by the externally applied electric field. The electrons can have ionizing collisions with neutrals. In this way the electron density can develop exponentially to an electron avalanche. The avalanche is increasingly accelerated towards the anode by an internal electric field in the streamer 'head'. If the avalanche reaches the anode, the electrons are accumulated at the dielectric and the remaining (positively charged) ions allow a cathode directed streamer, which is grown by the absorbance of secondary avalanches, e.g. initiated by ionization due to recombination emitted radiation. (Figure edited from[37, 43])](image)

When a streamer is formed from the cathode to the anode, the impedance of the discharge gap will drop. The creation of a conducting plasma channel results in a large conduction current and a large dissipation of power.[41] The power dissipation is reduced by the placement of a dielectric barrier in between the electrodes. Due to charge accumulation at this dielectric, the effective electric field in the discharge gap will be reduced and the discharge will already be quenched within several tens of nanoseconds after breakdown.[40, 41] After electron current termination, ionic charges remain in the micro-discharge volume. Positive ions of the micro-discharge slowly diffuse towards the electrodes resulting in a low intensity, slow-decaying ion current.[41] The duration of the stages in a streamer micro-discharge are shown in Table 2.1, together with the transferred charge in each of the steps.
Duration time | Charge transferred
---|---
A. Micro-discharge | 40 ns | $10^{-9}$ C
A1. Electron avalanche | 10 ns | $10^{-11}$ C
A2. Cathode directed streamer | 1 ns | $10^{-10}$ C
A3. Plasma channel | 30 ns | $10^{-9}$ C
B. Micro-discharge remnant | 1 ms | > $10^{-9}$ C

Table 2.1: Duration of the different stages of a micro-discharge, together with the transferred charge in this period. If this micro-discharge is quenched, positively charged ions remain present in the discharge gap, which results in a low, though very long, ion current. The duration and charge transfer of this micro-discharge remnant are also shown.[41]

In order to ignite the discharge again after quenching, an AC voltage should be applied to the plate electrode of the system. Depending on the applied voltage, it is possible to have one or multiple discharges at each of the up-going flanks of the absolute value of the applied voltage. If the effective electric field, after a discharge, is increased sufficiently, another discharge becomes possible. Depending on the applied voltage frequency, it is also possible that multiple discharges are ignited during the period that the needle electrode is 'down'. This can also be derived from Figure 2.3, since the applied voltage frequency is much larger than the up-and-down frequency of the needle electrode. The applied voltage and voltage frequency will be discussed in the next sub-section.

Properties of DBD plasmas

In the field of plasma-induced surface modifications, the µPlasmaPrint dielectric barrier discharge (DBD) setup allows polymer treatment at atmospheric pressure and compatibility with roll-to-roll processing.[4, 44, 45] Due to the accumulation of the charge carriers at the dielectric surface, as well as the short breakdown time, the power dissipated in a DBD setup is relatively low. Current densities during these short lived discharges are in the range of $100 - 1000 \, \text{A/cm}^2$.[40, 41]

In a DBD setup usually two different discharge regimes are identified. The most common regime is a streamer (filamentary) discharge regime, but also a very uniform glow discharge is possible. The difference between a filamentary discharge and a glow discharge is determined by the electric field needed for plasma ignition each time the applied voltage is switched. Plasma ignition by a low electric field becomes possible if sufficient seed electrons remain present in between two consecutive discharges ($n_e > 10^6 \, \text{cm}^{-3}$), e.g. by Penning ionization of nitrogen metastables.[46]

The difference between a glow discharge and a filamentary discharge in a parallel plate setup is often easily observed.[47] In the limit of a single streamer-like plasma in a pin-to-plate setup, however, this difference becomes less pronounced. Hence, the plasma regime should be determined from current measurements. Current-voltage characteristics of the two regimes are shown in Figure 2.5. A filamentary discharge consists of one or multiple short current pulses (10 – 100 ns each, Figure 2.5a), which are created due to the repeatedly formation and quenching of streamer discharges when the applied voltage increases. The current profile in a glow discharge, on the other hand, consists of a single, broad and continuous current peak per increasing flank of the applied voltage (Figure 2.5b, [46]), due to seed electrons present in between the discharges and the smaller electric field needed for plasma ignition.[46]

The difference between the two plasma regimes (and their current-voltage profiles) is important, since they are also different in terms of absorbed plasma power and thus strongly influence the polymerization mechanism. Since the plasma is quenched, the power needed to generate a new discharge in a filamentary discharge regime is higher than for a glow discharge. For a parallel plate DBD setup, the estimated power in a filamentary discharge is $\sim 100 \, \text{W/cm}^3$, for a glow discharge the power is usually lower, $\sim 10 \, \text{W/cm}^3$.[38, 46]
Figure 2.5: Current-voltage (I-V) characteristics of a filamentary (a) and a glow discharge (b), as determined by Gherardi et al.\cite{46} In a filamentary discharge multiple streamer discharges results in $10^{-100}$ ns current peaks when the applied voltage is increased, while in a glow discharge a continues, broad conduction current is measured.

From the measurement of the I-V characteristics on a µPlasmaPrint-like setup by Huiskamp (Figure 2.6a, \cite{48}) and the comparison with the current profile derived by Wagner et al. for a filamentary discharge (Figure 2.6b, \cite{44}), it can be concluded that the µPlasmaPrint setup is in a filamentary plasma regime. This conclusion is supported by a relatively high absorbed plasma power (Table 2.2), the (very) non-uniform electric field and the significant presence of metastable quenchers.

Figure 2.6: Huiskamp determined the I-V characteristic of a µPlasmaPrint like setup (a, \cite{48}), which is comparable with the current profile of a filamentary discharge as determined by Wagner et al. (b, \cite{44}). Based on this comparison, together with the considerations discussed in the text, it is derived that the µPlasmaPrint is in a filamentary regime.

When the I-V characteristics from Wagner et al. and Huiskamp in Figure 2.6 are compared with the results of Gherardi et al. in Figure 2.5, it can be concluded that due to a difference in the measurement method, a displacement current is observed in Figure 2.6, which originates from a changing electric field, according to Maxwell's addition to Ampère's law. Next to that, the results of Gherardi et al. and Wagner et al. are determined for a parallel plate setup, while the µPlasmaPrint setup consists of a pin-to-plate setup. A larger surface of the electrode results in more streamer discharges and thus more current peaks.
Based on I-V measurements in Figures 2.5 and 2.6, some of the properties of the plasma can also be derived. Other parameters are estimated based on experiments and literature. If a voltage of $6.5 \text{kV}_{pk-pk}$ is applied, from Figure 2.5 the peak conduction current is found to be $\sim 30 \text{mA}$. Such parameters result in a current density of $\sim 95 \text{A/cm}^2$. The calculation of the current density, as well as other relevant plasma parameters is shown in Table 2.2.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>discharge voltage in the gap for a single streamer discharge</td>
<td>$U = 1.5 \text{kV}$ [4, 35]</td>
</tr>
<tr>
<td>peak current per streamer</td>
<td>$I_{max} = 30 \text{mA}$ [49, 50]</td>
</tr>
<tr>
<td>average current during streamer</td>
<td>$\langle I \rangle = 12 \text{mA}$ [49, 50]</td>
</tr>
<tr>
<td>number of streamers per cycle</td>
<td>$n = 2$ [49, 50]</td>
</tr>
<tr>
<td>duration of a single streamer</td>
<td>$t_{streamer} = 40 \text{ns}$ [41, 46]</td>
</tr>
<tr>
<td>frequency of the applied voltage</td>
<td>$f = 57 \text{kHz}$ [30]</td>
</tr>
<tr>
<td>duration the plasma is 'on'</td>
<td>$t_{pulse} = 300 \mu\text{s}$ [30]</td>
</tr>
<tr>
<td>radius of a streamer</td>
<td>$r = 100 \mu\text{m}$ [40, 41]</td>
</tr>
<tr>
<td>minimum spacing between needle electrode and substrate</td>
<td>$h = 200 \mu\text{m}$ [50]</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Plasmoproperty</td>
<td>Value</td>
</tr>
<tr>
<td>current density $I_{max}/A = I_{max}/\pi r^2$</td>
<td>$95 \text{A/cm}^2$</td>
</tr>
<tr>
<td>energy per plasma 'dot'</td>
<td>$E_{dot} = n \cdot U \cdot \langle I \rangle \cdot t_{streamer} \cdot f \cdot t_{pulse}$</td>
</tr>
<tr>
<td>power per surface area</td>
<td>$P/A = n \cdot U \cdot \langle I \rangle \cdot t_{streamer} \cdot f \cdot \pi r^2$</td>
</tr>
<tr>
<td>power per volume</td>
<td>$P/V = n \cdot U \cdot \langle I \rangle \cdot t_{streamer} \cdot f \cdot \pi r^2 \cdot h$</td>
</tr>
</tbody>
</table>

Table 2.2: Estimation of interesting plasma parameters, based on measurements at InnoPhysics and literature. A plasma 'dot' is the time when the needle electrode is 'down' and the plasma is ignited.

In Table 2.2, it can be observed that a plasma dot of the µPlasmaPrint setup 'contains' approximately 25 µJ, which results in an average power per surface area, during the time the plasma is on, of $265 \text{W/cm}^2$. This is consistent with literature results. [40, 41] Since the plasma gap ($h = 200 \mu\text{m}$) is much smaller than the one reported in the experiments according to the literature ($h = 1 \text{mm}$, [40, 41]) , the current density is smaller than in literature, while the power density per volume is much larger. For the power density per volume, it should also be mentioned that in a parallel plate DBD setup, there is also a significant volume which is not filled with a filamentary discharge (otherwise it would have been a uniform discharge). Therefore, the measured power density per volume in literature are an underestimation, compared to the µPlasmaPrint setup.

Since the variations compared to literature are effects of plasma gap distance and method of power density measurement, it is derived that the µPlasmaPrint plasma can be compared relatively well to filamentary discharges described in literature.[4, 38, 40, 41, 44, 46]

### 2.2 Plasma deposition of vaporized monomers

One way of functionalizing a polymer surface is by the deposition of a thin film, which contains the desired functional group. The reactive species in a (micro-) plasma contribute to the deposition/polymerization of such a thin film.[51]

**Fragmentation-recombination plasma polymerization**

The creation of polymer-like structures from gaseous or vaporized monomers, enhanced by plasma ignition, is referred to as plasma polymerization. Plasma polymerization is usually defined as the
fragmentation and the subsequent deposition of (organic) monomers.\cite{13, 51} This mechanism of polymerization was proposed by Yasuda\cite{27} and can be described by Eq. 2.2. An example of such a process is given by the plasma polymerization of toluene in Figure 2.7.

\[
ABCDEF + \text{plasma} \rightarrow A + B + CD + E + F \quad \text{(fragmentation)}
\]

\[
n(A + B + CD + E + F) \rightarrow [FCABDE]_n \quad \text{(recombination)}
\]

(2.2)

Figure 2.7: Plasma polymerization of toluene according to the atomic polymerization mechanism of Yasuda.\cite{27, 51}

The radicals obtained by means of plasma fragmentation can interact with the surface, leading to a heterogeneous growth process.\cite{45} Depending on the Yasuda factor, \(Y = \frac{W}{F \cdot M}\), the monomer can either be just activated or completely fragmented. Therefore, by changing power \((W)\), flow rate \((F)\) or molecular weight of the monomer \((M)\), films can be deposited which differ in chemical structure, stoichiometry and/or density.\cite{38} By the variation of the Yasuda factor, the film growth process becomes either flow rate controlled (high \(\frac{W}{F \cdot M}\)) or discharge power controlled (low \(\frac{W}{F \cdot M}\)). In the flow rate controlled case, the precursor molecules are quantitatively activated and participate to the process of polymerization, since sufficient power is present to activate the monomer (see Figure 2.8).\cite{4, 13, 27}

In the previous section (Sect. 2.1) it was derived that in the \(\mu\)PlasmaPrint system the power-to-volume ratio is relatively high. This suggests a large Yasuda factor and thus a flow rate controlled polymerization regime. The polymerization regime is further investigated in Sect. 4.2.

![Figure 2.8: Influence of the Yasuda factor \((Y = \frac{W}{F \cdot M})\) on the deposition rate of plasma polymerized films. (edited from \cite{13})](image.png)

**Competitive ablation and polymerization**

In a plasma, however, many different processes can play a role in the functionalization of a (polymer) surface. As discussed, the starting monomer or precursor can be fragmented and the fragments can subsequently be deposited onto the substrate (indicated as plasma polymerization in Figure 2.9), but it is also possible that the monomer is retained almost completely and that it is adsorbed at the surface, e.g. at a reactive surface site (plasma induced polymerization). On the other hand, ion bombardment
towards the surface or plasma (V)-UV radiation can lead to ablation of fragments of the substrate or growing film.[13] These fragments, once ablated, can participate to the deposition process. All these plasma surface interactions are summarized in Figure 2.9. Unfortunately, not much is known in this field, since analysis are often limited to the properties of the depositing plasma or the deposited films and their potential applications.

![Figure 2.9: Schematic diagram of the competition between ablation and polymerization. (edited from [13])](image)

**Plasma-induced radical chain-growth polymerization**

The activated monomer and/or its fragments are able to undergo polymerization reactions at the surface. While the plasma phase is characterized by many non-selective processes, the growth of a plasma polymer film is usually dominated by a few selective processes.[52] At atmospheric pressure, the average electron energy usually remains relatively low (∼ 1 eV), compared to most bond dissociation energies (3 – 5 eV) and ionization energies (∼ 10 eV). Since the fraction of electrons in the high-energy tail of the electron energy distribution function, which have enough energy to perform these dissociation and ionization reactions, decreases exponentially, the ionized fraction in atmospheric pressure plasmas is usually relatively low and plasma deposition is dominated by radicals.[43]

A well-described polymerization mechanism, which is governed by radicals, is plasma-induced radical chain-growth.[51] This polymerization mechanism is governed by the continuous addition of monomer molecules (M) to activated (fragments of the) monomers, as indicated in Eq.2.3. First, the plasma activates a monomer by the dissociation of one or multiple bonds. Then, specific radical fragments can bind other monomers. The newly formed radical fragments continue to bind monomers, until the polymerization is terminated. A termination reaction occurs if radicals react with each other, as shown in the last equation of Eq.2.3. An example of such a polymerization mechanism, is the polymerization of a vinyl unit hosting a functional group (X) in Figure 2.10. During plasma polymerization, functional groups are usually much more retained than the structure of the monomer itself.[51]

$$
M + \text{plasma} \rightarrow \text{fragments}^* \quad \text{(generation/activation)}
$$

$$
\text{fragment}^* + M \rightarrow \text{fragment} - M^* \quad \text{(growth)}
$$

$$
\text{fragment} - M^* + M \rightarrow P_n^* \quad \text{(continuation of growth)}
$$

$$
P_n^* + P_n^* \rightarrow P_n - P_n \quad \text{(termination)}
$$

(2.3)

Chain-growth polymerization is actually a chemical process which is initiated by radicals generated in the plasma. Chemical polymerization processes are equilibrium reactions, which are controlled by thermodynamics, i.e. they proceed if the standard Gibbs energy ($\Delta G_p^0$) of the reaction is negative
Figure 2.10: Example of plasma-induced radical chain-growth polymerization of vinyl containing a functional group ($X$). Functional groups in plasma polymerization are often retained.[51]

(exothermic).[51] As can be observed in Eq 2.4, the Gibbs energy is related to the standard polymerization enthalpy ($\Delta H^0_p$) of the molecule, i.e. the enthalpy of the bonds which are dissociated and formed. Furthermore, the Gibbs energy is related to the entropy ($\Delta S^0_p$) via the absolute temperature ($T$) of the molecules. The polymerization enthalpy and -entropy are combined in an equilibrium constant ($K_n$), using the ideal gas constant ($R$) and the absolute temperature:

$$\Delta G^0_p = \Delta H^0_p - T\Delta S^0_p = -RT \ln K_n$$

(2.4)

Typical bond enthalpies for the APTMS molecule are summarized in Table 2.3. Especially silicon oxide bonds have a high bond energy, which is difficult to dissociate, and which can be formed relatively easy in polymer films.

### Table 2.3: Bond dissociation enthalpies of different bonds related to the APTMS molecule.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Enthalpy (eV)</th>
<th>Ref.</th>
<th>Bond</th>
<th>Enthalpy (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si – O</td>
<td>5.9</td>
<td>[53]</td>
<td>C – O</td>
<td>4.2</td>
<td>[54]</td>
</tr>
<tr>
<td>C – C</td>
<td>3.7</td>
<td>[27, 51]</td>
<td>C – N</td>
<td>3.7</td>
<td>[55]</td>
</tr>
<tr>
<td>C – H</td>
<td>4.3</td>
<td>[27, 51]</td>
<td>N – H</td>
<td>4.0</td>
<td>[27]</td>
</tr>
</tbody>
</table>

### Plasma polymerization in adsorbed- or gas phases

A last polymerization mechanism which should be encountered is the plasma polymerization of monomers in an adsorbed- or gas phase, as illustrated in Figure 2.11.[51] Especially at low-pressure conditions, where electrons have a relatively long mean free path and relatively low collision rate, polymer growth can occur in an adsorbed layer. After switching off the plasma, the adsorbed monomers can react with radicals at the surface or in the deposited film to form more conventional polymers with a high degree of regularity and relatively low surface roughness.[51] Such processes can already occur in a DBD plasma, when the plasma is quenched with the same frequency as the frequency of applied voltage (Sect.2.1), but usually the plasma-off times are larger, e.g. 0.5 – 50 ms.[30]

Comparable to the monomer adsorption and polymerization process, powder formation can also occur, i.e. monomers polymerize in the plasma phase before they get adsorbed at the surface. This process adversely results in a relatively rough surface. Differences in polymerization processes are shown in Figure 2.11 and may be explained by differences in internal and/or adhesion forces for different monomers and substrates.[36]

### Polymerization of organosilicon films

The plasma induced polymerization mechanism of APTMS is only briefly presented in literature. Borris et al. suggest that the APTMS monomer, $H_2N-C_3H_6-Si-(OCH_3)_3$, is reduced to a polymeric silicate, $(O_{3/2}Si-C_3H_6-NH_2)_n$, via the hydrolysis of the methoxy silanes to silanols and the subsequent condensation of these groups to form silica like networks, still containing the aminopropyl chain.[32, 57] This polymerization mechanism is similar to APTES (3-aminopropyl triethoxysilane) sol-gel polymerization.[31] For plasma afterglow polymerization of APTES a similar, but much more
fragmented polymer film was observed. The suggested APTMS polymerization process, which is similar to the sol-gel growth method is shown by Eq. 2.5:

\[
H_2N \cdots Si - OCH_3 + H_2O \rightarrow H_2N \cdots Si - OH + HOCH_3
\]

\[
H_2N \cdots Si - OH + HO - Si \cdots NH_2 \rightarrow H_2N \cdots Si - O - Si \cdots NH_2 + H_2O
\]

The polymerization mechanism, as described in Eq. 2.5, results in a polymer structure as shown in Figure 2.12. Due to the relative weak binding energy of the silicon-methyl and silicon-methoxy bonds, as well as the relative high binding energy of a Si-O bond, a reaction mechanism comparable to that as mentioned by Borris et al. is possible. The type of plasma regime used (direct, remote or afterglow and glow or filamentary) as well as the absorbed plasma power will significantly influence the polymerization process according to the Yasuda factor. The dominant deposition and polymerization mechanism is therefore also subject of this research project.

The polymerization process can be explained by the following reaction:

\[
H_2N \cdots Si - OCH_3 + H_2O \rightarrow H_2N \cdots Si - OH + HOCH_3
\]

\[
H_2N \cdots Si - OH + HO - Si \cdots NH_2 \rightarrow H_2N \cdots Si - O - Si \cdots NH_2 + H_2O
\]

Figure 2.12: Illustration of the idealized APTMS polymer. Hydrolysis and condensation reactions have taken place to form a silica-like network, while retaining the aminopropyl chain.[11, 31]
Chapter 3

Experimental setup

APTMS films are deposited using a μPlasmaPrint setup, developed by InnoPhysics. The μPlasmaPrint setup is described in Sect.3.1. The deposition parameters and the different substrates which are used, are addressed in Sect.3.2. After deposition, several methods are utilized to analyze the deposited APTMS films. The basic principles of these techniques are addressed in Sect.3.3 of this Chapter.

3.1 Deposition setup

The principle of plasma generation is based on actuated needle electrodes in a multi pin-to-plate, dielectric barrier discharge (DBD) geometry. The needles are grounded, while a high voltage is applied to the plate electrode. This high-voltage plate electrode is covered by a polyimide dielectric foil (∼100 µm). The substrate is placed on this dielectric. The polyimide foil and the substrate itself act as dielectric, reducing the conduction current and the dissipated power in the discharge, as discussed in Sect.2.1. A schematic drawing of the deposition setup is shown in Figure 3.1, together with the bubbler system which is used to vaporize the liquid APTMS monomer. The \(N_2\)/APTMS gas mixture is led to the μPlasmaPrint head, where the applied electric field allows the ignition of a micro-discharge between the needle electrode and the substrate if a needle is moved ‘down’. The needle electrode is actuated towards the surface by the leverage effect of a small magnet, which is attracted by the magnetic field of a current through a small coil. The needle electrode is pulled back by a spring in order to end the discharge within 100 – 500 µs (not shown).[50] The principle of needle actuation is also visualized in Figure 3.1b.

A picture of the actual setup is shown in Figure 3.2. The print head contains 24 needle electrodes which are positioned in two rows into a XY-Z movable print head for a patterned functionalization of the dielectric surface. An illustration of the print head itself is shown in Figure 3.2b. The print head also directs the gas mixture towards the plasma region underneath the print head, parallel to the surface, to allow different plasma treatments and precursor gases. The gas mixture is supplied in front of the needles, while the exhaust gas is removed from behind. An in-line camera is present to visualize the generated micro-discharges. The in-line camera is only shown in Figure 3.2a.

3.2 Experimental details

Amine containing films are deposited onto fluorinated ethylene propylene co-polymer (FEP) foil (Goodfellow) using the μPlasmaPrint setup, as described in Sect.3.1. The FEP substrate has a thickness of 75 µm. A digital pattern of micro-plasmas is used to functionalize the polymer surface using a gas mixture of nitrogen (purity > 99.996 %, Praxair) and 3-aminopropyl trimethoxysilane (APTMS,
Figure 3.1: Schematic drawing of the bubbler (left) and the deposition setup (right) for the plasma polymerization of a vaporized precursor. The setup is fed by a gas mixture, which contains a combination of pure $\text{N}_2$ gas (0.20 slm) and $\text{N}_2$ gas which is lead through the bubbler (0.10 slm). The ratio of these flows is controlled by mass flow controllers (3.1a). If one of the grounded needles (a,b) in 3.1b is actuated, a micro-discharge is ignited which spreads over the dielectric substrate (c,d,e). The substrate lays on the high-voltage plate electrode, which is covered by a $\sim\!100\,\mu\text{m}$ polyimide dielectric foil (f). The high-voltage is supplied by an AC power supply (g). The needle electrodes are actuated towards the surface by the leverage effect of a small magnet, which is attracted by the magnetic field of a current through a small coil, while the needles are pulled back by a spring [50].

Figure 3.2: $\mu$PlasmaPrint setup. The print head is mounted on a XY-Z movable stage, above the high-voltage substrate carrier. The print head is also equipped with an inline camera for plasma inspection (a). The print head hosts 24 needle electrodes, positioned between the gas inlet and exhaust (b).
$H_2N(CH_2)_3Si(OCH_3)_3$, purity 97% (Sigma Aldrich). The substrate is used after isopropanol cleaning in an ultrasonic cleaner for at least 15 minutes and heating at 40°C for at least 30 minutes. The substrate is cooled down before use. The chemical structures of FEP and APTMS are shown in Figure 3.3.

![Chemical structure of FEP and APTMS.](image)

Digital patterning is possible with a spot size down to $\sim 200 \mu m$ diameter, due to the sharp tip of the needle electrodes ($\sim 30 \mu m$). For analysis purposes, however, thin films of plasma polymerized APTMS have been deposited in squares of $\sim 20 \times 20 \text{mm}^2$. The films have a thickness $< 200 \text{nm}$, depending on the number of $\mu$PlasmaPrint repeats, if the films are printed using a single row of 12 needles and a print speed of $10 \text{mm/s}$. The printed digital pattern has a resolution of 282 dpi (dots-per-inch), which results in a print frequency (i.e. oscillation frequency of a single needle) of 112 Hz. The voltage was set to $6.5 \text{ kV}_{pk-pk}$ and the minimum spacing between needle and substrate was $150 \mu m$. The voltage was applied at the resonance frequency of the system. The resonance frequency is determined by the capacitance of the discharge gap, together with the capacitance of the different cables and the inductance of the coil in the HV transformer. The frequency for optimal power transfer to the plasma is found to be $\pm 57 \text{kHz}$.

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The print head and the high-voltage substrate table are integrated in a Roland EGX 350 desktop engraver, which allows translation in the X-, Y- and Z-direction. Using this platform, the print head is able to move with $10 - 50 \text{mm/s}$ in both the X- and Y-direction. To ensure sufficient precursor gas in the plasma region, $10 \text{mm/s}$ is used. A typical motion pattern of the print head above the substrate is shown in Figure 3.4. At 282 dpi the print head moves with the 12 odd numbered needle electrodes in the positive Y-direction to create plasma dots every $90 \mu m$. After that, the print head shifts $90 \mu m$ to the positive X-direction, moves to the original Y position and starts creating plasma dots again. After repeating this procedure a third time, the print head shifts its entire size ($3.24 \text{mm}$) to the positive X-direction, to start the procedure again. In order to create a $\sim 20 \times 20 \text{mm}^2$ area, the 3-line procedure is repeated 6 times. After this, a single print repeat (PR) has been performed. The print head moves to its pristine position and is ready to start a new printing pattern. When multiple print repeats are carried out, the home position is usually shifted a bit to prevent that areas are covered by the same needle every print repeat.

![Typical motion pattern of the $\mu$PlasmaPrint print head above the substrate.](image)
The total gas flow was set to be 0.30 slm of which 0.10 slm \( N_2 \) was first passed through the bubbler, containing liquid APTMS at room temperature (see Figure 3.1a). The APTMS containing nitrogen gas is mixed with 0.20 slm of pure \( N_2 \) prior to the introduction of the gas mixture into the plasma region. The gas flows were set using a Bronkhorst MV-302 flow meter.

A summary of all the experimental details is shown in Table 3.1.

### Table 3.1: Summary of experimental details.

<table>
<thead>
<tr>
<th>Gas mixture composition</th>
<th>Plasma properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 ) via APTMS</td>
<td>Needle tip size</td>
</tr>
<tr>
<td>( N_2 ) (pure)</td>
<td>Minimum plasma gap</td>
</tr>
<tr>
<td>Total flow</td>
<td>Applied voltage</td>
</tr>
<tr>
<td></td>
<td>Voltage frequency</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Printing properties</th>
<th>Dielectrics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Print head speed</td>
<td>Polyimide</td>
</tr>
<tr>
<td>Resolution</td>
<td>Glass</td>
</tr>
<tr>
<td>Print frequency</td>
<td>FEP</td>
</tr>
</tbody>
</table>

### 3.3 Analysis methods

The analysis techniques which are used in this project are described in this section. For each of the techniques, their theoretical principles are discussed and the setups are introduced.

The bulk of the deposited films is analyzed by X-ray photoelectron spectroscopy (XPS, Sect.3.3.1), which mainly provides the elemental composition of the deposited films, together with information on the chemical environment of each of the elements. The chemistry of the films is further analyzed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Sect.3.3.2), which provides information on the ro-vibrational excitation of the deposited film. The thickness of the deposited films is determined using spectroscopic ellipsometry (SE, Sect.3.3.3).

The surface of the deposited films, on the other hand, is investigated by water- and diiodomethane contact angle measurements and by the subsequent determination of the surface energy (Sect.3.3.4). The measurement of these contact angles is surface sensitive, providing information about the different functional groups which are present in the top 0.5 – 1 nm of the deposited films. At last, in order to detect the amine functionalities at the surface, fluorescent labeling of the amine functionalities (Sect.3.3.5) is performed.

#### 3.3.1 X-ray photoelectron spectroscopy (XPS)

The first method which is used to analyze the deposited films is X-ray photoelectron spectroscopy (XPS). This method is able to characterize the surface by the determination of the elemental composition with a probing depth of \( \sim 10 \) nm.[59, 60, 61] XPS provides a semi-quantitative elemental analysis and is able to identify the chemical environment of the atoms, based on the electronegativity of its nearest neighbors.[60]

XPS is governed by the emission of a core electron after the irradiation of the surface by an X-ray source. The kinetic energy of the expelled electron relates to the nature of the specific atom and its chemical environment:

\[
E_{\text{binding}} = h\omega - (E_{\text{kinetic}} + \phi)
\]  

(3.1)
In Eq. 3.1, it is shown that the binding energy of an electron to its nucleus \( E_{\text{binding}} \) can be derived from the X-ray photon energy \( (\hbar \omega) \), the remaining kinetic energy of the electron \( E_{\text{kinetic}} \) after it has been expelled from the sample and the work function \( (\phi) \), being the minimum thermodynamic energy needed to remove an electron from the film to a point immediately outside the solid surface (i.e. vacuum level). By measuring the kinetic energy with a hemispherical electron energy analyzer, \( E_{\text{binding}} \) can be derived. The measured kinetic energy is influenced inside the material, which leads to a broader distribution in kinetic energy and, thus, in the derived binding energy. Another point of care is the depletion of the material from electrons, which results in surface charging. The kinetic energy of negative electrons is reduced, due to the positive charged surface.[61]

The XPS spectra are recorded on a K-Alpha Thermo Fisher Scientific X-ray photoemission spectroscope using a monochromatic Al Kα X-ray source (1486.7 eV). For the determination of the film content and chemical environment of the atoms, the interesting elemental peaks – carbon (C 1s), nitrogen (N 1s), oxygen (O 1s), silicon (Si 2p) and fluorine (F 1s) – are first observed in a broad band spectrum. The high-resolution spectra are recorded around the main peaks of the elements using a 50 eV pass energy at an emission angle of 90°. Charge compensation at the sample is accomplished. After deposition in the μPlasmaPrint setup, the films are stored and transported in vacuum using a desiccator. The XPS analysis is performed within 4 hours after deposition.

Depending on the difference in electronegativity between the element under investigation and its neighbor atom, the binding energy of the element undergoes a shift, which allows determining the chemical environment for the specific element by peak fitting of the high-resolution XPS spectra. In this report the various peaks are assigned according to the literature, as summarized in Table 3.2. For the analysis of the XPS data, the peak positions are allowed to move by ±0.1 eV from a fixed fit position in order to optimize the fit, while the peak shape is fixed by a mixture of a Lorentzian shape (30%) and a Gaussian shape (70%).[29, 62] For the semi-quantitative analysis, the sensitivity factor is applied to determine the relative content of each element. For silicon, oxygen, carbon, nitrogen and fluorine the factors are 0.814, 2.449, 0.919, 1.210 and 4.407, respectively.

As can be observed in Figure 3.3, the FEP substrate only contains carbon and fluorine atoms. Due to the binding to fluorine the carbon peak in the substrate is shifted to higher binding energies than in the APTMS film (∼292 eV). If more fluorine atoms are bonded to carbon, the carbon binding energy increases, because more energy is needed to expel an electron. Fluorine in the substrate, on the other hand, is always bonded to carbon. Its binding energy (∼689 eV) is also slightly shifted if more fluorine atoms are bonded to the neighboring carbon atom. The small shift in binding energy between a carbon atom or a fluorine atom adjacent to the carbon atom which is bonded to the measured fluorine atom, allows differentiation in the chemical environment of fluorine. Also if fluorine is in an aliphatic environment, the binding energy is decreased significantly, since in that case the fluorine atom is the only (strong) electronegative atom in a certain environment.

The contribution of carbon in the APTMS film to the XPS spectrum, on the other hand, shows much lower binding energies, as observed in Table 3.2. Most authors calibrate the binding energy peak of aliphatic carbon (\( \text{C} - \text{C} \); \( \text{C} - \text{H} \)) at 285 eV [30, 62], but also the \( \text{C} - \text{Si} \) peak may be found in this region.[32] Next to this peak, there are usually two more contributions found in this region. These peaks are related to carbon which is single-bonded or double-bonded to oxygen and/or nitrogen.[30, 32, 62] The difference in electronegativity between oxygen and nitrogen is limited, which does not allow differentiation between these bonds, based on a shift in binding energy of the carbon peak.

The binding energy of carbon in APTMS is fitted with three peaks, according to literature. A similar fitting procedure is used to determine the nitrogen binding energy (∼399 eV) and its chemical environment. The derivation of the chemical environment of nitrogen is important to determine the concentration of amine functionalities in the deposited film and their potential to undergo further immobilization reactions. In contrast to carbon, the nitrogen binding energy is not only influenced by its nearest neighbors, but also by the neighbors of the carbon atom adjacent to the nitrogen functionality; as is the case for fluorine as well. Therefore, the first fitting peak is assigned to amine
functionalities \((C - NH_2)\) which contain a carbon atom which is only bonded to silicon, hydrogen and/or other carbon atoms. The second peak can either be assigned to oxidized amine functionalities, like amides \((O = C - NH_2)\), or to imine functionalities \((C = N)\), while a third peak is usually added to improve the fitting procedure, but which can also be related to other oxidized complexes, such as \(O = C - N - C = O\).[13, 30]

The binding energy of silicon may also provide information on the chemical structure of the deposited films. Since the silicon binding energy increases \(\sim 0.65\) eV for each oxygen atom which is bonded to silicon, the number of oxygen atoms bonded to silicon and the distribution over the various possibilities can be determined.[63] It should be noticed that the analysis of the silicon binding energy is performed in absence of other strongly electronegative atoms. Nitrogen and/or fluorine are present in the deposited APTMS films, which may influence this analysis.

The last element which is expected in the deposited films is oxygen. The oxygen binding energy does not provide as much information about its chemical environment as other elements. The oxygen binding energy can be fitted by single-bonded oxygen \((-O-)\) and double bonded oxygen \((=O)\).[29, 30]

<table>
<thead>
<tr>
<th>Carbon in FEP</th>
<th>Fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>C − F</td>
<td>289.5 − 289.8 eV [62]</td>
</tr>
<tr>
<td>O − C − F₂</td>
<td>290.5 − 291.4 eV [62]</td>
</tr>
<tr>
<td>C − F₂</td>
<td>291.8 − 292.2 eV [62, 65, 66]</td>
</tr>
<tr>
<td>C − F₃</td>
<td>293.5 − 294.2 eV [62, 65, 66]</td>
</tr>
</tbody>
</table>

Table 3.2: Overview of binding energies (eV) and peak assignments, as reported by different authors.

Based on the elemental content of the deposited films for several print repeats and the assignment of the fitting peaks to the chemical environment of the elements, it is possible to determine the thickness of the deposited film after 1 PR. If an element, or a specific peak in the binding energy spectrum of an element, is present in the substrate, while it is not present in the deposited APTMS film, its intensity follows an exponential decay due to the coverage of the deposited film[68]:

\[
I^X = I_0^X \exp \left( -\frac{d}{\lambda_{APTMS}^X} \right) \tag{3.2}
\]

Using Eq.3.2, the thickness, \(d\), of the deposited film can be determined, based on the intensity of the element \((X)\) in the pristine substrate \((I_0^X)\) and the intensity of these peaks after deposition \((I^X)\).
The measured intensity after film deposition is influenced by the average collisional mean free path of the expelled electrons in the APTMS film, $\lambda_{APTMS}^X$, which depends on its kinetic energy, $E_{\text{kinetic}}$, as derived in Eq.3.1:[59]

$$\lambda_{APTMS}^X = 0.087 \sqrt{E_{\text{kinetic}}}$$

(3.3)

### 3.3.2 Infrared spectroscopy (ATR-FTIR)

Infrared spectroscopy is used here as a complementary technique, next to XPS, for the analysis of the different bonds in the deposited films. By using infrared absorption, functional groups can be detected and information on the polymerization mechanisms can be inferred.[60] Attenuated total reflection (ATR) infrared spectroscopy is used, in order to be more surface sensitive.[69]

![Analysis setup for the ATR-FTIR measurements. An evanescent wave penetrates the sample, due to total internal reflectance in the crystal.](image)

The principle of ATR-FTIR is shown in Figure 3.5. Due to total internal reflection of an infrared light beam in an ATR crystal, an evanescent wave penetrates the sample. Total internal reflection occurs if the angle of incidence of a light beam relative to the normal of the interface between two media, $\theta$, becomes larger than the critical angle, $\theta_c$:

$$\theta_c = \arcsin \left( \frac{n_2}{n_1} \right)$$

(3.4)

In Eq.3.4, which can be derived from Snell’s law, the refractive index of the crystal, $n_1$, should be larger than the refractive index of the sample, $n_2$. The generated evanescent wave follows an exponential decay in the sample:

$$I_e = I_0 \exp \left( -\frac{x}{d_p} \right)$$

(3.5)

As indicated in Eq.3.5, the intensity of the evanescent wave, $I_e$, is proportional to the intensity of the incident light, $I_0$. The intensity follows an exponential decay with the penetration depth, $d_p$, which is dependent on the wavelength of the light, $\lambda$, as well as on the refractive indexes of the crystal, $n_1$, and the polymer film, $n_2$, and the angle of incidence, $\theta$: 
\[ d_p(\lambda) = \frac{\lambda}{2\pi \sqrt{n_1^2 \sin^2 \theta - n_2^2}} \]  

(3.6)

In this project, ATR-FTIR measurements are carried out using a Thermo Avatar 330 spectrometer equipped with a single reflection diamond crystal. The angle of incidence of the diamond crystal was 45°. The spectra are collected with a resolution of 4 cm\(^{-1}\) and averaged over 32 scans for wavenumbers from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The refractive indexes of the ATR crystal (\(n_1 = 2.40\)) and the FEP substrate (\(n_2 = 1.344\), [70]) result in penetration depths of 3.8 \(\mu\)m and 0.38 \(\mu\)m for wavenumbers of 400 cm\(^{-1}\) and 4000 cm\(^{-1}\), respectively.

The absorption of the APTMS film (\(A_{\text{APTMS}}\)) can be determined by the ratio of the transmitted infrared intensity of the pristine FEP substrate (\(I_{\text{R,FEP}}\)) and the substrate with the APTMS film (\(I_{\text{R,APTMS+FEP}}\)). This absorption can be related to specific bonds present in the film, according to the Beer-Lambert law (Eq. 3.7), which allows comparison of the different spectral absorbance peaks for the various plasma polymerized samples. The absorption of specific bonds in the film (\(\alpha\)) is based on their cross-section for absorption and their concentration. The absorption also depends on the effective path length (\(l\)) of the light.[69]

\[ A_{\text{APTMS}}(\lambda) = -10 \log \frac{I_{\text{R,APTMS+FEP}}}{I_{\text{R,FEP}}} = \alpha \cdot l \]  

(3.7)

Since the infrared absorption measurements are not obtained in transmission mode, the effective path length (\(l\)) is influenced by the penetration depth of the evanescent wave according to:

\[ l(d_p) = \frac{2n_1n_2 \cos \theta}{n_1^2 - n_2^2} \cdot d_p \]  

(3.8)

Variations in the clamping of the sample and variations due to interference phenomena of the thin APTMS films, however, impede on a quantitative analysis. The absorbance (\(A_{\text{APTMS}}(\lambda)\)) of the deposited APTMS films is, therefore, only quantitatively compared.

In the absorption spectra several different peaks can be observed. Since the deposited APTMS films are relatively thin (< 200 nm), the absorption of the FEP substrate is dominant. Contributions of the substrate to the infrared absorption spectrum for the \(C - F\) stretching bonds in \(CF_2\) and \(CF_3\) are clearly found in the region from 1100 – 1300.[71] Close to the substrate absorption, multiple peaks are reported which are related to \(Si - O - Si\) and \(Si - O - C\) bonds (1000 – 1200 cm\(^{-1}\)). The \(Si - O - Si\) bond is present if polymerization is done via the formation of a siloxane network, while the \(Si - O - C\) is present in the APTMS precursor. Unfortunately, separation between the contributions of \(Si - O - Si\) and \(Si - O - C\) is not possible.[31, 45] Differences in chemical environment lead to significant broadening and potential peak shifts.

Furthermore, there is a region from 2800 cm\(^{-1}\) to 3600 cm\(^{-1}\), which contains \(CH_2\) absorptions, but also peaks which are related to \(-OH\) and \(-NH\) functional groups. Amine functionalities are therefore difficult to distinguish from hydroxyl groups in infrared spectra. Other peaks, especially in the 1500 – 1700 cm\(^{-1}\) region provide more information about nitrogen related functionalities. An overview of the peaks which are expected in the infrared absorption spectrum is shown in Figure 3.3. The specific assignment of the measured absorption peaks will be discussed in Sect. 4.2.

### 3.3.3 Spectroscopic Ellipsometry (SE)

The thickness of the deposited APTMS films is determined using spectroscopic ellipsometry (SE). Using this technique, the deposition rate of the plasma polymerized APTMS films per print repeat
Table 3.3: Overview of dominant infrared absorption regions.

| Absorption of FEP |  
| --- | --- |
| $C - F_2$ | $1100 - 1300 \text{ cm}^{-1}$ |
| $C - F_3$ |  |

| Absorption of APTMS and potential functionalities |  
| --- | --- |
| $Si - O - Si$ | $1000 - 1200 \text{ cm}^{-1}$ |
| $Si - O - C$ |  |
| $N - H$ | $1400 - 1700 \text{ cm}^{-1}$ |
| $C = O$ |  |
| $C = N$ |  |
| $C - H_2$ | $2180 - 2240 \text{ cm}^{-1}$ |
| $N - H$ | $2800 - 2960 \text{ cm}^{-1}$ |
| $-OH$ | $3000 - 3600 \text{ cm}^{-1}$ |

can be determined. The influence of the substrate on the deposition rate can also be determined. The thickness measurements are performed using a Woollam M2000 Multi-Angle Ellipsometer.

![Figure 3.6: The basic principle of SE.][74]

The principle of SE is shown in Figure 3.6. Linearly polarized light is directed towards the sample. The polarization of the light is changed as a function of the wavelength due to the electrical and structural properties of the sample layers. The change in the polarization can be depicted using psi ($\Psi$) and delta ($\Delta$). These are the variables measured as a function of the wavelength of the light, which can be converted to the complex reflection coefficients $r_p$ and $r_s$, parallel (p) and perpendicular (s) to the plane of incidence, via

$$\rho = \tan \Psi \exp (i \Delta) = \frac{r_p}{r_s} = \frac{E_{rs}/E_{ip}}{E_{rp}/E_{is}}$$ (3.9)

An optical model should be used to fit the results found for $\Psi$ and $\Delta$. All refractive indexes and absorption coefficients are brought together in the complex reflectance ratio, $\rho$,

$$\tan \Psi \exp (i \Delta) = \rho (N_0, N_1, N_2, d, \theta_0)$$ (3.10)

In Eq.3.10, only the refractive indexes and absorption coefficients of a model with a single thin film on a substrate are included, as shown in Figure 3.7. The model consists of the FEP substrate ($\sim 75 \mu m$)
and the deposited APTMS film. Measurements were performed at an angle of incidence of 65°, 70° and 75°.

![Figure 3.7](image)

**Figure 3.7**: The basic model for the determination of the APTMS film thickness using SE. The incoming light ray is reflected at the various interfaces, where the refractive index changes. Also part of the light is transmitted.

In order to determine the thickness of the deposited film, the parameters of Eq.3.10 are modeled using a B-Spline model. A B-Spline fit function models the measured Ψ and Δ as a function of the wavelength (λ) by a polynomial function. A pristine FEP film is first analyzed and modeled. The resulting refractive index and absorption coefficient are subsequently kept constant to optically define the substrate for the modeling of the deposited film. For the modeling of the APTMS film, the wavelength region up to 3 eV is adopted to be transparent. If the polymer would exhibit absorption in this region, this is disregarded. Using this transparent region, the fitting procedure is carried out over the total wavelength range (1 – 5 eV) of the APTMS layer and results in a physically acceptable and Kramers-Kronig consistent fit.[68, 75, 76]

### 3.3.4 Contact angle measurements

The surface of the APTMS films is studied by the measurement of the contact angle of liquid droplets. The surface tension of a liquid and its contact angle provide information on the surface tension of deposited film. The surface tension can be determined from Young’s equation:

\[
\gamma_{lv} \cos (\theta_Y) = \gamma_{sv} - \gamma_{sl} \tag{3.11}
\]

Young’s equation follows from the different surface tensions, shown in Figure 3.8. The contact angle according to Young’s equation (θ_Y) is a result of the equilibrium between the surface tensions at the interface between the solid surface and air (γ_{sv}), the test liquid and air (γ_{lv}) and the solid surface and the test liquid (γ_{sl}).

To determine the tension, both the tension of the surface in air (γ_{sv}) and the surface tension between the liquid droplet and the solid surface (γ_{sl}) should be known. One method to determine γ_{sl}, which focuses on the polar character of the surface, is the Owens-Wendt-Rabel-Kaelble (OWRK) approach.[77, 78]

In the OWRK approach, the surface tension is separated in a dispersive and a polar component. The dispersive component accounts for Van-der-Waals forces and other non-site specific interactions from the surface with the applied liquid, while the polar surface tension reflects site specific forces as dipole interactions and hydrogen bonding. The separation of dispersive and polar interactions is represented by equations 3.12 and 3.13. Eq.3.13 is also known as Good’s equation[79]:

\[
\gamma = \gamma^D + \gamma^P \tag{3.12}
\]

\[
\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2 (\gamma_{lv} \gamma_{sv})^{1/2} - 2 (\gamma_{lv} \gamma_{sv})^{1/2} \tag{3.13}
\]
Figure 3.8: Schematic view of the surface tensions and the contact angle, involved in the determination of the solid surface tension using Young’s equation. The surface tension between the solid film and air, $\gamma_{sv}$, can be determined from the surface tension between the test liquid and air, $\gamma_{lv}$, the solid film and the test liquid, $\gamma_{sl}$, and the contact angle of the liquid, $\theta_{v}$. Since both $\gamma_{sv}$ and $\gamma_{sl}$ are unknown at least two liquids are needed for the surface tension determination of $\gamma_{sv}$.

In Eq.3.12 and Eq.3.13, $\gamma^{D}$ and $\gamma^{P}$ represent the dispersive and polar component of the surface tension. As shown in Eq.3.12, by simply adding them up, the total surface tension can be determined.

In order to determine the dispersive-, polar- and total surface tension of the film or substrate using the OWRK approach, two different liquids with known dispersive and polar components are used. These liquids are placed on the surface using an Eppendorf reference pipette, while the contact angle is determined by the fit of a home-built contact angle goniometer. The droplet size is 2.0 $\mu$l. Diffuse backlighting is used to clarify the edges of the droplet and improve the fitting procedure.

The first liquid is diiodomethane ($\text{CH}_2\text{I}_2$). Diiodomethane is used because of its completely dispersive character:

$$\gamma_{lv} = \gamma_{lV}^{D} = 50.8 \text{mN/m}$$  \hspace{1cm} (3.14)

The second liquid is deionized water. Water has a strong polar character, while it also possesses a dispersive component:

$$\gamma_{lv} = \gamma_{lV}^{D} + \gamma_{lV}^{P} = 26.4 + 46.4 = 72.8 \text{mN/m}$$  \hspace{1cm} (3.15)

The surface tension, $\gamma$, as determined from the contact angle measurements of multiple liquids allows differentiation between dispersive and polar effects in the contact angles. Water contact angles, however, are usually more important, since the polar character of water is more able to reflect changes in the polar character of the surface, induced by polar functional groups.

Static contact angle measurements are often performed in literature, using a comparable method to the one described in this section.[14, 80] The comparison of the measured contact angle with literature, however, remains difficult due to non-ideal measurement conditions. When performing contact angle measurements on ideal surfaces it is assumed that the measurement provides a unique 'equilibrium' contact angle. Deviations from this equilibrium contact angle are caused by assumptions, such as perfect smoothness and chemical inertness of the surface. Also physical and chemical homogeneity of the surface are assumed, while all surface tensions should remain constant, in time as well as with or without the liquid. These remarks also mean that the liquids should be pure and no evaporation of the liquid may take place.[81, 82]

These assumptions are not (completely) true for plasma polymerized films. The surface is, for example, not homogeneous. The concentration of amine functionalities and the film thickness vary as function of the plasma printing position; each needle has a slightly different distance to the surface and/or
a different tip shape, which results in variations in the plasma energy per needle and subsequent variations in the deposited film. These variations influence the contact angle. Also the orientation of the functional groups may be changed by the placement of a test liquid on the surface.

The focus of this project is on the changes of the contact angles for samples which are deposited with the same deposition setup and the same plasma properties. Since physical and chemical inhomogeneities in the deposited films are approximately constant, static contact angle measurement is an easy-to-use method. In the interpretation of the contact angle measurements, the static contact angle is usually found to be close to the advancing contact angle, which results in a stronger sensitivity for hydrophobic functionalities compared to hydrophilic groups.[82]

### 3.3.5 Fluorescence labeling of surface species

The identification of amine functionalities in the plasma polymerized APTMS films is already carried out by the above discussed techniques. For the determination of the ability of the amine functionalities to participate in further immobilization reactions, however, fluorescamine is used as an amine specific labeling technique, showing fluorescent emission when bonded to an amine functionality.

In this project, XPS is used for detecting and quantifying the amine functionalities in the film. This determination of the amine content by the deconvolution of the nitrogen peak, however, may be subject to a large error due to the small difference in binding energy between amine and amide/imine groups. The infrared absorption measurements are influenced by the $-OH$ absorption, occurring in the proximity of the $-NH_2$ absorption peak.

In order to improve the specificity of the detection of amine functionalities, chemical labeling is utilized. Chemical labeling allows specific binding of a marker molecule to the amine functionality. The marker molecule can be chosen so that it can be detected much easier than the amine functionality itself. Common detection methods using a marker molecule are XPS and fluorescence detection.[83, 84] With XPS a marker molecule, which contains an element which is not present in the deposited film, binds to the amine functionality. By the subsequent detection of this new element it becomes possible to determine the surface concentration of amine functionalities ($[NH_2]/[C]$) compared to the carbon concentration in the film.[1] TFBA (4-trifluoromethyl-benzaldehyde) is often used for this binding procedure, but in our case the new element, fluorine, is already in the FEP substrate, which makes TFBA less favorable for amine detection by XPS.[2, 30, 32, 85]

Labeling with a molecule which is fluorescent or becomes fluorescent when it is bonded to an amine functionality is another approach for amine characterization, e.g. in plasma polymerization and surface wetting research, but also for biological applications as protein adsorption of biosensor fabrication. A big advantage of fluorescent labeling compared to chemical derivation XPS is its use at atmospheric conditions. No vacuum equipment is needed. Fluorescent labeling is also the detection method which has the highest sensitivity. Since the background signal is zero, in principle, the detection limit goes down to $10^{-5} [NH_2]/nm^2$. In the case that the fluorescent marker only becomes active if bonded to an amine functionality, the fluorescent intensity is found to be linearly related to the concentration of amine functionalities. This is usually the case in characterization techniques, which directly measure the signal from the amine binding marker. With indirect characterization one can think of a reversible reaction, which unbinds the marker molecules, for a subsequent analysis of these marker molecules, e.g. in a solution.[83] In this case, the surface is recovered and the detection method is completely non-destructive.

When applying an indirect method, instead on a direct method, however, the measurement becomes more sensitive to side reactions. The specificity of a labeling molecule, for direct and indirect characterization methods, is one of the two key properties for accurate amine detection. The labeling molecule may only bind to the specific functional group. For example, the TFAA (trifluoroacetic anhydride) binds with $-OH$ groups as well as with primary and secondary amines.[30, 32, 85]

The marker molecule should not leave target functional groups unlabeled. The labeling reaction should, therefore, be fast and no side reactions should be possible. Depending on the size of the
labeling molecule, steric hindrance can occur. Also saturation of the fluorescent signal may occur upon quenching by vicinal marker molecules[84, 86], leaving the maximum detectable concentration of amine functionalities by fluorescent labeling to be $\sim 6 \times [NH_2]/\mu m^2$.[84]

The fluorescence analysis of the APTMS samples is governed by spontaneous photon emission. If an electron is electronically excited by the absorption of a photon with the energy matching the difference between two states, a photon can again be emitted if the electron is de-excited, e.g. to the ground state. This principle is shown in Figure 3.9a. This so-called Jablonski diagram shows that the absorption of a photon with a certain energy, $\hbar \omega$, results in the excitation of an electron. After some (non-fluorescent) internal conversion, photon emission occurs.[86] As can be observed in Figure 3.9b, this results in the emission of light, which has a larger wavelength than the light used for excitation. Both the excitation and emission spectra are significantly broadened, which is the result of a great variety of transitions between the electronic states due to multiple ro-vibrational states per electronic state. The given excitation and emission curves in Figure 3.9b are shown for fluorescamine.[87]

![Jablonski diagram](image)

Figure 3.9: Fluorescent emission is governed by the electronic excitation of an electron by the absorption of a photon. After internal conversion a photon is emitted with a higher wavelength (a, [86]). The excitation and emission curves are shown for fluorescamine, if bonded to an amine functionality (b, [87]).

In this project, fluorescamine is used for the fluorescent labeling and detection of amine functionalities. The reaction of fluorescamine with an amine functionality results in a chemical bond, which allows for fluorescence phenomena, while free fluorescamine remains non-fluorescent.[84, 85, 87, 88, 89, 90, 91] Also potential side reactions are non-fluorescent. The reaction of fluorescamine with amine functionalities is shown in Figure 3.10, together with the fluorescamine side reaction with water. The reaction time with water is much longer than with an amine functionality.

If the amine bonded fluorophore is exposed to light with a wavelength 390 nm, it will become fluorescent and emit light at a wavelength of 475 nm.[84, 85, 87, 88, 89, 90, 91] In order to achieve excitation and fluorescent detection an Olympus BX-40 fluorescence microscope is used, which is equipped with an OSRAM HBO 100-W mercury lamp and an Olympus ultraviolet filter set. The filter set is composed of an excitation filter ($380 \pm 15$ nm), a dichroic mirror ($420$ nm) and a barrier filter ($460 \pm 25$ nm). The dichroic mirror works as a beam splitter; it reflects wavelengths below $420$ nm towards the sample, while it allows wavelengths above this value to pass towards the detector. The total setup is shown in Figure 3.11, together with the transmittance of the applied filter set, as provided by the manufacturer of the filter set.
Figure 3.10: Fluorescamine and its possible decay reactions. Fluorescamine only becomes fluorescent of it reacts with an amine functionality. The probability for fluorescamine to react with an amine functionality is much larger than to react with water, as can be concluded from the half-life times.\cite{88}

Figure 3.11: Setup for the detection of surface amines using fluorescamine (a). The light of a HBO-100 W mercury lamp is filtered by an excitation filter and reflected towards the sample. The fluorescent light from the sample is allowed to pass through the dichroic mirror and is detected by a photosensitive detector after it has been filtered by a barrier filter. The amplification of the used lenses is 4x. The transmission of the different filters and the dichroic mirror are also shown (b).

In order to bind fluorescamine to the amine functionalities at the surface, the deposited APTMS samples are placed into 15 ml of buffer solution (0.20 M NaBO$_2$ · 4H$_2$O) for 5 minutes. A buffer solution allows fluorescamine binding at pH = 8.5 – 9.0, which enhances the binding process.\cite{85, 87, 88} Next, fluorescent binding is achieved by the addition of 5 ml fluorescamine solution (0.25 g/l in aceton) to this buffer solution.\cite{88, 89} As shown in Figure 3.10, all fluorescamine has reacted within 5 minutes. The samples are rinsed with ethanol and water (twice) afterwards.

The emission spectrum of a fluorescamine derivated APTMS sample is shown in 3.12. The sample was deposited with 5 PR, according to Sect.3.1 and 3.2. A pristine FEP sample is shown for comparison, together with the difference spectrum between the samples.

Based on the difference spectrum it can be observed that fluorescamine is bonded to amine functionalities. The measured fluorescence signal is increased for the sample with plasma polymerized APTMS compared to the pristine substrate. The measured emission contains a relatively large background signal, though the difference with the fluorescamine emission spectrum is still sufficiently large to
determine the fluorescence from the amine containing films.

The measured spectrum contains roughly two regions. The first region, from 445 − 490 nm, contains a background signal which has similar shape as the transmission of the barrier filter en the dichroic mirror (Figure 3.11). The second region, a sharp peak around 425 − 445 nm, originates from the mercury lamp. This peak is able to reach the detector by its reflection at the surface. Other peaks from the source are also observed (e.g. at 413, 418, 423, 503 or 508 nm), but these peaks are filtered much better. The resulting fluorescamine related spectrum is in close agreement with literature. The fluorescamine emission spectrum contains a very broad peak (≈ 440 − 600 nm), which has its maximum around 475 nm.[85, 87, 90] Due to the use of the ultraviolet filter set, however, approximately half of this spectrum, as well as another potential amine related peak at 520 nm, are filtered.[85, 90]

After spectral analysis of the detected light fluorescent pictures are recorded using a Canon EOS 6D camera. Due to the small differences in the measurement results, digital analysis of the signal is preferred. Appendix A shows the translation from the optical emission spectrum of the sample to a fluorescent intensity, as measured by the optical camera.

Fluorescamine is found to be a good marker molecule to determine the presence and immobilization potential of amine functionalities in the deposited APTMS film. Quantification of the concentration of amine functionalities at the surface, however, is more difficult. In order to create a reference surface, limited concentrations of APTMS are dissolved in toluene. Toluene is found to be a good solvent for APTMS and is often used for formation of self-assembled monolayers from the APTMS liquid monomer.[80, 91] The amine groups are subsequently functionalized by the admixture of fluorescamine. The fluorescamine is abundantly admixed to assure that all amines are bonded.

The mixture is subsequently placed between a microscope slide and cover slide and the fluorescence is analyzed similar to the APTMS films. The volume which is used is 3 μl. With a cover slide surface area of 18 × 18 mm the test films have a thickness of ≈ 9 μm. The fluorescence cannot be calibrated around the expected range of 0.5 − 5 [NH₂/μm²][28, 92], due to quenching of the fluorescent signal, as can be observed in Figure 3.13. This figure shows the calibration curves for two differently sized cover slides. Since the calibration volume remained constant (3 μl), the thickness of the film increased to ≈ 13 μm,
which resulted in an increase of the fluorescent quenching. For concentration from $0 - 0.01\,[\text{NH}_2]/\text{nm}^2$, however, the quenching appears negligible, as would be in agreement with literature.\cite{87} The absence of fluorescent quenching in this region allows the linear extrapolation of the fluorescent intensity towards the expected range of $0.5 - 5\,[\text{NH}_2]/\text{nm}^2$\cite{28,92}. The fluorescent intensity of the deposited APTMS films allows the subsequent determination of the amine surface concentration in the deposited films.

Figure 3.13: Test measurement for the quantification of the fluorescent signal. For thinner liquid films in between microscope slides (larger area), less fluorescent quenching is observed.
Chapter 4

Results and Discussion

As discussed in Chapter 1, the goal of this project is to incorporate amine functionalities on a dielectric surface. This incorporation is achieved by the plasma polymerization of vaporized APTMS (3-aminopropyl trimethoxysilane) using the µPlasmaPrint system. In Sect. 4.1, the APTMS films which are deposited with a single print repeat (1 PR) are analyzed by XPS, which allows determining which chemical bonds are present in the polymerized APTMS film. Furthermore, hypotheses can be formulated on the dissociation mechanism of the APTMS molecule in the plasma. The XPS C1s and N1s peaks are also included in this analysis, e.g. to determine the presence of amine functionalities in the deposited film. The thickness of the deposited film per print repeat is inferred by means of ellipsometry and XPS. The above-mentioned analysis provides answers to questions related to the polymerization process, therefore paving the way to the optimization of the amine concentration for the different applications.[7, 18, 19]

The film structure and the amine concentration are influenced by the plasma exposure time. In Sect. 4.2 the deposited APTMS films are analyzed as a function of the number of print repeats of the µPlasmaPrint setup. Changes at the surface and in the bulk of the films are monitored by means of contact angle, XPS and ATR-FTIR measurements. The stability of the films is investigated as well. The loss of amine functional groups in time is defined as ageing. Dominant ageing mechanisms are inferred using contact angle measurements and XPS.

In the last section of this chapter, Sect. 4.3, the amine functionalities are further investigated by studying their reaction with fluorescamine, followed by the detection of the fluorescent signal. The influence of the number of print repeats of the µPlasmaPrint system is again determined. Next to a qualitative analysis, an attempt has been made to determine the concentration of amine functionalities at the surface of the deposited film by the derivation of a calibration procedure. The ability of the amine functional groups to improve metal-polymer adhesion is also subject of investigation in Sect. 4.3.

4.1 Chemical structure of plasma polymerized APTMS films

The analysis of plasma polymerized films usually show a large variation in chemical bonds. Reactive species in the plasma, such as ions and radicals, create reactive sites at the surface which are able to bond with the various species in the plasma. In order to define the structure of plasma polymerized APTMS films in their early stages of growth, a single µPlasmaPrint repeat (1 PR) has been carried out and the film has been analyzed by XPS (Sect. 3.3.1). The results of the XPS measurement of the silicon Si2p and oxygen O1s peaks are shown in Figure 4.1.

The analysis of the silicon Si2p peak shows a single component at a binding energy of 102.1 eV. A fit of this peak provides a "Full Width at Half Maximum" (FWHM) of 1.44 eV. This FWHM is consistent with values reported in literature[31, 63], while it is larger than the resolution of the XPS analyzer.
Figure 4.1: High-resolution XPS spectra of the silicon Si2p peak (a) and the oxygen O1s peak (b). The assignments of the fitting peaks are also shown.

of $\sim 1$ eV. The FWHM is broadened due to the amorphous character of the plasma polymerized film.[31, 63]

The position of the silicon Si2p peak provides information on the chemical environment of the silicon atom. Since oxygen has a significantly higher electronegativity than the other elements present in the APTMS monomer (carbon, nitrogen and hydrogen), based on the Si2p peak position at 102.1 eV it can be derived that each silicon atom is bonded to two oxygen atoms, out of the four covalent bonds available.[63, 73] This result is consistent with a siloxane chain structure.[63, 73]

As discussed in Sect.3.3.1, the oxygen O1s peak is fitted with two components. The first one at 530.7 eV is a minor contribution, which is assigned to double bonded oxygen. The small contribution of $C = O$ bonds may be attributed to oxidation processes in the film or to the presence of impurities at the surface.[13] The second component at 531.9 eV, is assigned to (single) silicon-oxygen and carbon-oxygen bonds. As can be observed, the second contribution to the oxygen O1s peak is much more dominant.

**Film stoichiometry and bond dissociation**

Based on the previous analysis, it is derived that the backbone of the deposited APTMS film is constituted by siloxane chains. This siloxane network is formed by the specific dissociation of bonds in the APTMS monomer. The bond dissociation process, as well as the functional groups and side chains in the siloxane network, can be determined by the analysis of the stoichiometry of the deposited film using XPS. The stoichiometry of the APTMS film which is deposited with 1 PR, is shown in Table 4.1. The derived stoichiometry is compared to that of the APTMS monomer.

| Table 4.1: Elemental composition (at.%) of the APTMS film, which is deposited with 1 PR and measured by XPS. Based on the elemental composition the stoichiometry of the film is derived. The elemental composition and stoichiometry of the APTMS monomer are included for comparison. |
|-------------|---|---|---|---|---|
|            | Si | O  | C  | N  | F  | Stoichiometry       |
| APTMS monomer | 9.1 | 27.3 | 54.5 | 9.1 | 9.1 | $SiO_{3.0}C_{6.0}N_{1.0}$ |
| pp-APTMS (1 PR) | 12.5 | 27.5 | 41.6 | 13.2 | 5.2 | $SiO_{2.2}C_{3.3}N_{1.1}F_{0.4}$ |

Table 4.1 shows the presence of fluorine, which can be the result of the incorporation of fluorine into
the APTMS film, or due to the detection of the FEP substrate, in the case the APTMS film would be thinner than the $\sim 10$ nm escape depth of the ejected electrons during XPS analysis. Both options will be discussed at the end of Sect.4.1.

The origin of the changes in contribution of the different elements is related to the chemical structure of the deposited APTMS film. Further investigation of the structure is done by the analysis of the XPS spectra of carbon and nitrogen. The spectra are shown in Figure 4.2, together with the result of the peak deconvolution. Peak convolution has been performed according to literature, as summarized in Table 3.2.

![Figure 4.2](image)

**Figure 4.2.** High-resolution XPS spectra of carbon (a) and nitrogen (b) for 1 PR. Peak fitting is performed to determine the chemical environment (also shown) as discussed in Sect.3.3.1. The C1s and N1s measurements and peak deconvolutions are examples of the performed measurement series, while reported concentrations (at.%) of the deconvolutions are averaged over all measurements.

Four peaks are adopted to deconvolute the carbon C1s signal: it can be observed that the carbon peak predominantly consists of a contribution due to aliphatic carbon atoms ($C_1$, 284.4 eV), followed by a contribution due to $C - N$ and/or $C - O$ bonds ($C_2$, 285.7 eV) and a minor contribution of $C = O$ bonds ($C_3$, 287.5 eV). At last, a contribution is found at elevated binding energy values, which is attributed to $C - F$ bonds ($C_4$, 291.2 eV).

For the nitrogen N1s peak in Figure 4.2b three peaks are adopted for the deconvolution. The dominant contribution, here, is the amine-related peak ($N_1$, 398.8 eV), but also amides or amines in the vicinity of a more electronegative environment (i.e. containing oxygen) are present ($N_2$, 399.7 eV and $N_3$, 400.8 eV).

Based on the stoichiometry reported in Table 4.1, a repeating unit of the APTMS plasma polymer contains approximately one nitrogen atom. From Figure 4.2 it can be determined that the nitrogen content predominantly consists of amine functionalities. For the carbon content on the other hand, it was found in Table 4.1 that approximately three carbon atoms are present per silicon atom. From Figure 4.2a it can subsequently be derived that approximately one of these carbon atoms is bonded to oxygen or nitrogen, while the other two atoms are bonded to hydrogen, carbon or silicon. Since the nitrogen atom is bonded to carbon, the contribution of the peak at 285.7 eV ($C_2$) is attributed to $C - N$ bonds. The retention of the amine functionality in an aliphatic environment and the $C_1/C_2 + C_3$ ratio of approximately 2 is most likely to be accomplished by the retention of the complete aminopropyl chain.

$^1$Most authors calibrate the C1 peak at 285.0 eV to correct for surface charging.[29, 30, 62] In our measurements charge compensation is accomplished during the measurements and the C1 peak is found at 284.4 eV. The C1s fitting peaks may therefore be shifted approximately 0.6 eV compared to Table 3.2.
The stoichiometry of Table 4.1 and the chemical environment of carbon and nitrogen in Figure 4.2 show that the dissociation process of the APTMS monomer occurs via the abstraction of at least two of the three methyl groups present. Hydrolysis reactions, as shown in Eq.2.5, which result in the formation of silanol groups (≡ Si – OH) and molecular methanol (CH₃OH), are expected to occur during the deposition. The condensation of the silanol groups to ≡ Si – O – Si ≡ then leads to the formation of the siloxane network.

Similar monomer dissociation pathways are already observed in literature.[32, 57] In their parallel plate DBD setup, Borris et al. also deposited APTMS at atmospheric pressure and suggested that the deposited film structure was the result of the hydrolysis of the Si – O – CH₃ groups to silanols, ≡ Si – OH, followed by the condensation of these groups to ≡ Si – O – Si ≡. The plasma conditions in the system of Borris et al. are comparable to the µPlasmaPrint setup - as far as they are described in their paper - in terms of a filamentary discharge regime and absorbed plasma power, explaining the derivation of a comparable polymerization mechanism and comparable properties of the deposited APTMS films.

The retention of the aminopropyl chain, together with the formation of a siloxane network, almost completes the analysis of the chemical structure of the deposited films. Chemical (polymerization) reactions occurring at the fourth covalent binding site of the silicon atom, however, are under discussion. Based on the stoichiometry reported in Table 4.1, it may be suggested that at this site retention of silanol groups (≡ Si – OH) after the hydrolysis reaction or retention of the complete methoxy group (≡ Si – O – CH₃) leads to an [O]/[Si] ratio of approximately 2 and a [C]/[Si] ratio slightly above 3.

The binding of a third oxygen atom to silicon, however, would lead to a binding energy peak shift of the silicon Si2p peak from 102.1 eV to 102.8 eV.[63] Due to the complete lack of such a binding energy peak shift, the peak position of the silicon Si2p and its implications for the chemical structure of the APTMS films are given more weight than the derived stoichiometry, which may be influenced deviating sensitivity factors. This chemical structure based on the silicon Si2p peak, however, would lead to an [O]/[Si] ratio of 1. The increased oxygen content is attributed to a combination of several different processes. The incorporation of oxygen during and/or immediately after deposition of the film is one of them. The presence of oxidation processes is supported by contributions at higher binding energies in the N1s and C1s peaks (N2, N3, C2 and C3), as well as by the oxygen O1s contribution at 530.7 eV. These processes will be discussed extensively in Sect.4.2. Furthermore, it is possible that silanol- and methoxy groups are retained in the film as a results of incomplete hydrolysis and condensation reactions.[57] Retention of these groups results in a limited polymer chain length, increasing the [O]/[Si] ratio.

In absence of a third silicon-oxygen bond, the last silicon binding site is tentatively described by the binding of plasma radicals and/or monomer fragments (−R), which result in a Si – R bond with an electron negatively comparable atom to silicon, e.g. carbon or silicon itself. The formation of Si – Si bonds, e.g. from two siloxane chains, or the adsorption of −CH₃ functional groups are possible explanations for this bond.

### Initial growth of the APTMS films on FEP substrate

After the analysis of the chemical structure of the deposited APTMS films for 1 PR, it is investigated how the film is chemically bonded to the FEP substrate. By the elemental analysis of the substrate and the investigation of the shifts in binding energy when an APTMS film is deposited, the role of the substrate in the deposition process can be determined.

First the FEP substrate itself (Figure 3.3) is analyzed by XPS. It is found that the substrate only contains carbon and fluorine, as expected. No oxygen or carbon contaminations are found. Also the ratio between the fluorine and carbon content is consistent with their theoretical value: [F]/[C] = 2.0. The XPS spectrum of the carbon peak of the FEP substrate is shown in Figure 4.3. The C1s peak is deconvoluted in three components, assigned to CF, CF₂ and CF₃ contributions. More fluorine atoms
lead to an increase in the binding energy of carbon due to the electronegativity of fluorine. The peak assignment is again performed according to the literature described in Table 3.2.

![High-resolution XPS spectrum of the carbon C1s peak of the pristine FEP substrate.](image)

Figure 4.3: High-resolution XPS spectrum of the carbon C1s peak of the pristine FEP substrate.

From Figure 4.3, the ratio between the two components of the FEP co-polymer can be determined. It can be derived from the ratio between the $CF_2$ and the $CF_3$ peak, that the concentration of the ($CF_2CF_2$) component of the co-polymer is approximately ten times higher than the ($CF_2CFCF_3$) component.

In order to infer information on the early stages of growth of APTMS polymers on FEP substrates, the binding energy of fluorine is also analyzed as a function of the number of print repeats. The results are shown in Figure 4.4. The measured intensity is scaled in order to visualize the contributions of all different peaks (F1 to F5).

The fluorine peak is deconvoluted in five contributions. We discuss first the case of 1 PR and compare that film to the measurement on the pristine FEP substrate. The fluorine peak, which is presented at upon 1PR indicates either that the APTMS film is rather thin or that fluorine is incorporated in the film during deposition. After 1 PR, the fluorine binding energy is shifted towards lower values by ~1 eV. The $CF_3$ peak is no longer detected. Due to the coverage of the deposited film, the probability for the F1s electrons to escape from the sample becomes smaller. The same observation holds for the $CF_2$ peak. The $CF_2$ peak, however, is reduced by a factor ~ 400, which is a large reduction compared to the reduction of the $CF$ peak. The latter is only reduced by a factor ~ 2, suggesting an additional interpretation.

Based on the difference in peak reduction, it is suggested that the APTMS-derived radicals bond to the surface of the polymer via available $Si – OH$ groups to form $Si – O – C$ bridges with the FEP polymer, accompanied by fluorine abstraction (e.g. by $HF$ formation), therefore replacing in the outer surface of the polymer, fluorine with oxygen. The substitution of fluorine by oxygen leads to a decrease in binding energy, both for the carbon atom in the $Si – O – C$ bond and for remaining fluorine atom which is bonded to that carbon atom. As a result, in the fluorine spectrum the F3 peak is increased at the expense of the F4 (and F5) peak; i.e. the $F – C \equiv (C, C, F)$ bond, indicated in green in Figure 4.4, is replaced by $F – C \equiv (C, C, O)$, which is indicated in blue. The formation of $Si – O – C$ bridges is consistent with the binding energy of the carbon C1s peak. In Figure 4.2a, the small contribution
Figure 4.4: High-resolution XPS spectra of fluorine as a function of the number of print repeats (PR). Peak fits are performed to determine the chemical environment of the fluorine atoms, according to Sect. 3.3.1. The peaks assignments are also shown. The peaks are scaled to visualize all contributions.

which is related to $C - F$ bonds is in between the $C - F$ and $C - F_2$ contributions from the substrate from Figure 4.3, indicating the presence of $O - C - F$ bonds.[62]

The development of APTMS films deposited by 1 PR is sketched in Figure 4.5. This figure shows the abstraction of methyl groups by hydrolysis reactions, forming silanol groups ($\equiv Si-OH$) and molecular methanol ($CH_3OH$), as derived in the previous sub-section. It also shows the polymerization via the formation of siloxane chains and the suggested binding to the substrate by $Si - O - C$ bonds.

It is not included in Figure 4.5 that the fluorine spectrum in Figure 4.4 shows two more contributions. These contributions only are visible only when the APTMS film is deposited. The highest binding energy peak of those two peaks (F2, 686.8 eV) can be assigned to fluorine which is bonded to carbon in an aliphatic environment[64], indicating that local plasma-surface interactions are responsible for ablation of fluorine which is then embedded in the deposited APTMS film by the formation of $C - F$ bonds. This incorporation of fluorine atoms remains visible for a higher number of print repeats than the contributions of the FEP polymer. The second peak is also related to fluorine embedded in the APTMS film, since it has an even lower binding energy (F1, 684.8 eV). According to the peak position and its presence for more print repeats, it is suggested that the F1 peak is related to fluorine embedded in the film by silicon-fluorine bonds, since silicon has a lower electronegativity than carbon, resulting in a lower binding energy of the fluorine atom. Because of the small contribution of this peak ($< 0.5 \text{ at.\%}$) and because XPS has a much smaller sensitivity for the silicon atom than for the fluorine atom, the presence of $Si - F$ bonds cannot be confirmed by the silicon Si2p spectrum.

The second remark on the schematic representation of the plasma polymerized APTMS film in Figure 4.5 and the above-derived APTMS film structure is that the measured $[O]/[Si]$ ratio is higher than the content predicted by the polymerized monomer structure. As discussed, this difference is attributed to a combination of multiple effects, including oxidation processes, incomplete hydrolysis and condensation reactions and/or relatively short polymer chains. The effect of oxidation processes during and/or immediately after deposition is not included in Figure 4.5. The retention of methoxy groups, on the other hand, is illustrated.
Figure 4.5: Hypothesis for the formation of the APTMS plasma polymer in the early stages of the film growth. The APTMS monomer (a) is partially dissociated by hydrolysis reactions, removing the methyl groups, while forming silanol groups and molecular methanol (b). The APTMS fragments polymerize via the formation of siloxane bonds as a result of condensation reactions, while the aminopropyl chains remains intact. It is suggested the deposited film is bonded to the FEP surface via $\text{Si}^{-}\text{O}^{-}\text{C}$ bridges, replacing in the outer surface of the FEP polymer fluorine by oxygen (c).

**Deposition rate per print repeat**

Based on the peak assignment in the fluorine spectrum, it is also possible to derive the thickness of the deposited film after 1 PR using Eq.3.2. The attenuation length for fluorine atoms in APTMS is 2.46 nm, which is based on Eq.3.3. Using Eq.3.2 and Eq.3.3 the thickness of the APTMS film for 1 PR is determined to be $7.5 \pm 1$ nm. This film thickness is derived by the analysis of the sum of fluorine peaks F3, F4 and F5, meaning that the presence of a potential intermixing film, due to interactions between the FEP substrate and the depositing plasma, is assigned to the deposited film. Ablated fluorine, which is then embedded in the APTMS film (F1 and F2), is excluded from the thickness calculation.

The deposition rate for 1 PR is consistent with the film thickness after 5 PR, which is determined from spectroscopic ellipsometry (SE) measurements. Using SE, the thickness of an APTMS film deposited with 5 PR is found to be $40 \pm 1$ nm, which again results in a deposition rate of $\sim 8$ nm/PR. The refractive index, $n$, and the absorption coefficient, $k$, of the deposited film and the substrate are shown in Appendix C, together with the uniqueness of the SE fit as a function of the thickness of the film.

Based on the comparison of the deposition rates, determined by XPS and SE, it is concluded that the deposition rate is constant during film deposition.

**4.2 Oxidation processes during and after µPlasmaPrinting**

**APTMS film stoichiometry changes with increasing thickness**

The structure of the deposited APTMS films is influenced by the plasma exposure time, i.e. the number of print repeats (PR). As shown in the previous section, an increase in PR results in an increase in film thickness. Therefore, the film stoichiometry is determined by XPS for a sample which is deposited with 20 PR. The result is shown in Table 4.2.
Table 4.2: Elemental composition (at.%) of the deposited APTMS film, as measured by XPS.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>O</th>
<th>C</th>
<th>N</th>
<th>F</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTMS monomer</td>
<td>9.1</td>
<td>27.3</td>
<td>54.5</td>
<td>9.1</td>
<td></td>
<td>SiO$<em>{3.0}$C$</em>{6.0}$N$_{1.0}$</td>
</tr>
<tr>
<td>pp-APTMS (1 PR)</td>
<td>12.5</td>
<td>27.5</td>
<td>41.6</td>
<td>13.2</td>
<td>5.2</td>
<td>SiO$<em>{2.3}$C$</em>{3.3}$N$<em>{1.1}$F$</em>{0.4}$</td>
</tr>
<tr>
<td>pp-APTMS (20 PR)</td>
<td>12.4</td>
<td>33.3</td>
<td>41.3</td>
<td>13.0</td>
<td>-</td>
<td>SiO$<em>{2.7}$C$</em>{3.3}$N$_{1.0}$</td>
</tr>
</tbody>
</table>

The stoichiometry of an APTMS film, deposited with 20 PR, is close to the structure of a sample deposited with 1 PR. The measured content of silicon, carbon and nitrogen is approximately the same, while differences are found in the oxygen and fluorine content. Fluorine from the FEP substrate is not measured at the surface of a sample deposited with 20 PR, which is evident because of the large film thickness (∼160 nm) compared to the escape depth of the XPS electrons (∼10 nm). Also, ablation of fluorine from the FEP substrate (Sect.4.1), which is incorporated in the deposited film, does not play a role because of the large film thickness. The changes in the oxygen and fluorine content as a function of the number of print repeats are shown in Figure 4.6.

Figure 4.6: Evolution of the oxygen and fluorine content (at.%) in the APTMS film as a function of the number of print repeats. The fraction of fluorine which is assigned to the FEP substrate is also shown. The fluorine which does not originate from the substrate is embedded in the APTMS film. The fits are used as guide to the eye.

Figure 4.6 shows an increase of the oxygen content in the deposited APTMS films from 27.5% to 33.3% for 1 PR to 20 PR, respectively. The 'bulk' concentration of oxygen is reached after 5 – 10 PR, which is also the point where the fluorine contribution in the XPS measurement disappears. The maximum fluorine content of 5.2%, was found after 1 PR, where its contribution predominantly consisted of fluorine from the FEP substrate. For 2 PR and more, the contribution of fluorine from the substrate becomes negligible and the dominant contribution is from fluorine embedded in the APTMS structure. The small contribution of fluorine from the FEP substrate after 2 PR is consistent with the deposition rate derived in Sect.4.1. Based on the increase of the oxygen content and a decrease of the fluorine content, which is from the same order, it is suggested that C – F bonds in the APTMS film are progressively replaced by C – O and C = O bonds. For more than 5 – 10 PR fluorine is not detected and the film composition at the surface is saturated.
Oxidation processes during and after the deposition process

The increase in the oxygen content for an increasing number of print repeats is attributed to the incorporation of oxygen in the film, during and/or immediately after the deposition process, leading to a change in the chemical structure of the films. The chemical environment of silicon, however, is found to remain unchanged, since its binding energy was constant as a function of the number of print repeats, at 102.1 eV (Appendix B). Therefore, a further investigation of the changes in the APTMS film composition as a function of the number of print repeats is carried out by the deconvolution of the carbon C1s and the nitrogen N1s spectra of a film deposited with 20 PR, shown in Figure 4.7.

![Figure 4.7: Changes in chemical environment of carbon (a) and nitrogen (b) for an increase from 1 PR to 20PR. The binding energy of both peaks is deconvoluted. Changes in the contributions of the fitting peaks from 1PR (faded) to 20PR (bright) are indicated, as well as that they are shown in the legend. C2 (C−O, C−N), C3 (C=O, C=N), N2 (O=C−N−C=O) and N3 (O=C−N=CH2) are related to oxidation of the deposited APTMS film during deposition, while C1 (C−C, C−H, C−Si) and N1 (C−NH2) are predominantly present in the APTMS monomer and the plasma polymerized APTMS films, which are deposited with 1PR.](image-url)

It was already shown in Table 4.2 that the total carbon and nitrogen contributions remain approximately constant. The binding energy values of N1s and C1s, however, change significantly towards a chemical environment rich in oxygen. The C2 and C3 peaks (Sect. 3.3.1 and Sect 4.1), which are attributed to carbon which is single (C2) or double (C3) bonded to oxygen, increase from 27% to 41% and from 6% to 15%, respectively. The increase of C2 and C3 is accompanied by a decrease in the C1 component (aliphatic carbon bonds in the aminopropyl chain). The C4 component (fluorine bonded carbon) is absent after 20 PR. This last remark is consistent with Table 4.2 and Figure 4.6.

When examining the N1s peak, it can be concluded that oxidation occurs at the carbon atom adjacent to the amine functionality. The peak shift itself is again significant. Due to oxidation of the APTMS films the amide peak increases from 20% to 64% of the nitrogen content, while the amine peak decreases from 69% to 39%. The N3 peak decreases slightly from 11% to 7%.

The observation of the peak shifts in the carbon C1s and nitrogen N1s peaks as a function of the number of print repeats are supported by the the peak area ratio $C1/C2+C3$ and $N1/N2+N3$, as shown in Figure 4.8, quantitatively pointing out the oxidation which thicker films are undergoing during deposition. For carbon, $C1/C2+C3$ was found to be 2.0 for 1PR due to the retention of the aminopropyl chains, together with the dissociation of the methyl and methoxy groups (Sect.4.1). After 20 PR, however, the ratio is decreased to 0.8, meaning that a large fraction of the carbon atoms is oxidized, either by single bonded oxygen (C2) or by double bonded oxygen (C3).
Figure 4.8: Evolution of the XPS peak ratios of the carbon C1s (a) and nitrogen N1s (b) peaks as a function of the number of print repeats. C2, C3, N2 and N3 are related to oxidation of the deposited APTMS film. C1 and N1 are the dominant contributions for 1 PR, which decrease for more PR. The total carbon and nitrogen content in the film remains approximately constant.

For nitrogen, \( \frac{N_1}{N_2+N_3} \) was found to be 2.2 after 1 PR, reflecting that the majority of the nitrogen atoms was found in amine functionalities. After 20 PR, however, the \( \frac{N_1}{N_2+N_3} \) ratio decreases to 0.6, which indicates that approximately 60% the amine functionalities is oxidized, predominantly converted to amides (N2). This decrease can again be explained by the formation of oxidized nitrogen functionalities in N2 (amides) and N3, which are progressively formed by oxidation processes during and/or immediately after deposition.

Based on the measured oxygen content and the changes in the chemical environment of carbon and nitrogen atoms, it is suggested that APTMS films undergo oxidation during and/or immediately after the deposition process, which increases as a function of the number of print repeats. The observation that thicker films are more prone to these oxidation processes with respect to the 1 PR APTMS film, may be attributed to the fact that the film deposited at 1 PR contains fluorine: the hydrophobic character of \( CF_x \) groups in the film may impede locally the oxidation process.

The siloxane structure, both for a single print repeat and for multiple print repeats, as well as the oxidation of the amine functionalities for an increasing number of print repeats, are confirmed by the infrared absorption spectroscopy (ATR-FTIR, Sect.3.3.2). APTMS films are deposited with 1, 3 and 5 PR and their infrared absorption is subsequently measured. The absorbance spectra of the APTMS samples are shown in Figure 4.9. The measurements are related to the pristine FEP reference, according to Eq.3.7. An increased (positive) absorption is related to the deposited film, while a decreased (negative) absorption is related to the substrate.

In general, the infrared absorption spectra show a few interesting regions. In the region of 980 – 1160 cm\(^{-1}\), which is also shown in the inset, two peaks are found, which are both related to siloxane bonds, originating from \( Si - O - Si \) and/or \( Si - O - C \) structures in the film. Changes in the relative contribution of these peaks may be the result of changes in the ratio between \( Si - O - Si \) and \( Si - O - C \) bonds, changes in the chemical structure of the siloxane network and/or stress in the siloxane bonds.[45, 57] The siloxane absorbance region may also be influenced by the absorbance of the FEP substrate, which is partially overlapping, since it is spreads from 1130 to 1340 cm\(^{-1}\). This region decreases in absorbance for an increasing number of print repeats due to an increasing absorbance of the APTMS film on top of the FEP substrate.

Furthermore, a large absorbance region is found around 2800 – 3600 cm\(^{-1}\). This region is related to
multiple functional groups, which are difficult to separate. The peaks around 2890 cm\(^{-1}\) and 2935 cm\(^{-1}\) can be identified and assigned to the \(CH_2\) groups in the aminopropyl chains in the deposited film, but differentiation between hydroxyl and/or amine functionalities present in the 3000 – 3600 cm\(^{-1}\) region was not possible.

The last region, which is discussed, confirms the relative decrease of amine functionalities for an increase in the number of print repeats and is found from 1480 – 1740 cm\(^{-1}\). This region is also shown in the second inset in Figure 4.9. The first peak in this region, at 1575 cm\(^{-1}\), is assigned to \(NH_2\) scissoring vibrations. A second peak is found at 1655 cm\(^{-1}\), indicating the presence amide functionalities, since it is assigned to \(C=O\) bonds.[31, 32, 72] Amide functionalities are therefore represented in both peaks, while primary amines are only observed in the peak at 1575 cm\(^{-1}\). Based on the faster increase of the \(C=O\) peak, compared to the \(NH_2\) peak it can be concluded that freshly deposited amine functionalities are converted to amides due to oxidation processes during and/or immediately after deposition, which is consistent with earlier conclusions from the XPS measurements.

**Wettability**

The influence of the oxidation processes for an increased number of print repeats on the wettability and the surface energy of the deposited APTMS films is also investigated. The analysis is performed by the measurement of the contact angles of deionized water and diiodomethane and the subsequent determination of the surface energy, as discussed in Sect.3.3.4. The polar- and dispersive components of the surface energy are also quantified. The measurements are performed for several print repeats. Next to that, the APTMS films are deposited both on glass and FEP, in order to further analyze the influence of the substrate in the deposition process. These results are reported in Figure 4.10.

In Figure 4.10a the contact angles for water and diiodomethane are shown as a function of the number of print repeats. The contact angles on both FEP and glass are included in the same graph. The FEP polymer substrate has a water contact angle of 112 ± 1\(^{\circ}\), which reflects its hydrophobic nature.[14, 62] For 1 PR, however, the water contact angle drops to 10 ± 5\(^{\circ}\). When increasing the number of print repeats both the water and diiodomethane contact angles gradually increase from 10\(^{\circ}\) to 44\(^{\circ}\) and from 35\(^{\circ}\) to 44\(^{\circ}\), respectively. In Figure 4.10b the calculated surface energies (total, polar and dispersive)
Figure 4.10: Contact angle (a) and surface energy (b) of the plasma polymerized APTMS films, deposited on FEP and glass substrates using standard deposition conditions. The contact angles are measured for several print repeats using water and diiodomethane. After 10 PR the APTMS films exhibit the same surface properties when deposited on FEP or glass.

are shown. After 1 PR on the hydrophobic FEP substrate both the polar and dispersive component of the surface energy have increased significantly. With an increasing number of print repeats the total-, polar- and dispersive surface energies show a gradual decrease.

The behavior of the water contact angle on FEP is consistent with the wet-chemical growth of APTMS.[80] For thin films the surface is completely hydrophilic, while the film structure purely consists of siloxane chains, together with the aminopropyl chains. If the growth process continues for longer times, the surface concentration of amines decreases and the water contact angle increases to up to ∼45°.[50, 80]

The contact angles of APTMS on a glass substrate differ significantly from the results of the films deposited on FEP. The hydrophilic glass substrate has a low water contact angle of 33 ± 3°, which increases to a maximum of 57 ± 3° for 2 PR. After this maximum, the water contact angle decreases a bit, towards the same saturation value as for the films deposited on FEP (44 ± 3°). This saturation is reached after 10 PR. At the same time, the diiodomethane contact angle decreases from 50° for the glass substrate to 40°, as a saturated APTMS contact angle for 10 – 20 PR. The saturation of the diiodomethane contact angle is also reached after 10 PR. For less than 10 PR, both the contact angles of diiodomethane and water are larger on glass than on FEP.

The differences in diiodomethane and water contact angle between glass and FEP substrates are reflected in their surface energy. While the dispersive component is approximately the same for both measurement series, differences are observed in the polar component of the surface energy. Consequently, the reduced polar surface energy on glass substrates results in a reduced total surface energy up to 10 PR, indicating either the reduction of the concentration of polar functional groups at the surface and/or reduction the polarity of the surface functionalities. After 10 PR the contact angle and surface energy become independent of the substrate.

The described differences in contact angle and surface energy up to 10 PR reflect a different influence of the substrate on the deposition process. For < 10 PR fluorine is incorporated in the deposited APTMS film, impeding the oxidation process of the film during and/or immediately after deposition. The retention of the amine functionalities results in a lower contact angle, while the small contamination of fluorine does not influence the contact angle. Hydroxyl functionalities on the glass surface, on the
Is APTMS deposition performed in a flow rate or a discharge power controlled regime?

The different behavior of the water and diiodomethane contact angles of APTMS films deposited on glass substrates, compared to FEP, allows the derivation of the plasma polymerization growth regime, as discussed in Sect. 2.2. A decrease of the Yasuda factor \( Y = \frac{W}{F \cdot M} \) is accomplished by the increase of the monomer concentration in the precursor flow (also see Figure 2.8), which is achieved by a 0.30 slm nitrogen flow, which is completely led through the APTMS bubbler system, instead of leading 0.10 slm through the bubbler and mixing it with 0.20 slm pure nitrogen. The results of the increased precursor concentration on the contact angles of water and diiodomethane and on the surface energy of APTMS films are shown in Figure 4.11.

![Figure 4.11: Contact angle (a) and surface energy (b) of the plasma polymerized APTMS films as a function of the number of print repeats for an increased APTMS precursor concentration. The measurements are again performed on FEP and glass.](image)

In Figure 4.11a, the contact angles of the APTMS films, deposited with an increased APTMS precursor concentration, show a similar behavior as in the standard conditions. The water contact angle after saturation of 44º, however, is already reached after 1 – 5 PR. Next to that, the contact angles on glass and FEP substrates become similar after 1 – 2 PR, after which the deposited films are not influenced by the used substrate anymore. Apparently, due to the larger APTMS concentration in the precursor flow, a thicker film is deposited, which has similar properties as the films deposited with 10 – 20 PR at standard conditions. The increase in film thickness was also optically observed.

Based on the shift in saturation for an increasing APTMS concentration, the deposition rate is increased and the deposition setup is in a discharge power controlled regime. The discharge power controlled deposition regime is the result of a relatively high Yasuda factor due to the high \( \mu \)PlasmaPrint plasma power (filamentary plasma regime) and the relatively low precursor flow and/or precursor molecular weight.

The growth regime is in contrast to conclusions by Massines et al, who deposited HMDSO (hexamethyl disiloxane) in their atmospheric pressure DBD setup.[45] They derived that their growth mechanism mainly depended on precursor activation, since their deposition rate only slightly increased with an increase of the precursor concentration in the discharge, while a stronger increase was observed by the increase of the dissipated power. The power, however, was varied from 0.5 – 2.0 W/cm², which is approximately two orders of magnitude smaller than the estimated power in the \( \mu \)PlasmaPrint setup (Table 2.2). Due to the difference in dissipated power between the \( \mu \)PlasmaPrint setup and the setup of Massines et al., it appears reasonable to conclude that the deposition of APTMS is performed in a flow rate limited regime.
other hand, are suggested to promote the oxidation of amine functionalities, which results in a higher water contact angle than the saturation contact angle of 44°.

The derived surface energies in Figure 4.10b confirm the origin of the differences in the contact angle measurement between glass and FEP. The dispersive component of the surface energy is approximately the same for both glass and FEP substrates, but there is a clear difference in the polar surface energy. The APTMS films which are deposited on FEP have a higher polar surface energy up to 10 PR than the deposited films deposited on glass, which is caused by a lower polarity of the surface functionalities. When the deposition is performed on glass, oxidation processes are facilitated since there is no hydrophobic component impeding the oxidation process. Therefore, the oxidation of the APTMS films on glass, subsequently leads to oxidation of polar functionalities, i.e. amines, decreasing their polarity and leading to a decrease in the polar component of the surface energy.

Post deposition oxidation

The incorporation of oxygen in the APTMS films during the deposition process, further proceeds after deposition upon exposure of the modified layers to air. Water contact angle measurements are a valid approach to monitor this process. The measurement of the water contact angle also reflects processes such as oxidation by secondary reaction mechanisms and hydrophobic recovery (e.g. for surface modification of polymers or very thin plasma polymer films.).[13, 26, 73]

An increase of the water contact angle is observed as a function of ageing time for the deposited APTMS films, as shown in Figure 4.12. Figure 4.12a shows the contact angle changes of APTMS films for several print repeats, for ageing times of 20 and 42 hours. Figure 4.12b focuses on samples which are deposited with 2 and 20 PR. The ageing behavior of these samples was followed for a longer period (20 minutes to 5 weeks).

![Figure 4.12: Water contact angle ageing behavior of the plasma polymerized APTMS films as a function of time after deposition. The samples are measured immediately after deposition, after 20 hours and after 42 hours (a). The samples with 2 and 20 PR are measured for a larger ageing periods (b, 20 min. – 5 weeks).](image)

The results of the ageing analysis of the surface show a significant increase in water contact angle of the deposited APTMS films. Especially for the samples with 1 – 3 PR the changes are relatively large. For all samples, the water contact angle increases to approximately 60°. The samples with 1 – 3 PR reach even slightly higher contact angle values. Furthermore, contact angle changes for these samples
occur fast. The samples with 2 and 20 PR reach a contact angle of about 60° already within a few hours after deposition. After that the water contact angle keeps increasing, but slowly.

![Diagram of different ageing mechanisms](image)

**Figure 4.13:** Schematic representation of the different ageing mechanisms, as suggested from literature.

The functional groups can re-orientate themselves into the substrate or deposited film (a), oxygen can bond to the surface at dangling bonds (b) and/or functional groups can undergo secondary oxidation processes (c).

The change of the contact angle of the APTMS surface, usually referred to as ageing, can occur due to surface re-organization, dangling bond oxidation or secondary oxidation mechanisms. [13, 29, 73] These three most common ageing mechanisms are illustrated in Figure 4.13. Depending on the method of functionalization (film deposition or activation only), hydrophobic recovery and secondary oxidation mechanisms usually are relatively slow processes (several days - years). [29] The oxidation of dangling bonds, on the other hand, is very fast. [26, 93, 94] The fast change of contact angle is, therefore, assigned to oxidation of the film at dangling bonds. Static water contact angle measurements are more sensitive to hydrophobic functionalities, which explains the increase in water contact angle. [82] Oxidation of amine functionalities to amides reduces the polar surface energy and thus increases the water contact angle of the aged films.

Furthermore, APTMS films deposited with more PR (e.g. 10 or 20 PR), show less ageing than the films deposited with 1 – 3 PR. The difference in ageing behavior can be explained by the oxidation processes during film deposition. Since the films with more PR are already oxidized during the deposition process, e.g. by the oxidation of amine to amide functionalities, they are less prone to oxidation after deposition. In the water contact angle measurements, however, another ageing component appears present. The origin of this ageing phenomenon is less pronounced. The fact that the sample which was deposited with 2 PR ages faster in this region indicates that thinner films are more prone to hydrophobic recovery. [13, 26] The thin films 'feel' the substrate more, as well as they are less crosslinked. Crosslinking results in larger polymer chains which are less able to move or re-orientate themselves. [13, 26] Therefore, the second ageing mechanism is assigned to re-orientation of functional groups.

The oxidation of the deposited APTMS films is confirmed by the measurement of the oxygen content by XPS. After storage of the samples for four weeks under cleanroom conditions, the same samples were measured again. In Figure 4.14a, the increase of the oxygen content is shown. Except the measurement point at 5 PR, all measurements show a significant increase in the amount of oxygen present in the film.

Next to the oxygen content, in Figure 4.14b and Figure 4.14c, also the influence of the oxidation on the amine and amide content is shown. Due to the oxidation of the deposited film, the amount of amines in the film is reduced. Since the concentration of amides is increased, it can be concluded that oxidation predominantly takes at the amine functionalities. The oxidation of amines to amide is a well-known phenomenon in the degradation of amine functionalities. [13, 29, 73]
Figure 4.14: Oxygen and nitrogen content in the deposited film, measured immediately after deposition and after 4 weeks of ageing. The oxygen content (a) is increased, while the nitrogen content (b, c) is decreased. The individual nitrogen peaks are solved from high-resolution nitrogen spectra. Due to the dot-wise plasma printing technique, fluctuations in the measurements are possible, depending on the measurement position on the sample.

The ageing of the ∼30 nm APTMS films is also observed by Borris et al. They used chemical derivatization XPS with TFBA (4-trifluoromethyl-benzaldehyde) for the determination of the concentration of amine functionalities at the surface and found a reduction in amine concentration from 5.9% to 1.9% \( ([NH_2]/[C]) \) after four weeks of ageing in atmospheric conditions, which was accompanied by an increase of the oxygen content. The ageing of amines is comparable or even stronger than in this research project. They also showed post deposition oxidation via dangling bonds. By admixture of the addition of ammonia to the \( N_2/\text{APTMS} \) plasma, they suggested that dangling bonds were sealed and showed an improved stability of the amine functionalities after deposition, i.e. the amine concentration even increased from 3.6% to 4.0% \( ([NH_2]/[C]) \) within four weeks of ageing.\[32\]

4.3 Immobilization reactions after \( \mu\text{PlasmaPrinting} \)

Amine functionalities are incorporated in the APTMS films as discussed in the previous sections. These amines influence the wettability of the surface, but they can also be used for covalent bonding with other molecules. In this section fluorescamine is anchored to amine functionalities and the fluorescent signal is analyzed, according to Sect.3.3.5. Also an electroless plating process is performed to demonstrate the improved polymer-metal adhesion. By the coupling with amine functionalities, the presence of amine functionalities and their ability to immobilize molecules can be further derived.

**Fluorescamine coupling**

FEP samples are functionalized by the deposition of plasma polymerized APTMS films. The ability of the deposited amine functionalities to bind fluorescamine is investigated as a function of the number of print repeats. The measured fluorescence (Sect.3.3.5 and Appendix A) is strongly influenced by fluctuations in the amine content in the APTMS films, as shown in Figure 4.15. The fluorescent intensity increases linearly for an increasing number of print repeats to reach a maximum after 3–5 PR. After this maximum, the fluorescent intensity slightly decreases and reaches a plateau.

The behavior of the fluorescent intensity as a function of the number of print repeats is described by two different phenomena. Since fluorescamine specifically binds to amine functionalities and only emits fluorescence if it is bonded to an amine, the linear increase of the fluorescent signal is attributed to the number of amine functionalities summing up, within an increasing film thickness up to 3–5 PR. By the increase of the number of print repeats, the deposited film thickness increases further, while
Figure 4.15: Qualitative analysis of the fluorescent intensity of fluorescamine functionalized APTMS films as a function of the number of print repeats. The relative content of amines (at.%) in the films, as determined by XPS, is also shown.

The relative content of amine functionalities remains approximately constant, according to the XPS analysis (also shown in Figure 4.15). Based on the estimated film thickness per print repeat ($\sim 8$ nm, Sect. 4.1), it can be concluded that the fluorescamine molecules diffuse within $25$ nm into the film.

For more than $3 - 5$ PR the film depth which is available for fluorescent binding remains constant. The relative amount of amine functionalities in the top $10$ nm of the deposited APTMS films, however, decreases for an increasing amount of print repeats, as shown in Sect. 4.2. This decrease in amine functionalities explains the decrease in fluorescent intensity from $5$ to $10$ PR. For more than $10$ PR, on the other hand, the top $25$ nm of the APTMS is stable not only for the diffusion of the fluorescamine molecule into the film, but also for the film content and the concentration of amine functionalities in the film. Since for $10$ PR and $20$ PR the fluorescamine binding process is the same, a plateau is reached, showing a constant fluorescence for more than $10$ PR.

The anchoring of fluorescamine allows for an estimation of the amine surface density. The quantitative analysis of the amine surface concentration, however, is not straightforward. The key problem for quantification is the lack of a reference surface with known concentration of amine functionalities, which allows calibration of the exploited quantification method.

The linear relation between the amine bonded fluorescamine concentration and its fluorescent intensity, which is found in Figure 3.10, however, does allow the quantification of the amine surface concentration. By the extrapolation of the fluorescent intensity after background subtraction, it is found that a sample with $5$ PR contains $0.3 \pm 0.2$ $[\text{NH}_2]/\text{nm}^2$. The extrapolation is shown in Figure 4.16.

The measurement error for the quantification is relatively large, because of the measurement errors in the individual calibration points, as well as the large extrapolation. The large extrapolation is used, however, because fluorescent quenching is negligible for calibration samples with a relatively low amine concentration, while for larger concentrations the fluorescent intensity is significantly reduced.[87] The limited range over which the relation between the amine concentration and fluorescent intensity is linear, is also the reason that measurements were only performed at two different concentrations (without amines and $0.01$ $[\text{NH}_2]/\text{nm}^2$).

For the plasma polymerized APTMS sample, which was deposited with $5$ PR, on the other hand, flu-
Figure 4.16: Quantification of the amine surface concentration of the films deposited with 5 PR. The quantification is performed based on the extrapolation of the calibration curve for very low amine concentration. The low concentration part of the curve was used to minimize fluorescent quenching effects in the calibration samples.

Fluorescent quenching is not included in the determination of the concentration of amine functionalities. If fluorescamine is bonded to the amine functionalities on a surface instead of dissolved in a solution, they become immobile. As a result, quenching of the fluorescent signal by collisions or energy transfer is strongly reduced. Fluorescence measurements on immobilized functionalities are suggested to be possible for surface concentrations up to $\sim 6 \text{[NH}_2\text{]/nm}^2$[84], while fluorescamine measurements in solutions may already be influenced by quenching, starting from $0.01 \text{[NH}_2\text{]/nm}^2$. The measurement conditions and amine concentrations in this experiment are, therefore, optimized so that quenching of the fluorescent signal in the deposited films is of minor influence on the measured amine concentration.

The measured amine concentration is slightly lower than results found by other methods in literature. Most results found in literature show amine concentration in the order of $1 \text{[NH}_2\text{]/nm}^2$.[3, 8, 57] Depending on the size of the molecule which may be bonded to the aminated surface, however, the measured surface concentration is usually sufficiently high. Relatively small proteins have a diameter of $3 - 4$ nm, which results in a maximum surface density which is still smaller than the derived amine surface density.[13] On the other hand, one should be aware that amine functionalities may not be available for molecule immobilization if they are located 25 nm inside the deposited film. It may therefore be possible that not all amines are available for molecule immobilization and that the effective amine surface concentration may be much lower. Specific experiments on the immobilization of (bio-) molecules are therefore suggested to determine the efficiency of the deposited film in terms of molecule immobilization via surface functionalization.

**Electroless metallization**

Next to fluorescamine immobilization, amine functionalities can also be used for the improvement of polymer-metal adhesion of (hydrophobic) polymer surface. If the (amine) functionalization deposition is patterned, i.e. by the µPlasmaPrint system, it is possible to perform a low-cost electroless plating
process by the adsorption of palladium and the subsequent growth of a nickel or copper conducting grid. Such conducting grids can be used in flexible electronics.[7, 8, 10, 11, 12]

The adsorption of palladium can be performed on various differently terminated surfaces, but only if nitrogen containing functionalities are grafted, the adsorption can be performed in a single-step process.[10] Amine functionalities are preferred, here, because of their improved reactivity.[8] If 0.5 s/l \( \text{PdCl}_2 \) and 0.3 s/l \( \text{NaCl} \) are dissolved in deionized water, the solution allows palladium adsorption on amine functionalities if the APTMS samples are immersed in this solution for 4 minutes:

\[
-NH_2 + PdCl_2 \rightarrow H_2N^\delta^- + Pd^\delta^+Cl_2
\] (4.1)

The palladium grafted samples are subsequently immersed in a nickel plating bath. This bath contains 36 s/l \( \text{NiSO}_4 \cdot 6\text{H}_2\text{O} \) and 10 s/l \( \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} \) and is heated up to 80°C during the plating reaction of 12 minutes. The sodium hypophosphate in the solution allows removal of the \( \text{Cl} \) atoms, as well as the reduction of the \( \text{Pd}^{2+} \) ions to \( \text{Pd} \)[8]:

\[
\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2e^-
\] (4.2)

\[
Pd^{2+} + 2e^- \rightarrow \text{Pd}
\] (4.3)

On the \( Pd \) initiator atoms, \( Ni \) is able to form a conducting film where APTMS is deposited. The result of the electroless \( Ni \) plating is shown in Figure 4.17. The \( \mu \)PlasmaPrint head is kept at a fixed position, while a single needle electrode is actuated for 20 – 2000 pulses i.e. periods in which the needle electrode is actuated down, and up again (100 – 500\( \mu \)s each, see Figure 2.3). The APTMS films, deposited on FEP, are subsequently immersed in the above-described palladium and nickel baths.

![Image of nickel pads created by electroless plating](image)

**Figure 4.17:** Nickel pads, created by electroless plating according to the above described method. The sample is exposed to 20 – 2000 APTMS plasma pulses, i.e. periods in which the needle electrode is actuated down, and up again (100 – 500\( \mu \)s each, see Figure 2.3). The \( Ni \) spot size increases for an increasing number of plasma pulses from \( \sim 2 – 4 \) mm.

As can be observed in Figure 4.17, the spot size of the nickel pads is relatively large (\( \sim 2 – 4 \) mm). By the reduction of the number of plasma pulses this spot size can be reduced, e.g. down to \( \sim 200 \mu m \), which was reached with the \( \mu \)PlasmaPrint system for the deposition of HMDSO. If this resolution could be reached for the metallization process as well, low-cost, large-area electronics could be fabricated with a better resolution than found in literature (\( \sim 500 \mu m \)).[7]

Another method to reduce the resolution may be by a plasma post-treatment.[50] If an APTMS deposited pattern can be post-treated with a higher resolution air plasma, it appears possible to convert amine functionalities to less reactive amide functionalities, a high resolution pattern with amine functionalities may remain, e.g. for this electroless plating process. The effect of such a post-treatment, however, should be researched to a much larger extend, e.g. to confirm the modification of amines to amides, as well as the influence of the plasma gas mixture on the resolution of the plasma treatment.
Chapter 5

Conclusions

In this project, a FEP polymer surface is amine-functionalized by plasma polymerization of APTMS. The deposition process was performed using a µPlasmaPrint setup, as developed by InnoPhysics, which utilizes a (multi) pin-to-plate dielectric barrier discharge. Nitrogen was used as a carrier gas for the plasma deposition of APTMS in a flow rate controlled polymerization regime. Under the precursor flow and plasma conditions used in this research project, a growth rate of 8 nm was obtained per µPlasmaPrint repeat (PR). Answers to the research questions are given in Sect.5.1. Suggestions for further research, e.g. for a better understanding of the polymerization mechanism or for the determination and the optimization of the amine surface concentration, are given in the outlook in Sect.5.2.

5.1 Conclusions

The deposition of the APTMS films on a FEP substrate by the µPlasmaPrint provided the following answers to the research questions:

1. What is the chemical structure of the deposited APTMS films?

The APTMS film stoichiometry and chemical structure were first analyzed for a single print repeat. Analysis of the APTMS films by XPS showed a film stoichiometry of $SiO_{2.2}C_{3.3}N_{1.1}F_{0.4}$. Furthermore, the binding energy of the silicon Si2p peak showed that the films predominantly consist of a siloxane structure. Peak deconvolution of the C1s and N1s peaks showed that the aminopropyl chain of the APTMS monomer remained intact. Also the amine functionalities were predominantly retained after 1 PR. It was, therefore, derived that the plasma polymerization process was governed by hydrolysis and condensation reactions, dissociating methyl- and methoxy groups from the APTMS monomer and that binding of the APTMS film to the FEP substrate occurs through $Si-O-C$ bonds. It was suggested that the measured oxygen content was higher than in the derived polymerization mechanism due to oxidation processes during and/or immediately after deposition, incomplete hydrolysis and condensation reactions and/or relatively short polymer chains.

2. What is the influence of the number of µPlasmaPrint repeats (PR) on the structure of the deposited film?

When the deposited APTMS films were analyzed for 1 – 20 PR it was found that fluorine is embedded in these films for 1 – 5 PR. The fluorine stems from the FEP substrate in its early stages of exposure to the plasma; the ablated fluorine subsequently participates in the plasma deposition process. The
relative presence of fluorine in the film decreases as a function of the number of print repeats, while the oxygen content increases by approximately the same percentage. Since the APTMS films become more oxidized for more print repeats, during and/or immediately after deposition, as oxygen is progressively replacing fluorine. It is suggested that the presence of fluorine prevents the film from oxidation in the early stages of film growth. The oxidation processes are reflected in the amine concentration of the films. It was found that amine functionalities are progressively converted to amide functionalities by the bonding of oxygen at the carbon atom adjacent to the amine functionality. For 1 PR, the APTMS films yielded \( \sim 9 \) at.
\% of amine functional groups (according to XPS peak deconvolution), while for 20 PR the amine content was decreased to \( \sim 5 \) at.
\%. The other carbon atoms also become more oxidized as a function of the number of print repeats, according to the decrease in \( C_1/C_2+C_3 \) peak area ratio.

The decrease in amine functionalities at the surface as a function of print repeats is reflected in a change in the wettability of the films. For 1 PR the water contact angle is \( 10 \pm 5^\circ \), due to the high polarity of the amine functionalities, while for \( > 5 \) PR the water contact angle increased to \( 45 \pm 3^\circ \). The increase of the water contact angle is attributed to the conversion of amine functionalities to amide functionalities, as the increase in water contact angle was accompanied by a decrease in the polar component of the surface energy.

Degradation of the amine functionalities after deposition was also analyzed for a longer period of time. XPS measurements showed an increased oxygen content in the film, especially for the samples with 1 – 5 PR. Samples which were deposited with more PR already contained an increased concentration of oxygen, incorporated during and/or directly after the deposition. Oxidation of amine to amide functionalities was derived from XPS peak deconvolution and from a rapid change in water contact angle. All samples reach a water contact angles of \( \sim 60^\circ \) within several hours after deposition. The contact angle of the samples deposited with 1 – 3 PR aged faster and more than the samples which are deposited with 5 – 20 PR. This difference is assigned to structural re-organization of polar functional groups, like amines.

3. Are the deposited amine functionalities able to participate in further immobilization reactions?

The anchoring of fluorescamine to the aminated surface and the subsequent detection of the fluorescent signal allows confirmation of the presence of amine functionalities at the polymer surface, as well as that it shows the ability of the amine functionalities to participate in immobilization reactions. The variation of fluorescent intensity as a function of the number of print repeats showed that the fluorescamine diffused approximately 25 nm into the APTMS film. The fluorescent intensity is consistent with the derived amine concentration of the XPS nitrogen N1s spectrum, indicating that all amines are available as anchoring sites. By the use of thin liquid reference films, in which fluorescamine was bonded to APTMS, an attempt has been made to quantify the amine surface concentration. It was derived that the amine surface concentration for APTMS films deposited with 5 PR, is \( 0.3 \pm 0.2 \,[\text{NH}_2]/\text{nm}^2 \).

On the other hand, the ability of the amine functionalities to participate in further immobilization reactions is also shown by an electroless plating process, in which \( \text{PdCl}_2 \) was adsorbed at the amine, subsequently allowing nickel growth. Due to the presence of amine functionalities, the palladium adsorption process could be performed in a single-step process. Based on this plating process a minimum feature size was derived of 2 nm diameter. For this metallization process, as well as for the APTMS deposition itself, improvements in the resolution, however, appear possible after comparison with earlier investigations.

The different methods which are used, are consistent with each other, all showing the significant presence of amine functionalities in the deposited APTMS films. The amine concentration decreases as a function of the number of print repeats and as a function of ageing time, both due to oxidation of amines to amides. Contact angle measurements, the performance of an electroless plating process
and the immobilization of fluorescamine show that the deposition of amine containing APTMS films by the µPlasmaPrint setup is a good method for the local/patterned improvement of the wettability of (fluorocarbon) polymer substrates, its adhesion properties or the immobilization of (bio-) molecules.

5.2 Outlook

During this project, new (interesting) research questions showed up. Hypotheses were derived, of which some of them were only partially validated by measurement results. More research or different analysis techniques are required for answering the remaining research questions, as well as to confirm hypotheses derived in this M.Sc. thesis work. In this section, the "open-ends" of this research project will be discussed and suggestions will be done for answering the questions left.

The analysis of the chemical structure of the deposited APTMS film has led to a sufficient understanding of the polymerized structure. The last binding site of the silicon atom, however, is still under discussion. The binding of plasma radicals was suggested, together with the retention of silanol and silicon-methoxy groups due to incomplete hydrolysis and condensation reactions. The latter also explaining the increased oxygen and (to a smaller extent) oxygen content. Identification of this bond is the last step in the complete derivation of the chemical structure of the deposited APTMS films. The deposition of a thinner film, with a smaller variety of chemical structures and less oxidation processes occurring during and/or immediately after deposition, could provide more information on the early stages of film growth. The deposition of thinner films may be accomplished by the admixture of a smaller concentration of APTMS to the plasma gas. Also the deposition in a less powerful plasma regime (e.g. in a glow discharge) may result in a limited variety of chemical structures and oxidation processes. Performing deposition and film analysis in the sample (closed) reaction chamber may exclude oxidation effects completely; also allowing the determination of the influence of the admixture of oxygen, as is the case in the µPlasmaPrint setup, may be of interest for further investigation.

A thinner film may also help to further investigate the influence of the substrate, e.g. where the ablated fluorine exactly is embedded in the deposited film. Deposition on a different substrate and the subsequent analysis with XPS may also be of interest. Of course it can be confirmed that the incorporation of fluorine resulted in the complete wetting, because fluorine impedes on the oxidation processes in the early stages of film growth, but also the suggestion that a hydroxyl terminated surface increased oxidation of amines to amides could be determined, when the deposition was performed on a glass substrate.

On such a substrate, the stability of the incorporated amines may also be investigated. Based on water contact angle measurements and XPS it is suggested that thin APTMS show faster and more ageing than thicker films. Is the ageing also influenced by the chosen substrate? If the substrate is less hydrophobic, do the water contact angles for 'thin' and 'thick' films reach the same contact angle because of the absence of hydrophobic recovery effects? The influence of oxidation at dangling bonds present in the APTMS film during and after deposition could be investigated by the admixture of NH₃ to the plasma, since it was suggested in literature that NH₃ radicals may bond to surface radicals, impeding on the oxidation both during and after the deposition of the APTMS film.

Post-treatment of the deposited APTMS film with NH₃ plasma may also help to increase the amine concentration. A post-treatment, though, may also increase oxidation effects, reducing the amine concentration. Post-treatment of the APTMS with air plasma was, therefore, suggested to improve the resolution in the electroless plating process and maybe in other processes. Changes occurring at the surface of the film as a result of plasma post-treatment, however, should be investigated to a much larger extend, e.g. by XPS analysis.

A last issue for the use of amine functionalities in the different areas of application, is the exact determination of the amine surface concentration. In this report an attempt has been made for this quantification process, however, quenching effects, the diffusion of the marker molecule into the film and
the absence of a well-defined reference surface resulted in large error margins and left discussion on the applicability of the deposited APTMS film for further immobilization reactions. The immobilization of fluorescamine and the electroless plating of nickel via the site-specific adsorption of palladium, however, are a good start for future investigations of aminated surfaces.
Acknowledgement

This M.Sc. Thesis work describes the results of the graduation project performed to achieve a title in Master of Science at Eindhoven University of Technology. This graduation project is performed at InnoPhysics B.V. Therefore, I would like to thank InnoPhysics for the opportunity they gave me in performing this project at their company.

Next to learning the research and physics competences, I have established that working at a company like InnoPhysics is an experience which will help me in my further career. Great thanks to the people working at InnoPhysics for giving me their trust. I would also like to thank them for the nice working environment and the support.

Also thanks to Alquin Stevens and Peter Verhoeven for their scientific and technical support. Their feedback and their discussions were very helpful. The same holds for Adriana Creatore from the department of Applied Physics of Eindhoven University of Technology. Suggestions and discussions on the interpretation of the results, as well as on the writing of the report, were appreciated. At last thanks to Wytze Keuning for performing XPS and SE measurements and assistance with the processing of the data.
Appendix A

Calibration of fluorescent signal

As discussed in Sect.3.3.5, fluorescamine is selectively bonded to amine functionalities to derive the ability of the amine functionalities to participate in further immobilization reactions. Fluoresentcamine becomes fluorescent when it is bonded to an amine. In this way a qualitative analysis of the molecule immobilization ability of the amine functionalities at the surface of the plasma polymer can be investigated as a function of the number of print repeats.

In order to increase the sensitivity of the fluorescence measurement, a Canon EOS 6D optical camera is used to capture digital photos of the fluorescent samples. Subsequently, an intensity histogram is determined from this picture. In Figure A.1 two examples of these intensity histograms are shown: a fluorescent sample of plasma polymerized APTMS, deposited with 5 PR and a darker sample of a bare FEP substrate. Based on the intensity distribution, the average intensity of the picture and its standard deviation can be derived.

Figure A.1: The binding of fluorescamine to amine functionalities results in an increased intensity of the captured figures, which leads to a shift in the intensity distribution. The differences in intensity distribution and their average intensity are shown together with the captured figures for a cleaned FEP sample and a fluorescent sample of plasma polymerized APTMS, deposited with 5 PR.
The measured intensity also depends on the acquisition time of the camera. The dependence of the intensity, as measured by the camera, is shown in Figure A.2. It can be observed that the fluorescent intensity of a plasma polymerized APTMS sample, deposited with 3 PR, increases linearly with the acquisition time. If the shutter is opened for a longer time, more fluorescent light reaches the camera, so the measured intensity increases. It can be observed that this relation is linear for an acquisition time up to 6 s, but it deviates for longer times. At the same time, it is observed that the fluorescent intensity decreases significantly under UV irradiation (not shown). Therefore, the lower than linear intensity at pictures with an acquisition time larger than 6 s is related to a decrease in fluorescent intensity under UV irradiation. This form of fluorescent quenching occurs if a fluorescent molecule is changed to a non-fluorescent stable state, which prevents the molecule from excitation to the fluorescent state. Such transitions have a much smaller probability than the transition from the ground state to the fluorescent state or vice versa. Though, if a non-fluorescent state is stable, however, the quenching effect is accumulating, which decreases the fluorescent intensity significantly in time. This quenching effect is also called photobleaching.[86]

Next to photobleaching, an effect which may also play a role in the deviation from the linear relation between the acquisition time and the measured intensity, is the overexposure of the camera. It is determined, however, that the effects of overexposure of the camera are < 0.1 %.

![Figure A.2: The measured fluorescent intensity is dependent on the acquisition time of the camera. Up to 6 s, a linear relation is found between the acquisition time and the measured intensity.](image)

At last, it is shown that an intensity increase is caused by fluorescence in the region as expected. By the measurement of the optical emission spectrum, it is shown that 87 % of the increased fluorescence comes from the 437 – 487 nm region. As shown in Figure 3.12, this is the region where fluorescamine emission is expected. The analysis of this linear relation, based on the integration of the optical emission spectrum of the fluorescence, is shown in Figure A.3. APTMS samples with a different number of print repeats are used for calibration.
Figure A.3: The measured intensity of the samples, as captured by this camera, is linearly related to the fluorescent intensity as determined from the emission spectrum.
Appendix B

Extended results of the XPS measurements

In Chapter 4 several conclusions are drawn from the results of XPS measurements. These measurements were performed in two series with 1, 2, 3, 5, 10 and 20 print repeats. In the first measurement series, samples deposited with 1, 5 and 20 print repeats were measured, together with a pristine FEP substrate, at three different positions, while in the second measurement series most samples (including pristine FEP) were measured once; 1 PR and 2 PR were measured twice. For the determination of the film composition, all available results were averaged and a measurement error was determined. If figures of the deconvolution of the binding energy are shown only one typical example is shown. The data which is additionally provided with these figures, is based on the averaged data. All averaged data are shown in Table B.1.

Furthermore, typical data are shown for all print repeats and for peaks. This is done in Figure B.1.
Figure B.1: XPS spectra of the different elemental peaks, together with a survey spectrum.
Table B.1: Atomic composition of the deposited films as determined by XPS. The atomic concentrations and environmental information of the APTMS monomer are included for comparison.

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(eV) = electron volts; C1, C2, ..., C7 = carbon peaks; N1, N2, N3 = nitrogen peaks; F1, F2, ..., F5 = fluorine peaks.
Ageing experiments

The second series of measurements is stored at cleanroom conditions for four weeks after the measurement. After storage, the samples are measured again. The (averaged) film content is shown in Table B.2. The film composition of these films is compared to the measurement of the sample as deposited.

Figure B.2: XPS spectra of the different elemental peaks, together with a survey spectrum.
Table B.2: Atomic composition of 4-weeks aged APTMS films as determined by XPS. The atomic concentrations and environmental information of the APTMS monomer are included for comparison. The concentrations are compared to the measurements of the samples immediately after deposition.

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Appendix C

Results of the SE analysis

The thickness of the deposited films is determined using spectroscopic ellipsometry (SE), as discussed in Sect. 3.3.3 and Sect. 4.1. First the pristine FEP film is analyzed and the measured $\Psi$ and $\Delta$ are fitted using a B-Spline fit function. From the fit, the refractive $n$ and the absorption $k$ are derived as a function of the energy of the incident ray of light. These results are shown in Figure C.1. The refractive index of FEP is found to be $1.35 - 1.38$, which is consistent with the properties provided by the manufacturer.[70] The absorbance spectrum of FEP shows several fringes, which may be attributed to a thin film on top of the substrate (e.g. a planarization layer) or a separation inside the substrate, e.g. due to diffusion of one of the two components of the co-polymer towards or away from the surface. Next to that, the absorbance becomes negative, indicating that the film may be producing light at this wavelength. This negative absorbance is suggested to be a result of the fit of $n$ and $k$.

![Figure C.1: The refractive index, $n$, and the absorption coefficient, $k$, for the FEP substrate. The FEP substrate is used "as is".](image)

The properties of the substrate are subsequently used "as is" for the analysis of an APTMS film, which is deposited with 5 PR. The refractive index, the absorbance and also the thickness are again determined using a B-Spline fit function. The region up to 3 eV is fixed to be transparent in order to
be able to fit $n$, $k$ and $d_{APTMS}$ by the measurement of $\Psi$ and $\Delta$. In the fitting procedure the film composition is assumed to be stable as a function of the penetration depth of the incident ray of light. This is obviously not true (see Sect. 4.2 on the role of the substrate in the deposition process), but the derived variables will be a good indication. The $n$ and $k$ of the film are shown as a function of the energy of the incident ray of light in Figure C.2.

The thickness of the deposited APTMS film is also derived in the fit. The uniqueness of this fit is shown in Figure C.3. Increasing or decreasing the derived thickness of 40 nm would change the derived $n$ and $k$ and would lead to an increased "Mean Square Error".

Figure C.2: The refractive index, $n$, and the absorption coefficient, $k$, for the deposited APTMS film. The film is modeled to be transparent up to 3 eV.

Figure C.3: Uniqueness of the derived thickness, based on the mean square error of a fit, as a function of film thickness.
Bibliography


[74] Robin Roelofs. Optical analysis (se and fir-atr) of silicon oxide films on pen substrates by atmospheric pressure barrier discharge deposition. Report, Summer 2010.


