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Plasma-polymer interaction leading to interphase formation between poly(ethylene 2,6-naphthalate) and inorganic films

Lohmann, V.I.T.A.

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V.I.T.A. Lohmann

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Abstract

SiO$_2$-like moisture permeation barrier layers have been plasma-deposited on poly(ethylene 2,6-naphtalate) (PEN) substrates as a model system for the deposition of inorganic films on organic substrates. Two plasma deposition techniques are used: an Ar/O$_2$/HMDSO-fed Expanding Thermal Plasma (ETP), which is a remote, high density plasma, and a radio frequency (rf) O$_2$/HMDSO plasma, which is a direct, low density plasma. The plasma-polymer interaction and the interphase, defined as a region which differs from the bulk SiO$_2$ as well as from the polymer bulk, have been studied. The interphase affects the adhesion as well as the barrier performance of the film, both of which should be excellent for application in flexible electronics, such as flexible organic light emitting diodes (F-OLEDs) or flexible solar cells. The plasma-polymer interaction, the formation of the interphase and the growth of the SiO$_2$ layer are characterized chemically, mainly by means of XPS, as well as optically, by means of in situ spectroscopic ellipsometry, a sensitive and non-intrusive optical diagnostic tool.

The existence of a 10-15 nm-thick interphase is demonstrated by the presence of carbon and silicon-carbon bonds in thin ETP-deposited films, detected by means of XPS and confirmed by means of SE measurements. No interphase has been detected for films deposited in the rf parallel plate reactor, suggesting that the interphase is thinner than 5 nm. The difference in interphase formation can be explained by a lower (V)UV intensity and/or a lower ratio of the non-depositing radicals-to-depositing radicals flux in the rf plasma reactor, resulting in lower etch or modification rates and, thus, in a thinner interphase. XPS and contact angle measurements have demonstrated that the plasma modification consists of the insertion of O-containing functional groups at the PEN (sub-)surface.

The role of several types of radicals (O, H, OH) in the plasma-polymer interaction has been studied with SE in the ETP reactor using non-depositing plasmas. The modeled modification thickness is in the range of 2-2.5 nm after 10 s of plasma when the sample is shielded from the plasma beam (exposure to long-life radicals only), indicating significant modification. Without shielding, the modification rate is not negligible compared to the deposition rate, indicating a competition between modification/etching and deposition during the early stages of growth, which contributes to the formation of an interphase.
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1 Introduction

1.1 Technology assessment

Synthetic polymers are versatile materials and have, therefore, more and more replaced glass, metals, ceramics and wool because of their benefits, such as being lightweight, rugged, flexible, impact resistant and easy to process, i.e. moldable and compatible with both roll-to-roll and batch processing. Since the seventies synthetic polymers have proven to be very useful in a variety of fields, the earlier applications being packaging and clothing (synthetic fibers). Nowadays, polymers are also used for glazing applications in the automotive and architectural industry. Presently, synthetic polymers draw much attention in the field of flexible electronics and photovoltaics.

The use of polymers as substrates for the production of amongst others electronic devices has two major drawbacks. First, the glass transition temperature $T_g$ of the polymer limits the maximum processing temperature during all steps in the production of the device. Depending on the specific polymer that is used, the processing temperature is limited to ~100 °C or less. Second, polymers are poor barriers for oxygen and water vapour. Typical transmission rates of polymers are $10^{-1}-10^3$ cm$^3$ m$^{-2}$ day$^{-1}$ atm$^{-1}$ for oxygen and $10^{-1}-10^3$ g m$^{-2}$ day$^{-1}$ for water vapour. As shown in Figure 1.1, these transmission rates are orders of magnitude too large for many applications. The choice of measuring the transmission rates of mainly $O_2$ and $H_2O_{\text{vap}}$ derives from the food packaging industry. Oxygen and water vapour from the ambient permeate the polymer package and oxidize the packed food or drinks, thus shortening the shelf life of the packed product.

![Figure 1.1](image)

As Figure 1.1 shows, Flexible Organic Light Emitting Diodes (F-OLEDs) present the highest demands regarding the oxygen and water vapour transmission rates (OTR and WVTR respectively). Flexible OLEDs can be applied in many fields, e.g. rollable displays, displays on clothing and diffuse lighting systems (see Figure 1.2), and allow the designer absolute freedom with respect to the shape of the display. Figure 1.3 shows a schematic picture of an OLED. The cathode consists of a low work function metal, such as Ca, Ba or Li, to obtain efficient electron injection from the cathode into the organic luminescent layer. However, the low work function makes it vulnerable to oxidation. The maximum allowed OTR and WVTR as displayed in Figure 1.1 are calculated from the amount of oxygen/water needed to oxidize the cathode layer (typically 5-10 nm thick), and the required lifetime of the device [1-3], ranging from 1-2 years for displays for mobile phones to 5 years for transportable televisions [4]. If no barrier film is applied to reduce the OTR and WVTR, oxygen and water vapour from the ambient permeate the polymer substrate, causing shrinkage of the pixels, growth of pinholes.
and oxidation of the cathode [5, 6], degrading the device within hours. The degradation of a flexible OLED without barrier film is illustrated in Figure 1.4.

Figure 1.2. Applications of F-OLEDs include rollable displays (left) and light-emitting cars (right).

![Diagram of an OLED structure]

Cathode (usually Ca, Ba or Li)
Luminescent organic layer (phosphorescent small molecules or polymers)
Hole transport layer
Anode (usually indium tin oxide)
Substrate

Light

Figure 1.3. Schematic representation of an OLED.

![Degradation of a Flexible Organic Light Emitting Diode (F-OLED)]

Figure 1.4. Degradation of a Flexible Organic Light Emitting Diode (F-OLED). Left: a display without barrier film before exposure to the ambient. Right: the same display after a couple of hours of exposure.

To extend the device's lifetime, a barrier is required to reduce the OTR and WVTR. In the food packaging industry, this permeability problem is solved by the application of a barrier layer, which is a thin inorganic film, usually of aluminum, aluminum oxide, silicon oxide or silicon nitride. However, this solution is insufficient for the protection of electronic devices, where transparent barriers with much smaller transmission rates are required. As a consequence of the presence of defects in the films [7, 8], state of the art transparent barrier films currently yield a WVTR of as much as 0.05 g m$^{-2}$ day$^{-1}$ [1], which is far above the estimated maximum allowable WVTR of $10^{-5}$-$10^{-6}$ g m$^{-2}$ day$^{-1}$ for F-OLEDs [1, 2]. The key to meeting this stringent demand is the application of a multistack: a stack of alternating organic and inorganic layers. Figure 1.5 shows the encapsulation of an OLED in a barrier multistack.
Figure 1.5. Encapsulation of an OLED display in a barrier multistack on a polymer substrate [1].

Barrier layers deposited by means of Plasma-Enhanced Chemical Vapour Deposition (PECVD) outperform barrier layers deposited by means of sputtering or Physical Vapour Deposition (PVD) [7, 9-12] in terms of barrier performance and adhesion, as will be shown later in Chapter 2. As an example, Figure 1.6 compares the performance of a PVD- and a PECVD-deposited SiO₂ barrier film under the influence of strain. The formation of a so-called interphase is held responsible for the differences in adhesion and presumably for the differences in barrier performance as well. The interphase is a region between the polymer substrate and the inorganic barrier film, with properties different from both the substrate and the bulk of the film [11]. Active species from the plasma (radicals, energetic ions, (V)UV photons), are responsible for the formation of an interphase. During deposition by means of sputtering or PVD, none of these species are generated and thus no interphase is formed. The present work investigates the formation of an interphase in a rf parallel plate reactor (a direct plasma) and in an Expanding Thermal Plasma reactor (a remote plasma), because knowledge about the formation of the interphase is necessary to gain control over the interphase, and thus over the adhesion and barrier properties.

Figure 1.6. The OTR of a plasma-deposited and an evaporated (PVD-deposited) SiO₂ barrier as a function of the applied strain [9].
1.2 Research motivation

The combination of low temperature processing and good quality barrier layers poses a challenge where much research is still needed. Barrier films can be deposited in several ways, e.g. sputtering, PVD or PECVD. Plasma deposition (PECVD) is the preferable deposition technique for two reasons. First, the barrier properties and the adhesion of PECVD-deposited barrier films are generally found to be superior to films produced by PVD or sputtering [7, 9-12], which may be attributed to the formation of an interphase. Second, plasma deposition offers the freedom of tuning many parameters, e.g. gas flows, power and pressure, and thus a large influence on the material properties. From the many different types of plasma (e.g. radiofrequency (rf) plasma, microwave (MW) discharge, inductively coupled plasma) the choice in this work has fallen on the Expanding Thermal Plasma (ETP), because this plasma configuration allows to focus the study on the chemical action of the radicals involved in the polymer modification during the deposition, i.e., without the interference of the physical contribution of ion bombardment. If desired, the contribution of ion bombardment may be studied using external substrate bias. Deposition and interphase formation in a radiofrequency plasma, a direct plasma, is studied as well in order to make a reference to interphase studies reported in literature, which generally concern direct plasmas (dual frequency MW/rf reactor [11]; active glow zone of a distributed electron cyclotron resonance (DECR) [13, 14]).

The plasma deposition of silicon dioxide-like barrier layers is chosen as a model system for the deposition of inorganic films on polymer substrates in general, because SiO₂ is a widely studied barrier material (e.g. [8, 13, 15-18]). An organosilicon compound, namely hexamethyldisiloxane (HMDSO), is chosen as the silicon-providing precursor because it enables the deposition of a whole multistack in a single process chamber: decreasing the oxygen flow is sufficient to change from the deposition of inorganic SiO₂ to the deposition of organosilicon (SiOxCyHz) material.

The present work specifically looks into the plasma-polymer interaction and the formation of an interphase between a poly(ethylene 2,6-naphthalate) (PEN) substrate and the silicon dioxide-like bulk, but is presumably representative for PECVD of any inorganic material on an organic substrate. The formation and the properties of the interphase may be important for the performance of the polymer/inorganic film composite. For example, the adhesion of barrier films for application in flexible electronics (F-OLEDs, flexible photovoltaics) has to be excellent to prevent delamination. Furthermore, the formation of an interphase affects the initial growth and thus, as most deposition techniques are conformal, the subsequent growth of the bulk. By influencing the bulk growth, the interphase also affects the bulk properties, amongst which the barrier performance. This study only considers single layer films, but is related to the multistack configuration in the sense that many inorganic/organic interphases exist in a multistack. Therefore, a small improvement in the barrier properties and adhesion of a single barrier film on polymer may result in a much better performance of barrier multistacks. The present work also studies the plasma-polymer interaction, which causes the formation of the interphase, with the focus on the role of radicals in the plasma-polymer interaction. The role of (V)UV photons and energetic ions is considered less extensively. Knowledge about the interphase formation can lead to control over the interphase formation, which can be used to tune the properties of the polymer/inorganic film composite to the demands of a specific application.

The plasma-polymer interaction, the formation of the interphase and the growth of the barrier layer are, amongst others, characterized by in situ spectroscopic ellipsometry. SE is a powerful tool, because it is a sensitive, non-intrusive technology that probes the full thickness of transparent samples and gives information about the optical properties of the sample. These optical properties are related to other properties like chemical composition and density. The benefit of using an in situ instead of an ex situ configuration is that ageing is prevented and that both before and after deposition exactly the same spot is measured. Inhomogeneities in the polymer substrate will influence all measurements in an identical way, and therefore not affect the modeling of the deposited layer. Altogether, SE, if combined with other diagnostics, is a very suitable and useful diagnostic for the study of interphase formation and thin film growth. In the present work, SE is complemented with the following chemical,
optical and morphological \textit{ex situ} diagnostics: X-ray Photoelectron Spectroscopy (XPS), contact angle measurements, infrared spectroscopy (FTIR) and Atomic Force Microscopy (AFM).

This report starts with a discussion about plasma-polymer interaction, interphase formation and the transmission of oxygen and water vapour through single layer barrier films, based on reports in literature. The transmission through multistacks is briefly addressed as well. Chapter 3 describes the used materials, plasma reactors and diagnostics. The experimental results are presented in Chapter 4-7. In Chapter 4, the bulk properties of silicon dioxide-like films deposited in the ETP reactor and in the rf parallel plate reactor are compared. Chapter 5 follows with the identification and characterization of the interphase in SiO$_2$-like films deposited in both reactors. The results of an \textit{in situ} SE study of the interphase formation and the plasma-polymer interaction in the ETP reactor are presented in Chapter 6. In Chapter 7, the influence of energetic ions on the SiO$_2$-like bulk and on the interphase is investigated. Finally, the conclusions and recommendations from this report will be presented in Chapter 8.
2 Literature review

The present work investigates the growth of a plasma-deposited inorganic film on a polymer substrate and the formation of an interphase between the polymer substrate and the inorganic layer. The interphase is important, because it influences the properties of the polymer/inorganic film composite, e.g., its presence affects the adhesion between a polymer substrate and an inorganic barrier film [10, 19, 20] and the barrier properties [10]. In the first section of this chapter, the interphase formation and the plasma-polymer interaction, which has a major influence on the interphase formation, are discussed. The section concludes with some examples that illustrate the importance of the interphase. In the second section, the gas/moisture permeation process through barrier layers is discussed, highlighting the importance of the first stages of film growth.

2.1 Interphase formation and plasma-polymer interaction

Various authors [11, 13, 14, 19] have reported on the detection of an interphase between a polymer substrate and a plasma-deposited inorganic film. Da Silva Sobrinho et al. [11] investigated the interphase between a poly(ethyleneterephthalate) (PET) substrate and deposited layers of SiO₂ and Si₃N₄, amongst others by Elastic Recoil Detection (ERD). The interphase width observed for SiO₂ films deposited by means of Physical Vapour Deposition (PVD) (e.g. electron beam-induced evaporation) was narrower than the one for films deposited by means of Plasma-Enhanced Chemical Vapour Deposition (PECVD) in a microwave/radiofrequency (MW/rt) dual frequency plasma. During the deposition, an rf substrate bias of -150 V was applied, causing bombardment by highly energetic ions. Figure 2.1 shows that the apparent interphase width is 120 nm for PECVD-deposited SiO₂, and only 60 nm for the PVD sample. These values, however, are affected by the limited spatial resolution of ERD, because, using XPS, it was found that the interphase is very small (<5 nm) in the case of PVD-deposited samples [14]. Therefore, the true interphase thickness of the PECVD sample is estimated at (120-60) nm = 60 nm. The formation of the interphase is explained with an ablation/re-deposition mechanism: energetic species from the plasma (energetic ions and (vacuum) UV photons) induce scission of chemical bonds in the polymer and etching by creating volatile organic fragments. These fragments mix with the deposition precursors (radicals) in the plasma phase, and thus participate in the initial stages of film growth. Because of the presence of organic fragments, the initial film composition is expected to be organosilicon-like; gradually, as the film thickness increases, the film composition will reflect the (inorganic) plasma chemistry. This ablation/re-deposition mechanism can account for an interphase region with a thickness up to several tens of nanometers and highlights the importance of plasma-polymer interaction; in the case of PVD, no energetic particles or photons are available to cause ablation of the polymer, and thus no interphase is formed. Radicals may play a - possibly synergistic - role in the formation of the volatile species, but their role remains unclear in this study, as both energetic ions, (V)UV photons and radicals are present in this plasma. In the ETP setup on the contrary, no energetic ions are generated due to the very low sheath voltage (see Section 3.1), and thus only (V)UV photons and radicals may participate in the plasma-polymer interaction and the formation of an interphase. By shielding the substrate from the expanding plasma beam, the influence of (V)UV radiation is eliminated, leaving long-life radicals as the only active species being able to interact with the polymer surface. As will be shown later in Section 6.2, no deposition occurs in this situation, and thus this situation is suitable for studying the interaction of the polymer surface with non-depositing radicals.
Dennler et al. [13, 14] have shown that an interphase can form under the action of radicals alone. Figure 2.2 shows that with Rutherford Backscattering Spectroscopy (RBS), an interphase of 16 nm thick was observed for SiO₂ deposited on polyimide (PI) by means of PECVD, using a Distributed Electron Cyclotron Resonance (DECR) reactor and HMDSO and oxygen as feed gases. The substrate was placed downstream (18 cm below the glow zone) and shielded from VUV irradiation with a silicon wafer. Furthermore, by placing the substrates in different zones and measuring the interphase thickness, it was shown that the interphase thickness depends on the relative importance of etching and deposition: if the substrate is placed in the active glow zone of the plasma, exposed to VUV photons, energetic electrons (3-6 eV), energetic ions (10-20 eV) and radicals (mainly atomic oxygen), an interphase of 11 nm thick has to be included in the RBS model (Figure 2.3). If the substrate is placed downstream but not shielded, the sample was exposed to long-life reactive precursors and VUV, but presumably not to ions. In this case, no or almost no interphase was detected within the resolution of RBS (5 nm). The interphase in the case of thermal evaporation (PVD) was found to be smaller than the resolution of the measurement (5 nm), confirming what was commented earlier on PVD processing. These observations can be explained with a competition between deposition and plasma-polymer interaction (etching). In the active zone, plenty of energetic species are available for etching or modification of the substrate. Re-deposition of etched products results in the incorporation of hydrocarbon species in the inorganic film, creating an interphase. In the downstream region, the deposition rate decreases from 0.075 to 0.047 nm/s, but due to a very low concentration of active species, the deposition is much faster than etching, resulting in a very thin interphase. If the substrate is shielded from VUV radiation, the deposition rate decreases another factor of 3, apparently sufficient to allow a significant contribution of the etching and re-deposition process. In this situation, the etching can be attributed solely to the action of radicals.
In the above-described studies, invasive diagnostics are used for the characterization of the interphase. Bergeron et al. [19], on the other hand, used ex situ spectroscopic Ellipsometry (SE), a non-destructive, optical diagnostic tool, to study the interphase. The SE model is shown in Figure 2.4. A MW/rf dual frequency plasma was used for the deposition of Si₃N₄ and SiO₂ films on polycarbonate (PC). Without pretreatment of the polycarbonate, the measurements are not sensitive enough to define an interphase with a different refractive index for SiO₂ films. For Si₃N₄ films, an interphase has to be included between the polymer and the inorganic film in order to obtain a good fit. This interphase is modeled as a transition region with a refractive index lower by 0.03–0.05 than the bulk. If the PC is pretreated in a He/N₂ plasma, the transition region is thinner. This is attributed to cross-linking and stabilization of the polymer surface during the plasma pretreatment, decreasing the tendency to liberate volatile species. This study shows that, despite the limited sensitivity, SE can be used to detect an interphase. However, an ex situ diagnostic was used, although it is expected that the formation of an interphase can be investigated better in situ so that the influences of ageing and of measuring on different spots are avoided. Therefore, in the present work, SE is used in situ in order to obtain information about the film growth, interphase formation and plasma-polymer interaction in a non-intrusive way. Furthermore, in the work of Bergeron, only relatively thick films (60-600 nm) are considered, whereas in the present work thinner films (3-100 nm) are investigated, thus studying the initial growth and the interphase region in a more direct way, i.e. without the influence of the bulk.
Discussion

As interphases are observed for PECVD on polymer substrates but not for PECVD on crystalline silicon substrates [11], nor for PVD on polymer substrates [13], the interphase formation must be caused by plasma-polymer interaction. Three classes of particles from the plasma may affect the polymer, possibly in a synergistic way: (V)UV photons, radicals and energetic ions. Dennier et al. [13, 14] showed that radicals are capable of forming an interphase, but the role of VUV photons and energetic ions is unclear, as they have not been isolated. However, as their energy is large enough to break chemical bonds, it is very likely that they contribute to the etch process and/or to cross-linking. Da Silva Sobrinho et al. [11] reported a much wider interphase, which may be attributed to the higher ion energy (150 eV) compared to the ion energy in the work of Dennier (10-20 eV in the active glow zone, negligible in the downstream region), and to the larger susceptibility of PET with respect to PI toward etching. Another difference is that Da Silva Sobrinho used a low density-plasma ($p = 0.13$ mbar, $P = 150$ W), whereas Dennier used a high density-plasma ($p = 2.7 \cdot 10^{-3}$ mbar, $P = 400$ W). In the latter, the power is higher and the pressure lower, leading to a higher electron and ion density and a higher ionization degree, and thus to a larger ion flux. Thus, compared to the plasma used by Dennler, the ion energy in the plasma used by Da Silva Sobrinho was high but the ion density low, complicating the interpretation of the influence of the ion bombardment.

Ion bombardment

Literature has often reported on the positive role of ion bombardment in the densification of the bulk of plasma-deposited films [21]. Molecular-dynamics simulations have shown that the densest SiO$_2$ films are obtained if the energy delivered by ions is 12-15 eV per condensing SiO$_2$-unit [17]. Martínez et al. [18] determined experimentally, using a MW/rf dual frequency plasma, that the critical ion energy is 70 eV (rf bias). Lower ion energies result in less dense films, whereas higher ion energies can lead to the incorporation of hydrogen-rich species, gas entrapment, high internal stress and sputtering. The reported optimum ion-to-condensing SiO$_2$-unit ratio ($\Phi_{\text{ion}} / \Phi_{\text{SiO}_2}$) is 0.78 [18]. None of these studies, however, considered polymer substrates or the formation of an interphase when ion bombardment is involved. As ion bombardment affects the bulk growth, it also affects the initial growth and thus the interphase formation. By being able to break bonds and restructure the material in or near the interphase, the energetic ions can change the properties of the interphase and may increase its thickness. Altogether, the role of energetic ions during the deposition of barrier layers on polymer substrates is very interesting, as it influences the performance of the polymer/inorganic film composite both through the bulk properties of the film and through the interphase properties. If more knowledge is obtained concerning the effect of ion bombardment on the interphase region, ion bombardment may be used as a tool to control the interphase formation. The Expanding Thermal Plasma (ETP), which is used in the present work, combines a high density-plasma with a low self-bias (1-2 V, see Section 3.1), and is therefore ideal for studying the influence of energetic ions: ion bombardment is negligible without external substrate bias, but, due to the high ion density, significant if external substrate bias is applied. In this way, the ion bombardment is fully controlled and can be studied without affecting other plasma properties, thus isolating the effect of ion bombardment. In Chapter 7, a preliminary study of the influence of ion bombardment on the interphase formation is presented.
Interaction of radicals and (V)UV irradiation with polymers

The role of (V)UV irradiation and radicals has been investigated in non-depositing plasmas. It was found by Bergeron et al. [19] that the top 40-200 nm of polycarbonate is cross-linked when treated in helium or nitrogen plasma. The cross-linking can be detected by a decrease in solubility of the polycarbonate in acetone and an increase in refractive index $n$ of 1.5%-2.0% (see Figure 2.5). This cross-linking may improve the mechanical stability, and hence improve the adhesion and reduce the thickness of the interphase. The effect of He plasma on $n$ and the affected thickness $d$ appears to be larger than for N$_2$ plasma, most probably due to a more intense VUV radiation generated in the He discharge. On the other hand, for N$_2$ plasma, the thickness of the affected region is more pronounced with longer treatment times. The increase in $d$ as a function of the treatment time in N$_2$ plasma can be attributed to the formation of low molecular weight species at the surface. Presence of low molecular weight species should lead to a lower refractive index at the surface, but this may be masked by an increase of $n$ due to incorporation of nitrogen. Summarizing, it can be said that the polymer is cross-linked by (V)UV irradiation, and, in the presence of a non-noble gas, low molecular weight species form at the surface, accompanied by the incorporation of radicals from the plasma.

![Figure 2.5](image-url)

Figure 2.5. The refractive index $n$ (at $\lambda = 500$ nm) and the thickness $d$ of the cross-linked layer as a function of the treatment time in a helium plasma (left) and in a nitrogen plasma (right). The refractive index of untreated polycarbonate is 1.598 [19].

Holländer et al. [22] studied the effect of VUV irradiation of PET. In a non-oxidizing environment (e.g. vacuum or nitrogen), the main effects are cross-linking via radical recombination and the formation of double bonds. In oxygen or air, chain scission takes place, with carbon oxides, vinyl groups, and phenolic groups as main products. The previously discussed work of Bergeron [19] showed that a He/N$_2$ plasma pretreatment decreases the interphase width by cross-linking and stabilizing the polymer surface. However, the effect is probably reversed if the pretreatment is performed in oxidizing plasmas, where the main effect of plasma treatment is chain scission.

Fozza et al. [23] isolated the role of atomic oxygen (AO) and VUV irradiation on polymethylmethacrylate (PMMA), hexatriacontane (C$_{36}$H$_{74}$) and polyethylene (PE). It was shown that, even in vacuum, VUV photons are capable of etching (see Figure 2.6), confirming the conclusion of Bergeron and Holländer regarding (V)UV induced chain scission and the formation of low molecular weight species. AO is capable of etching as well, although the etch rates for AO exposure alone were very low compared to the etch rates for exposure to VUV + AO (see Figure 2.7). For all three organic materials studied, the etch rate increases in the following order: AO alone < VUV alone < VUV and AO, which, in view of the very low etch rates for AO alone, points out to a VUV/AO synergy. Thus, the influence of radicals alone on the formation of an interphase is probably limited, unless the radical flux is high compared to the deposition flux, as was the case in the experiment of Dennier et al. [13]. However, no quantitative information is available and therefore, the influence of radicals is not necessarily negligible during the deposition of inorganic films in the expanding thermal plasma used in the present work. The importance of VUV photons is not surprising, as their high energy (6 eV for $\lambda = 200$ nm) is sufficient to break any chemical bond. Truica-Marasescu et al. [24] investigated the
influence of VUV radiation on polymers and showed that the VUV-polymer interaction not only depends on the intensity of the radiation, but also on the photon energy. The formation rate of unsaturated bonds and the etch rate strongly depend on the photon energy and generally increase with increasing photon energy. Due to the absorption of VUV photons by the polymer, the interaction of these photons with the substrate is limited to the top 30-200 nm of the polymer [24].

Figure 2.6. The etch rates of (1) PMMA, (2) C₃₆H₇₄ and (3) polyethylene due to exposure to (a) both UV/VUV and AO, and (b) UV/VUV only [23].

Growth modes

With deposition, generally two growth modes can be observed: Volmer-Weber growth, also referred to as the island-coalescence mode, and Frank-Van der Merwe or layer-by-layer growth. Volmer-Weber growth occurs when the deposited atoms are more strongly bound to each other than to the surface. In the Volmer-Weber mode, the growth starts island-like at the so-called nucleation sites. The islands grow until the substrate is fully covered (coalescence of the islands), after which the growth becomes homogeneous. Frank-Van der Merwe growth on the other hand occurs if the deposited atoms are more strongly bound to the substrate than to each other. In this mode, the growth is homogeneous from the start.

Using thermal evaporation (PVD) of SiO on polyimide (PI) substrates, Dennler et al. [14] observed Volmer-Weber growth with island coalescence occurring at a film thickness of 1 nm. In a
radiofrequency (rf) plasma reactor on the other hand, the growth occurs in the Frank-Van der Merwe mode. This growth mode was observed for SiO₂ deposition from an Ar/HMDSO/O₂ plasma on PI, polyethylene terephthalate (PET) and polypropylene (PP) [15]. The occurrence of Frank-Van der Merwe growth is attributed to an increased surface free energy of the polymer due to plasma-polymer interaction (e.g. the near-surface oxidation observed by Fozza et al. [23]), which is absent during thermal evaporation.

The growth mode may be important for two reasons: (1) if the growth occurs via the Volmer-Weber mode, radicals and energetic ions have unimpeded access to the polymer until the islands coalesce, while in the Frank-Van der Merwe mode the substrate is faster completely covered by a protective barrier layer. Thus, in PECVD, Volmer-Weber growth would lead to a larger interphase. Apart from that, in both growth modes (V)UV radiation can interact with the polymer throughout the deposition, as SiO₂ and Si₃N₄ are transparent in this region. (2) Because most deposition techniques are conformal, the morphology and defects of the initial deposit will be reproduced in the bulk. For instance, in the Volmer-Weber growth mode, a grain boundary, which is a defect, may remain between two islands after their coalescence [25]. As will be discussed in the next section, defects like pinholes and grain boundaries limit the barrier performance of the films.

Performance of PECVD versus sputtering and PVD
It has been shown that interphases are absent in films deposited by means of sputtering or PVD, due to a lack of active species like (V)UV photons, energetic ions and radicals. Below, some examples are given, showing that plasma-deposited barrier films display better properties in terms of adhesion and barrier performance. The superior adhesion of PECVD films is attributed to the formation of an interphase [10, 19, 20]. The superior barrier performance of PECVD-deposited films may be due to the formation of an interphase, the higher density or the lower defect density with respect to sputtered or PVD-deposited films [10].

Chatham [7] and Da Silva Sobrinho et al. [10] compare the barrier performance of SiO₂-like films deposited by means of sputtering and PECVD. The oxygen transmission rate (OTR) for PECVD-deposited films is found to be one to three orders of magnitude lower than for PVD-deposited films. This is illustrated in Figure 2.8. PECVD films also display a better adhesion [11, 12], which is important for flexible applications, such as flexible solar cells and F-OLEDs. Moreover, Roulin et al. [9] showed that PECVD films outperform sputtered films under influence of stress (see Figure 2.9).

![Figure 2.8. The oxygen transmission rates of plasma-deposited and sputtered SiO₂-like films as a function of the film thickness. *: [26] #: [27] #: [28] #: [29].](image)
2.2 Barrier films

Permeation of single barrier layers

The barrier performance of a film is influenced by its chemical composition and the presence of defects. For instance, the presence of carbon or SiOH functionalities in SiO₂-like films decreases the barrier performance [30]. Defects like pinholes and grain boundaries are very important as well, because the minimum value of the gas permeation rate through barrier layers is determined by defects, as will be pointed out below. As the growth mode influences the number of grain boundaries (in the Volmer-Weber growth mode, grain boundaries between two islands may remain after the coalescence of the islands) and presumably the interphase formation, the growth mode also affects the barrier performance. The presence of carbon in the interphase for instance limits the minimum film thickness for which a good barrier performance can be obtained.

Figure 2.10 shows the oxygen transmission rate as a function of the film thickness \( d \) for plasma-deposited barrier layers. Initially, the OTR decreases only slightly with increasing film thickness. But when a certain critical thickness \( d_c \) (typically 10-30 nm [1]) is reached, the OTR quickly drops by about two orders of magnitude. If the thickness increases further, the OTR continues to decrease at a much lower rate. The same thickness dependence is observed for the water vapour transmission rate [10]. This behaviour reveals information about the gas/moisture transport through the barrier layers. Generally, gas transport through materials under the influence of a pressure gradient can occur via two mechanisms: (1) the solubility-diffusion mechanism and (2) flow through defects in the material like pinholes, microcracks, grain boundaries and porosities. The solubility-diffusion mechanism concerns transport through the material matrix itself and consists of several steps: absorption of the permeant onto the surface, solution of the permeant into the material, diffusion through it under the influence of the concentration gradient, dissolution of the permeant onto the opposite surface and, finally, desorption. From Ideal Laminate Theory it follows that the steady state gas transport via the solubility-diffusion mechanism through a two-layer structure, i.e. the polymer substrate and the barrier layer, decreases with increasing film thickness [7, 31]. This is clearly not the case with the data presented in Figure 2.10. Furthermore, Roberts et al. [8] have pointed out that if a SiO₂-like film had a similar structure to silica glass and contained no macroscopic defects, the transmission rates would be expected to be lower by many orders of magnitude: using the permeability of vitreous silica respectively silica glass and a film thickness of 100 nm, an OTR of only \( 10^{-9} \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1} \) and a WVTR of \( 10^{-10} \text{ g m}^{-2} \text{ day}^{-1} \) are calculated. The role of defects is further stressed by the high performance of Al₂O₃ barrier films deposited with the Atomic Layer Deposition (ALD) technique (WVTR 0.06 g m⁻² day⁻¹ for poly(ethersulfone) coated on both sides with 30 nm Al₂O₃) [32]. The excellent step coverage of this technique leads to a reduced defect density, e.g. by filling in pinholes. However, the very low growth rate (0.1 nm/cycle, typically 1-10 s/cycle) is a major drawback for the application of ALD for the deposition of barrier films.
The oxygen transmission rate as a function of the film thickness for SiO$_2$-like (left) and SiN$_x$ (right) films on 13 µm PET. The different symbols belong to series deposited with different PECVD reactor types: (•) dual frequency (microwave and radiofrequency), (*) microwave, (△) radiofrequency [10].

Therefore, the suggestion of Chatham [7] that the residual transmission through barrier layers occurs via flow through defects is generally accepted. Experimental proof for this defect-controlled transmission mechanism is presented by Da Silva Sobrinho et al. [33], who showed that the oxygen transmission rate and the defect density are highly correlated (see Figure 2.11): when the barrier thickness reaches the critical value, a sharp decrease not only in OTR, but also in defect density is observed. Defects in the barrier film are caused for example by dust particles on the polymer substrate prior to deposition, the surface roughness (which is influenced by plasma-polymer interaction [19]) or imperfections of the polymer such as anti-block particles$^1$, geometric shadowing during the deposition and scratches or cracks in the film, resulting from high stress or sample handling. Why the defect density decreases drastically for $d = d_c$ is not yet well understood. It is possible that at this thickness the deposited layer is thick enough to cover the substrate roughness and irregularities.

Additional proof for the defect-controlled transmission mechanism is presented by Tropsha and Harvey [34], who determined the activation energy of permeation through the structure from the temperature dependence of the transmission rates. This activation energy resulted to be much lower than expected for polymer coated with glass-like films and led to the conclusion that the PECVD-deposited SiO$_2$-like layers contain defects through which the oxygen and other permeants move freely.

$^1$ Anti-block particles are deliberately incorporated in commercial polymer sheets to improve the rollability by decreasing the adhesion between the layers on a roll.
The dominant transport mechanism was permeation through the PET substrate, followed by flux through available defects in the oxide layer.

The work of Prins and Hermans [35] presents an indication for the defect-controlled transmission mechanism as well. By solving the steady state diffusion equation for the gas flux through cylindrical defects (pinholes) in an otherwise impermeable film on a polymer substrate, it is obtained that the gas transmission rates are independent of the thickness of the barrier film, which corresponds to the experimental behaviour of the OTR for $d > d_c$.

**Multistack**

The permeability has to decrease five decades with respect to the current performance of barrier layers to fulfill the requirements for F-OLEDs, as already pointed out in Chapter 1. Therefore, it is very unlikely that it will be achieved with a single barrier layer only, especially when considering that the lower limit of the water vapour transmission rate of a single barrier layer is estimated to be $5 \cdot 10^{-2}$ g m$^{-2}$ day$^{-1}$ [1]. The solution to this problem is to engineer a stack of alternating organic and inorganic layers, a so-called multistack. As such a multistack comprises many organic and inorganic layers, it also comprises many interphase regions, provided PECVD is used, thus increasing the importance of the interphase.

Figure 2.12 shows the structure of Barix™ and how it can be used to encapsulate a F-OLED display. Barix™ is a multistack that consists of sputtered $\text{Al}_{2}\text{O}_{3}$ barrier layers alternated with polyacrylate. To deposit the acrylate interlayer, an acrylic monomer in the gas phase is condensed onto the cooled sample. Next, the condensed liquid is cured to form highly cross-linked polyacrylate. The oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) of Barix™ are below $5 \cdot 10^{-3}$ cm$^3$ m$^{-2}$ day$^{-1}$ atm$^{-1}$ and $5 \cdot 10^{-3}$ g m$^{-2}$ day$^{-1}$ respectively, the detection limits of the MOCON test [1]. With a calcium test, a WVTR as low as $8 \cdot 10^{-4}$ g m$^{-2}$ day$^{-1}$ was measured [36]. This value comes close to meeting the demands for F-OLED encapsulation, which is estimated at $5 \cdot 10^{-5}$ g m$^{-2}$ day$^{-1}$ [1-3].

![Diagram of Barix™ and OLED encapsulation](image)

**Figure 2.12.** Top: schematic representation of the production and structure of Barix™. Bottom: encapsulation of an OLED display.

Although the organic layers do not possess barrier properties, their presence appears to be significant. Figure 2.13 illustrates the effect of a multi-layer structure for a silicon nitride/acrylate multistack [37]. The silicon nitride is deposited using an Ar/N$_2$/Si$_x$ plasma and an expanding thermal plasma reactor similar to the reactor used in the present work. The acrylate inter-layers are obtained by spraying a diluted acrylic monomer mixture onto the sample, followed by evaporation of the solvent and UV-curing.
Instead of distinct organic/inorganic transitions, a film of gradually changing composition may be used, i.e., interphase regions may be created deliberately. In this way, the disadvantage of abrupt changes in composition, namely the tendency to introduce stress in the film structure where delamination can easily occur, is avoided [38, 39]. Kim et al. [38] obtained such a graded-composition barrier film in a continuous process using one plasma reactor. The WVTR of a polycarbonate substrate coated with the graded-composition barrier was less than $1 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$, thus meeting the stringent OLED substrate requirements and demonstrating the feasibility of a fully plasma-deposited 'multistack'. A rf parallel plate reactor was used with SiH$_4$, NH$_3$ and O$_2$ as precursor gases for the inorganic zones (Si$_x$N$_y$) and Ar and an organosilicon (Si$_x$H$_y$) precursor gas for the deposition of the organic zones (Si$_x$H$_y$). The transition zones are obtained by changing the feed gas mixture gradually.

In literature, different theories explaining the beneficial effect of the organic interlayer are found. Affinito [40] suggests that the organic material fills up defects in the inorganic layer, thus repairing them and decreasing the transmission rate. This is illustrated in Figure 2.14. Burrows et al. [1] state that planarization is the main action of the inorganic layer: irregularities at the surface are planarized by a non-conformal, ultra-smooth film (rms roughness < 1.0 nm), effectively decoupling the non-uniformities of the barrier layers. The model suggested by Graff et al. [41] also states that the organic interlayer decouples the defects, the effect being an increased diffusion path length and thus an increased diffusion time. This is illustrated in Figure 2.15. According to ideal laminate theory calculations, this results in a diffusion time of as much as 73 days for a defect distance of 100 µm and a stack of five dyads. Figure 2.16 shows that for larger distances between the defects, the lag time can increase to as much as a couple of years. The steady-state water vapour transmission rates are still in the order of $1 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$, but due to the large lag time, this steady-state transmission rate is only reached after a couple of years. This theory is supported by the increasing inconsistency between calculated steady-state and reported WVTR values as a function of the number of dyads. These values are reported in Table 2.1 for an aluminum oxide/acrylic layer multistack.
Figure 2.15. The organic interlayer decouples the defects in the inorganic layers, thus increasing the diffusion path length [41].

Figure 2.16. The calculated lag time as a function of the number of dyads for different defect spacings [41].

Table 2.1. Predicted and measured WVTR (steady-state) values for multilayer barrier films on PET. The calculated values originate from ideal laminate theory equations [41].

<table>
<thead>
<tr>
<th># dyads</th>
<th>Reported WVTR (g m⁻² day⁻¹)</th>
<th>Calculated WVTR (g m⁻² day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.7</td>
<td>6.8</td>
</tr>
<tr>
<td>1</td>
<td>0.07</td>
<td>0.036</td>
</tr>
<tr>
<td>2</td>
<td>&lt;0.005</td>
<td>0.0181</td>
</tr>
<tr>
<td>3</td>
<td>&lt;0.005</td>
<td>0.0121</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.005</td>
<td>0.0091</td>
</tr>
<tr>
<td>5</td>
<td>~10⁻⁵</td>
<td>0.0073</td>
</tr>
</tbody>
</table>

Van Assche et al. [3] demonstrated that within the temperature range compatible with polymer processing, the substrate processing temperature has a crucial influence on the barrier performance of a multistack. An inductively coupled plasma (ICP) with SiH₄ and NH₃ as precursor gases has been used for the deposition of SiNₓHᵧ barrier films. As Figure 2.17 shows, the WVTR of a stack of three dyads decreases by as much as four decades when the substrate processing temperature is increased from 60 °C to 140 °C.
Figure 2.17. The WVTR of barrier multistacks at 50 °C and 50% relative humidity as measured using a Ca-test, as a function of the substrate temperature during SiN₃Hₓ deposition. The multistacks consist of three SiN₃Hₓ layers separated by thin (<100nm) organic films.
3 Experimental setup

This chapter reports on the substrates used for the plasma deposition, the deposition precursors, the two plasma deposition setups (the expanding thermal plasma, ETP, and the capacitively coupled parallel plates, CCP, reactors), and the applied ex situ and in situ diagnostics, i.e., Spectroscopic Ellipsometry. This latter is described in detail because it represents a key diagnostics in this work and it is used for the first time in situ (real time) to study the formation of an interphase during the deposition of an inorganic layer on a polymer substrate.

3.1 Materials

The polymer substrates are cut from a roll of 100 μm-thick foil of poly(ethylene 2,6-naphthalate), PEN. The chemical structure of PEN is shown in Figure 3.1a. The optical grade Teonex PEN is manufactured by DuPont Teijin under the tradename Q65. The defect density is estimated from AFM pictures. On average, one defect was found per scan area of 10 x 10 μm², corresponding to a defect density of 10⁴ mm⁻². Figure 3.2 shows an AFM and a SEM picture of a defect. The polymer is bi-axially oriented and its refractive indices are 1.78, 1.82, and 1.55, along the optical axes, x, y and z, respectively. PEN is chosen as a substrate because of its transparency (85% for λ>400 nm [42]), relatively low cost (1 €/m²) and a relatively high glass transition temperature Tg (121 °C, which allows a larger (plasma) processing temperature). The substrates are washed in a sonic bath with ethanol for fifteen minutes, and then dried in a convection oven at 60 °C for thirty minutes. Single side polished boron-doped p-type silicon (100)-wafers with a thickness of (525 ± 25) μm and a resistivity of 7-21 Ω·cm are also used as substrates. After fifteen minutes cleaning in ethanol in a sonic bath, the Si samples are dried with a flux of nitrogen. The silicon substrates are used as reference, since it is reported in literature (and, later on, also shown in the Results chapter), that only very thin interphases (<5 nm) are formed on Si substrates during the SiO₂ film growth. Consequently, the bulk optical and chemical properties of the deposited SiO₂ films on Si can be studied and compared with the growth, under the same experimental conditions, on polymer [43].

![Figure 3.1. The chemical structure of (a) poly(ethylene 2,6-naphthalate), PEN, and (b) hexamethyldisiloxane (HMDSO).](image)

![Figure 3.2. AFM picture (left) and SEM (right) picture of PEN, showing a defect.](image)

Hexamethyldisiloxane (HMDSO) is an organosilicon precursor, liquid at room temperature, with a boiling point of 101 °C, and a rather high vapour pressure (44 mbar at 20 °C). Together with O₂,
HMDSO is plasma-activated in both the ETP and the rf parallel plate reactor to deposit SiO₂-like films. Its chemical structure is shown in Figure 3.1b. Silane (SiH₄) may also be used as silicon-supplying precursor instead of HMDSO. In this study, however, HMDSO is used because organosilicon compounds are less hazardous than the pyrophoric silane. Moreover, the use of organosilicon molecules allows for a versatile chemistry of the deposited films, since this can be tuned towards carbon-free SiO₂-like films or carbon-containing SiO₂ films, often referred to as organosilicon-like films, i.e., Si₃CₓOᵧHₓ. These latter have been reported in literature for the deposition of anti-scratch films on polymers for glazing applications, i.e., replacement of glass for transportation and architectural windows [16, 44, 45]. Moreover, Si₃CₓOᵧHₓ is known to improve the adhesion between polymer substrates and inorganic layers: Korzec et al. [46] report on the gradual transition in chemical composition from organosilicon-like towards hard quartz-like films for improving the scratch resistance of windshields and automobile reflectors. On the other side, inorganic SiO₂ coating applications range from anti-corrosion coatings on steel [47], to gas/vapour diffusion barriers and membranes.

3.2 Expanding Thermal Plasma reactor

The Expanding Thermal Plasma is a remote plasma, which means that the plasma generation is separated from the plasma treatment/etching/deposition region. The plasma is generated at high pressure (0.4-2.0 bar) in the arc and expands into the downstream region (0.1-0.3 mbar), where the (deposition) precursor gases are injected. The ETP can be referred to as the ultimate remote plasma configuration (when compared to other remote plasma sources, such as electron cyclotron resonance, ECR, or microwave, MW) because of the independent control of the downstream properties (precursors chemistry, pressure) from the plasma source (plasma parameters), due to the large difference in pressure. Furthermore, because the expansion process reduces the electron temperature to about 0.3 eV in the downstream region [48], the deposition process is generally defined as chemically-driven, since a low self-bias voltage and therefore a negligible ion bombardment develop at the substrate, according to Equation (3.1) [49]. Due to the expansion of the plasma, the transport of the active species towards the substrate is convective (directed velocity 100-1000 m/s [50, 51]) and not diffusive like in e.g. radiofrequency plasmas, resulting in a larger deposition rate. The expansion reduces the electron temperature $T_e$ from 1-2 eV in the plasma source to 0.1-0.3 eV in the reaction chamber [52]. This results in a low self-bias voltage and thus negligible ion bombardment, as the ion energy $E_i$ at the wall is given by Equation (3.1) [49]. This equation assumes a collisionless sheath, thermal ions and a Maxwellian velocity distribution of the electrons.

$$E_i = \frac{T_e}{2} \ln \left( \frac{3m_i}{m_e} \right) \approx 4 - 6 \ T_e = 0.4 - 1.8 \ eV$$  \hspace{1cm} (3.1)

where $E_i$ and $T_e$ are given in eV, $m_i$ is the mass of the respective ion and $m_e$ is the mass of an electron. The approximation is based on the consideration that hydrogen and argon are the lightest respectively heaviest ions in the plasma. The low ion energy implies that dedicated studies of the effect of ion bombardment on the film growth as well as on the polymer/inorganic film interphase development, can be carried out by means of an external substrate bias. The low electron temperature in the downstream region implies that electron-impact dissociation channels can hardly occur; therefore, the HMDSO and O₂ dissociation paths in an argon-fed expanding thermal plasma have been investigated recently [48, 53] in order to shed light on the mechanisms of molecule dissociation. Briefly, charge exchange reactions between argon ions and O₂ or HMDSO molecules provide molecule activation, which is followed by dissociative recombination with low energy electrons ([54-56]). Equation (3.2) schematically shows the reaction for O₂ molecules and Equation (3.3) shows the first step of the dissociation of HMDSO.
\[
\begin{align*}
\text{Ar}^* + \text{O}_2 & \rightarrow \text{Ar} + \text{O}_2^* \\
\text{O}_2^* + e^- & \rightarrow O + O^* \\
\text{Ar}^* + \text{Me}_2\text{SiOSiMe}_3 & \rightarrow \text{Ar} + \text{Me}_2\text{SiOSiMe}_3^* + \text{Me} 
\end{align*}
\] (3.2)
(3.3)

where O* indicates an oxygen metastable and Me a methyl group. The reaction product of (3.3) can be further dissociated by recombination reactions with electrons, leading to Si-O and Si-C bond dissociation.

Figure 3.3 shows a scheme of the ETP reactor and the plasma source. The plasma source is a so-called cascaded arc. It consists of three cathodes, a stack of copper plates insulated from each other by boron nitride rings, and a grounded anode plate. The plasma is ignited in a current-controlled dc discharge in argon at high pressure (0.4-1.0 bar). Oxygen is added through the nozzle gas inlet; HMDSO is injected through a ring located ~5 cm below the arc. The substrate is clamped on a substrate holder, which is in turn mounted on a chuck 60 cm below the arc. The substrate holder is loaded in the reactor via a loadlock system with a base pressure of 10^{-6} mbar. The chuck temperature is actively controlled via ohmic heating and liquid nitrogen/water cooling with an accuracy of 10 °C [57]. To improve the thermal contact between the substrate holder and the substrate, a small helium backflow of 1.5 sccs is applied in the case of silicon substrates. No backflow is used for PEN substrates, since it causes slight bulging of the flexible substrate. This is troublesome for spectroscopic ellipsometry (SE), since the bulging changes the angle of incidence on the substrate and thus affects the optical alignment. A stainless steel shutter is used to shield the sample from the plasma during the first ten seconds after plasma ignition, when the ignition is not yet stabilized. The pressure in the expansion chamber is controlled via a pumping unit, which consists of two main pumping lines. One line is formed by two mechanical booster pumps (Edwards EH2600, 2600 m^3 h^{-1}; Edwards EH500A, 500 m^3 h^{-1}) and one

\[1\] At room temperature, HMDSO is in the liquid phase. Therefore, it is evaporated at 65 °C and mixed with an accompanying argon flow rate of 1.8 sccs in a Bronkhorst Controlled Evaporator/Mixer before injection in the reaction chamber.
rotary piston pump (Edwards, 240 m$^3$ h$^{-1}$) and is used to control the pressure during deposition within the range 10$^{-2}$–1 mbar, via a moveable valve. The other line consists of a turbo-molecular pump (Leybold Turbomex 1500, 90 m$^3$ h$^{-1}$) and a rotary pump (Edwards, 40 m$^3$ h$^{-1}$) and it is used overnight to maintain a base pressure of 10$^{-6}$ mbar. Table 3.1 lists plasma and external parameters characterizing the ETP setup.

Table 3.1. Some properties of the Expanding Thermal Plasma [58]. Besides the typical values for this type of plasma, the specific properties of the standard plasma as used in this work are listed.

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical</th>
<th>In this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (plasma on)</td>
<td>0.4 – 2 bar</td>
<td>0.6 bar</td>
</tr>
<tr>
<td>Electron temperature</td>
<td>1-2 eV</td>
<td></td>
</tr>
<tr>
<td>Electron density</td>
<td>10$^{22}$ m$^3$</td>
<td></td>
</tr>
<tr>
<td>Degree of ionization</td>
<td>5 – 10%</td>
<td>5 % [48]</td>
</tr>
<tr>
<td>Arc current</td>
<td>30 – 100 A</td>
<td>75 A (= 25 A/cathode)</td>
</tr>
<tr>
<td>Arc voltage</td>
<td>30-80V</td>
<td>60V</td>
</tr>
<tr>
<td>Reactor chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base pressure</td>
<td>10$^{-6}$ mbar</td>
<td>10$^{-6}$ mbar</td>
</tr>
<tr>
<td>Pressure (plasma on)</td>
<td>0.1-0.3 mbar</td>
<td>0.23 mbar</td>
</tr>
<tr>
<td>Electron density</td>
<td>10$^{15}$-10$^{19}$ m$^3$ [52]</td>
<td></td>
</tr>
<tr>
<td>Electron temperature</td>
<td>0.1 – 0.3 eV</td>
<td></td>
</tr>
<tr>
<td>Plasma sheath voltage</td>
<td>1-2 eV</td>
<td></td>
</tr>
<tr>
<td>Directed velocity at the substrate</td>
<td>100-1000 m/s [50, 51]</td>
<td>200 m/s [51]</td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>30 – 100 sccs$^a$</td>
<td>100 sccs</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>5 – 30 sccs</td>
<td>5.0 sccs</td>
</tr>
<tr>
<td>HMDSO flow rate</td>
<td>0 – 0.5 sccs</td>
<td>0.25 sccs$^b$</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>-90 – +300 °C</td>
<td>50-100 °C</td>
</tr>
</tbody>
</table>

$^a$ Electron density in a pure Ar plasma (without O$_2$/HMDSO injection).

$^b$ If external substrate bias is applied the HMDSO flow is increased to 0.4 sccs.

**External substrate bias**

The substrate holder can be biased with either a radiofrequency bias (13.56 MHz) or the so-called Ion Energy Selective (IES) bias. Radiofrequency (rf) biasing at a frequency of 13.56 MHz is commonly practiced to accelerate ions in the plasma sheath towards the surface, in order to supply the substrate with energy to enhance the surface mobility and certain reactions like bond rearrangements, therewith possibly densifying the deposited film. As Figure 3.4 illustrates, rf biasing results in a broad, double peaked Ion Energy Distribution Function (IEDF) [59, 60]. This is because the ion energy depends on the phase of the bias signal during the ion transit of the plasma sheath. To improve the control over the ion energy, the IES bias creates a constant negative bias voltage instead of a sinusoidal voltage on the substrate [61]. The IES bias signal and IEDF are illustrated in Figure 3.5. To prevent problems due to positive charging by the ion current from the plasma to the substrate, short pulses of negligible bias voltage are included. During these pulses, electrons can neutralize the positive charge of the ions on the substrate. The setup is schematically depicted in Figure 3.6.

$^1$ 1 sccs is 1 cm$^3$ per second at standard pressure (1 bar).
Figure 3.4. The substrate potential (left) and the Ion Energy Distribution Function (right) when rf bias is applied.

Figure 3.5. The substrate potential (left) and the IEDF (right) when Ion Energy Selective bias is applied.

Figure 3.6. Scheme of the IES setup. The signal at channel 1 of the oscilloscope is the input bias signal, the signal at channel 2 is the output bias signal, i.e. the voltage at the substrate holder.
During the ion collection phase of each period, arriving ions reduce the negative charge and thus the bias voltage at the substrate and the substrate holder. This ion current is compensated by increasing amplitude of the input bias signal. Figure 3.7 shows an example of the signals. The difference in slope between the input and output bias voltages is used to calculate the ion flux $\Phi_{\text{ion,IES}}$:

$$dQ_{\text{capacitor}} = dQ_{\text{c}}$$
$$\Leftrightarrow C \cdot (dV_{\text{output}} - dV_{\text{input}}) = \Phi_{\text{ion,IES}} \cdot A \cdot e \cdot dt$$

$$\Leftrightarrow \Phi_{\text{ion,IES}} = \frac{C \cdot d(V_{\text{output}} - V_{\text{input}})}{e \cdot A} \quad (3.4)$$

The first equation states that the change in electrical charge on the capacitor $Q_{\text{capacitor}}$ equals the charge delivered by the ion current ($Q_{\text{c}}$). The charge $Q_{\text{capacitor}}$ is expressed as a function of the capacitance $C$ and the voltage over the capacitor $V$. The charge $Q_{\text{c}}$ is a function of the ion flux, the ion collecting surface area $A$ and the elementary charge $e$. Since $C$ and $e$ are known, $A$, $V_{\text{output}}$ and $V_{\text{input}}$ are measured in order to calculate the ion flux. Equation (3.4) is valid when silicon substrates are used, but the situation is different when PEN, a dielectric, is used because in that case, the voltage drops across the substrate. The parasitic capacitance $C_{\text{dil}}$ formed by the PEN substrate is given by

$$C_{\text{dil}} = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad (3.5)$$

where $\varepsilon_0$ is the permittivity of the vacuum ($8.85 \times 10^{-12}$ F m$^{-1}$), $\varepsilon_r$ the dielectric constant (3.16 for PEN), $A$ the surface area of the dielectric and $d$ the thickness of the dielectric (100 $\mu$m). This results in a parasitic capacitance of 1.8 nF for the used sample size of 64 cm$^2$. The voltage at the topside of the sample is calculated with Equation (3.6) and the situation is illustrated in Figure 3.8.
Figure 3.8. Because the PEN substrate is a dielectric, the parasitic capacitance of the PEN has to be taken into account. The result is a series connection of the two capacitors.

\[ \Delta V_C = V_{\text{output}} - V_{\text{input}} = \frac{Q}{C} \]

\[ \Leftrightarrow Q = C \left( V_{\text{output}} - V_{\text{input}} \right) \]

\[ \Delta V_{\text{diel}} = V_{\text{substrate}} - V_{\text{output}} = \frac{Q}{C_{\text{diel}}} = \frac{C \left( V_{\text{output}} - V_{\text{input}} \right)}{C_{\text{diel}}} \quad (3.6) \]

\[ V_{\text{substrate}} = V_{\text{output}} + \frac{C}{C_{\text{diel}}} \left( V_{\text{output}} - V_{\text{input}} \right) \]

A small capacitor \((C = 1.12 \, \text{nF})\) is used, because according to Equation (3.6) it has to be as small as possible to reduce the voltage drop over the parasitic capacitance \(C_{\text{diel}}\). On the other hand however, the capacitance should not be too small, because with a small capacitance, a given ion flux will reduce the bias voltage faster \(\left( V = \frac{Q}{C} \right)\).

In the case of rf biasing, the ion flux is given by Equation (3.7):

\[ \Phi_{\text{ion,rf}} = \frac{I_{\text{bias}}}{e \cdot A} = \frac{P_{\text{bias}}}{e \cdot V_{\text{bias}} \cdot A} \quad (3.7) \]

To compare the ion flux with the depositing flux, the depositing flux is calculated from the deposition rate \(R_d\) under the assumption that the film is stoichiometric SiO\(_2\):

\[ \Phi_{\text{dep}} = \frac{R_d \cdot \rho \cdot N_A}{m_{\text{SiO}_2}} = \frac{R_d \cdot 2.2 \cdot 10^5 \cdot 6.02 \cdot 10^{23}}{60} = 2.2 \cdot 10^{28} \, \text{m}^{-3} \cdot R_d \quad (3.8) \]

In this formula \(\Phi_{\text{dep}}\) denotes the flux of depositing particles in terms of SiO\(_2\)-units \(\text{m}^{-3} \, \text{s}^{-1}\). \(N_A\) is Avogadro’s number and \(m_{\text{SiO}_2}\) is the mass of one SiO\(_2\)-unit expressed in atomic mass units. \(\rho\) represents the density of the SiO\(_x\) and is approximated with 2.2 g cm\(^{-3}\), the density of fused silica.

The energy per SiO\(_2\)-unit \(E_{\text{SiO}_2}\) delivered by ion bombardment is calculated as follows:

\[ E_{\text{SiO}_2} = \frac{E_i \cdot \frac{\Phi_{\text{ion}}}{\Phi_{\text{dep}}}}{e \cdot V_{\text{bias}}} = \frac{\Phi_{\text{ion}}}{\Phi_{\text{dep}}} \quad (3.9) \]

The bias voltage \(V_{\text{bias}}\) is as depicted in Figure 3.4 and Figure 3.5 and is obtained using Channel 2 of the oscilloscope. Figure 3.9 shows the ion flux as a function of bias voltage for rf biasing and for IES biasing. During these measurements, the HMDSO flow was 0.4 sccs instead of the default 0.25 sccs. In the case of IES biasing, the ion flux is independent of the bias voltage and much lower than in the case of rf biasing, where the ion flux increases with increasing bias voltage. So, the rf biasing leads to ion production. When either the IES or the rf bias is switched on while the ETP plasma is switched
off, a plasma is visible. Therefore, to exclude any differences between differently biased and unbiased samples before the start of the deposition, the bias is not switched on until the shutter is opened and the deposition starts.

![Figure 3.9. The ion flux as a function of the bias voltage for rf biasing and IES biasing.](image)

3.3 *Rf parallel plate reactor*

The rf plasma reactor for HMDSO processing at the Fraunhofer Institute for Interfacial Engineering and Biotechnology is a capacitively coupled rf parallel plate reactor, described in detail by Hegemann [62]. A schematic picture of the reactor is shown in Figure 3.10. The HMDSO is heated to 35 °C to increase its vapour pressure. The vapour is mixed with oxygen and injected into the reactor chamber through a showerhead located 86 mm above the lower electrode. Substrates are placed on the lower, powered electrode. The pressure during depositions is 0.15 mbar, the base pressure is $10^{-2}$ mbar. In a rf plasma, the ion energy due to the acceleration in the plasma sheath is given by Equation (3.10) [49]. This formula assumes that the velocity of the ions $v_i$ equals the Bohm velocity $v_{Bohm}$ (Equation (3.11)):

$$E_i = \frac{T_e}{2} + \frac{T_e}{2} \ln \left( \frac{m_i}{2 \pi m_e} \right) \approx 3 - 5 T_e$$  \hspace{2cm} (3.10)

$$v_i = v_{Bohm} = \sqrt{\frac{k_B T_e}{m_i}}$$  \hspace{2cm} (3.11)

where $k_B$ is Boltzmann's constant.
Table 3.2. The experimental conditions for deposition in the rf parallel plate reactor. The conditions for the ETP reactor are shown as well for comparison.

<table>
<thead>
<tr>
<th></th>
<th>rf parallel plate default conditions</th>
<th>ETP – default conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>0.15 mbar</td>
<td>0.23 mbar</td>
</tr>
<tr>
<td>Argon flow</td>
<td>-</td>
<td>100 sccs</td>
</tr>
<tr>
<td>Oxygen flow</td>
<td>3.3 sccs</td>
<td>5.0 sccs</td>
</tr>
<tr>
<td>HMDSO flow</td>
<td>0.05 sccs</td>
<td>0.25 sccs</td>
</tr>
<tr>
<td>Power</td>
<td>375 W</td>
<td>4.5 kW</td>
</tr>
<tr>
<td>Plasma sheath voltage</td>
<td>10 V*</td>
<td>1-2 V</td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.4 nm/s</td>
<td>2.0 nm/s</td>
</tr>
</tbody>
</table>

* Estimation based on Equation (3.10) and an electron temperature of 2-3 eV.

3.4 Diagnostics

3.4.1 Spectroscopic Ellipsometry

Theory [63]

Spectroscopic ellipsometry (SE) is an optical technique that is used to obtain information about the deposited layers, e.g. the thickness, refractive index and surface roughness. SE exploits the difference in reflectance of the two polarization directions of incident light, as schematized in Figure 3.11. The incident light is linearly polarized and consists of two components. The electric field of the first component oscillates in the plane of incidence and is referred to as p-polarized light. The electric field of the second component oscillates in the direction perpendicular to the plane of incidence and is referred to as s-polarized light. When the light is reflected on the sample surface, the intensity and phase of both components change independently, resulting in elliptically polarized light. The reflected light is then detected and analyzed as a function of the wavelength $\lambda$ in a multi-channel analyzer. This yields $\Psi$ and $\Delta$, the two main quantities in ellipsometry. $\Psi$ represents the ratio of the intensity of both polarizations and $\Delta$ represents the difference in phase shift. $\Psi$ and $\Delta$ are defined as
\[
\tan \Psi = \frac{|I_p^2 / I_1^2|}{|I_p^1 / I_1^1|} \\
\Delta = (\delta_p^2 - \delta_s^2) - (\delta_p^1 - \delta_s^1)
\]

where \( I \) is the absolute intensity and \( \delta \) the phase of the light. The superscript \( p \) (s) refers to \( p \)-(s-) polarized light and a subscript 1 (2) to the situation before (after) reflection on the sample. The measured (experimental) values of \( \Psi \) and \( \Delta \) as a function of the wavelength can be compared with the theoretical values of a given model. This model then is modified until it fits the experimental data, yielding the thickness and optical constants of the layer(s). The theoretical spectra are calculated from Fresnel’s equations, Snell’s law and Drude’s equations. The reader is referred to Tompkins [63] for more information about these equations. When using models, it is important to note that a fit is not necessarily unique: different models can result in a good fit.

1. Linearly polarized light

2. Reflection on the sample

3. Elliptically polarized light

Figure 3.11. Linearly polarized light from the SE source reflects on the sample.

To reduce the number of regression parameters, a model has to be used rather then the fundamental equations. For the modeling of SiO\(_x\) usually the so-called Cauchy model is used because it is a simple yet powerful model for describing the refractive index of dielectric and semiconducting materials [63]. This model assumes no absorption and is thus valid for transparent materials only. The following dependence of the refractive index \( n \) on the wavelength \( \lambda \) is assumed:

\[
n(\lambda) = A_n + \frac{B_n}{\lambda} + \frac{C_n}{\lambda^4}
\]

where \( A_n, B_n, \) and \( C_n \) are fit parameters. Typical values for SiO\(_2\) are \( A_n = 1.3-1.5 \) and \( B_n = (1-6) \cdot 10^3 \) \( \text{nm}^{-1} \). Because the refractive index and the fit quality are not sensitive to \( C_n \), this parameter is fixed at 0.

A mixture of materials is commonly described with the Bruggeman Effective Medium Approximation (BEMA), which calculates the dielectric function of the composite material from the following equation

\[
f_a \frac{\tilde{\varepsilon}_a - \tilde{\varepsilon}}{\tilde{\varepsilon}_a + 2\tilde{\varepsilon}} + f_b \frac{\tilde{\varepsilon}_b - \tilde{\varepsilon}}{\tilde{\varepsilon}_b + 2\tilde{\varepsilon}} = 0
\]

where \( \tilde{\varepsilon} \) is the effective dielectric function of the composite material, and \( \tilde{\varepsilon}_a \) and \( \tilde{\varepsilon}_b \) are the complex dielectric functions of the constituent materials. \( f_a \) and \( f_b \) are the volume fractions of the two constituent materials. The complex dielectric function can be written as
\[ \varepsilon = \varepsilon_1 + i\varepsilon_2; \quad \varepsilon_1, \varepsilon_2 \in \mathbb{R} \quad (3.15) \]

\[ n = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}} \]
\[ k = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}} \quad (3.16) \]

The BEMA can also represent surface roughness by setting vacuum \((n = 1, k = 0)\) as one of the two constituent materials.

**Modeling of Spectroscopic Ellipsometry**

All measurements are performed *in situ* with a Woollam M2000 spectroscopic ellipsometer at an angle of 68° with respect to the sample surface normal. The light source is a Xenon arc lamp. Data are recorded for 470 wavelengths in the 247-1000 nm range and averaged over 200 scans. When monitoring a deposition real-time, the recorded spectrum is averaged over 10-15 scans, resulting in a time-resolution of 1.5-2.5 s. The program WVASE32 is used for the data acquisition and the modeling of the spectra. The material files (*.mat) mentioned in this section are included in this program. In the remainder of this thesis, the values of the refractive index are reported for a wavelength of 633 nm.

In order to be able to model the deposited SiO₂-like film, the substrate has to be known accurately from an optical point of view. Therefore, every substrate is measured before the start of the deposition. Silicon substrates are modeled with a temperature-dependent silicon material file with a thin native silicon dioxide layer. The fit parameters are the temperature \(T\) and the thickness of the oxide \(d\). Although it results in an excellent fit, the fit is further optimized by subsequently fitting the silicon layer with a so-called point-by-point (pbp) fit. That means that for every measured wavelength, the optical parameters \(n\) and \(k\) are optimized within the limits of the Kramers-Kronig consistency\(^f\).

The modeling of PEN substrates is more complicated due to the birefringence of the material. The refractive index profiles have been determined by J.A. Woollam Co. The in-plane anisotropy has been determined by normal incidence anisotropic transmission ellipsometry; the out-of-plane anisotropy has been determined by variable angle transmission anisotropic ellipsometry. Figure 3.13 shows the refractive indices of the x-, y- and z-axis. Unfortunately, at the time of writing the information about the anisotropy is limited to the \(\lambda = 500-1000\) nm range. Therefore, all modeling in this work, including the modeling of SiO₂-like films on silicon substrates, is confined to this range. As Figure 3.12a shows, this has little influence on the accuracy of the refractive index: a refractive index of 1.42 and a film thickness of 104 nm are found for SiO₂ deposited on a silicon substrate using both the full wavelength range \((\lambda = 247-1000\) nm\) and the limited range \((\lambda = 500-1000\) nm\). Furthermore, Figure 3.12b shows that, using the small range, the error in the refractive index is acceptable, i.e. smaller than 0.01, as models using a refractive index of 0.01 higher (respectively lower) than the optimum value of 1.42 clearly deviate from the experimental spectrum.

\[^f\text{From first principles, } n \text{ and } k \text{ are not independent quantities. They are related by the Kramers-Kronig relation:} \]
\[ n(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE', \text{ where } P \text{ means principal value.} \]
Figure 3.12a. Experimental spectrum of 104 nm ETP-deposited SiO₂ on a silicon substrate (straight line). The dashed lines represent the best fit \((n = 1.42)\) using the full wavelength range \((\lambda = 247-1000 \text{ nm})\) and the small wavelength range \((\lambda = 500-1000 \text{ nm})\), respectively. Figure 3.12b. Experimental spectrum of the same sample (straight line). The dashed lines represent the best fit \((n = 1.42, \lambda = 500-1000 \text{ nm used for fitting})\) and the best fits obtained fixing \(n\) at 1.41 and 1.43, respectively.

The anisotropy is taken into account with the model depicted in Figure 3.14, which defines three optical axes, each with its own optical constants \(A_n, B_n\) and \(C_n\) from the Cauchy relation (Equation (3.13)). The basis is formed by the optical constants of the x-axis; the refractive indices of the y- and z-axis are described relative to the x-axis (‘y-x’ and ‘z-x’). The information from these layers is combined in ‘Biaxial’. To adapt the model to each individual substrate, the anisotropy is conserved by fixing the optical constants of ‘z-x’ and ‘y-x’ and fitting \(A_m, B_n\) and \(C_n\) of ‘x-axis’, therewith automatically changing the refractive indices of ‘y-axis’ and ‘z-axis’ accordingly. The thickness of the roughness layer, which is modeled as a BEMA layer consisting of 50% voids and 50% ‘Biaxial’, is fitted as well. Figure 3.15 shows the result of neglecting the birefringence: real-time scans, recorded during the deposition of SiO₂ on a PEN substrate, are modeled using both the biaxial model from Figure 3.14 and an isotropic substrate layer for the PEN. The thickness that is obtained with both models is nearly equal, but the refractive index is up to 0.04 higher if the substrate is treated as if it were isotropic.

Figure 3.13. The refractive indices of the x-, y- and z-axis of the PEN used in this work as a function of the wavelength.
Roughness (BEMA) ~1 nm
Biaxial (x-axis, y-axis, z-axis) 0.1 mm
z-axis = x-axis + (z-x) 0 nm
y-axis = x-axis + (y-x) 0 nm
z-x 0 nm
y-x 0 nm
x-axis 0 nm

Figure 3.14. The biaxial model used to describe birefringent substrates.

Figure 3.15. The thickness and the refractive index of a SiO₂-like film on PEN as obtained with the single Cauchy model from real-time scans. The substrate has been modeled with the biaxial model (●) and as an isotropic material (△).

For transparent substrates like PEN, care has to be taken to avoid backside reflection, which generates an interference pattern in the acquired spectrum due to the polymer thickness. This is schematically represented in Figure 3.16. Therefore, the backside of the PEN is scratched with fine sandpaper (1200 Grit) before the cleaning procedure. Due to the roughness of the surface the light at the backside is scattered and does not contribute to the reflected light beam. Figure 3.17 illustrates the difference in SE spectrum between scratched and unscratched PEN.

Figure 3.16. If the backside of the PEN substrate is smooth, multiple reflections cause an interference pattern (left). But if the backside is roughened, light is scattered at the backside and does not contribute to the detected SE signal.
When a SiO$_2$-like film is deposited on the polymer, several approaches have been pursued in order to model the corresponding optical spectrum. The simplest model assumes the deposition of a SiO$_2$-like film homogeneous in depth, i.e. neglecting any polymer sub-surface modification prior to deposition and the development of an interphase. This model is schematically reported in Figure 3.18, together with the refractive index evolution along the film depth. The fit parameters are the SiO$_2$ thickness $d$, and the parameters $A_n$ and $B_n$ as defined in the previous section. A roughness layer can be added to represent the surface roughness and is modeled as a BEMA-layer (BEMA.mat) consisting of 50% voids and 50% of the underlying Cauchy layer is known. However, roughness layers are not used in this study because it does not improve the fit. This is in agreement with AFM measurements that showed that the roughness does not exceed 5 nm.

3.4.2 FTIR

Fourier Transform Infrared (FTIR) spectroscopy is a light absorption-based technique that compares the IR light intensity (400-4000 cm$^{-1}$) before and after perpendicular transmission through the sample. The photon energy is usually expressed in terms of wavenumbers and is linked to rotational-vibrational transitions characteristic of a specific chemical bond. The absorption peaks relevant for SiO$_2$-like layers are listed in Table 3.3.

If the thickness $d$ of the layer is known, the intensity $I_t$ of a band can be calculated from the Beer-Lambert law:

$$T = T_0 \exp(-\alpha d)$$

$$I_t = \int a \nu = \int_0^\nu \frac{1}{d} \ln \left( \frac{T}{T_0} \right) d\nu$$

(3.17)
where $T$ is the transmittance of the sample (substrate plus film), $T_0$ the transmittance of the bare substrate, $\alpha$ the absorption coefficient, and $\nu$ the wavenumber. If the so-called proportionality constant $P$, the integrated absorption coefficient, is known, the bond density can be calculated according to Equation (3.18) [64]:

$$ P_i = \int \frac{\alpha}{\nu} d\nu $$

$$ n_i = P_i \cdot I_i $$

Equation (3.18)

In this thesis, the fit procedure described by Van de Pas [65] for obtaining $I_i$ from the transmission spectrum is followed. It calculates the intensity $I_i$ of the peak by integrating over the width of the peak and corrects for the exponential behaviour of the transmission and for the dependence of the electromagnetic field on the wavenumber, which is induced by interference in the SiO$_2$ film. Because no proportionality constants are available for the AS1 and AS2 modes, only the OH density is calculated. The proportionality constant for the SiOH$^1$ and SiOH$^2$ modes together is $4.4 \cdot 10^{-19}$ cm$^{-2}$ [66].

Table 3.3. SiO$_2$-related infrared absorption peaks [47, 67, 68].

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1076$^a$</td>
<td>AS1</td>
<td>Asymmetric SiO-Si stretch. Two adjacent oxygen atoms oscillate in phase with each other.</td>
</tr>
<tr>
<td>1200$^a$</td>
<td>AS2</td>
<td>Asymmetric SiO-Si stretch. Two adjacent oxygen atoms oscillate 180° out of phase with each other.</td>
</tr>
<tr>
<td>457$^a$</td>
<td>R</td>
<td>Rocking of an oxygen atom about an axis through the two silicon atoms.</td>
</tr>
<tr>
<td>810$^a$</td>
<td>SS</td>
<td>Symmetric SiO-Si stretch</td>
</tr>
<tr>
<td>2950$^b$</td>
<td>CH</td>
<td>C-H stretch.</td>
</tr>
<tr>
<td>1250$^b$</td>
<td>SiCH$_3$</td>
<td>Si-CH$_3$ wagging mode.</td>
</tr>
<tr>
<td>840$^b$</td>
<td>Si(CH$_3$)$_x$</td>
<td>Si-(CH$_3$)$_x$ stretch mode.</td>
</tr>
<tr>
<td>885$^b$</td>
<td>Si(CH$_3$)$_x$</td>
<td>Si-(CH$_3$)$_x$ stretch mode.</td>
</tr>
<tr>
<td>2170$^c$</td>
<td>SiH</td>
<td>Si-H stretch mode.</td>
</tr>
<tr>
<td>3450$^c$</td>
<td>SiOH$^1$</td>
<td>Si-OH stretching of hydrogen bonded SiOH</td>
</tr>
<tr>
<td>3650$^c$</td>
<td>SiOH$^2$</td>
<td>Si-OH stretching of non-hydrogen bonded SiOH</td>
</tr>
<tr>
<td>920$^c$</td>
<td>SiOH$^3$</td>
<td>Si-O-H stretch mode.</td>
</tr>
</tbody>
</table>

$^a$ from Kirk [67] $^b$ from Angelini et al. [47] $^c$ from Piskin [68]

The FTIR measurements are performed with a Bruker Vector 22 instrument. The samples are measured in transmission mode in the 400 – 5000 cm$^{-1}$ range with a resolution of 4 cm$^{-1}$. All FTIR measurements are performed on SiO$_x$ on silicon substrates, because PEN is opaque to infrared radiation.
3.4.3 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a common analysis technique used to examine the chemical composition of the sample surface. This technique is described in detail by Watts and Wolstenholme [69]. Only the specific aspects relevant for this study are presented in this section.

In XPS, a sample is exposed to an X-ray beam with a specific photon energy $h\nu$. When an atom absorbs an X-ray, a core electron can be ejected, the so-defined photoelectron. The kinetic energy $E_k$ of such an electron is measured in a spectrometer. From $E_k$, the binding energy $E_b$ of the electron is calculated according to

$$E_b = h\nu - E_k - W$$

In this formula $h$ represents Planck's constant, $\nu$ the frequency of the incident X-ray, and $W$ the spectrometer work function. Atomic species are identified by their characteristic binding energies. Even different bond types can be distinguished, as the electronegativity of the neighboring atoms influences the total charge on an atom and therewith the binding energy of the electrons. Table 3.4 lists the binding energies that are relevant for this study. The Si2p peaks at 102.1 and 102.8 eV correspond to silicon atoms with only two respectively three Si-O bonds instead of four. The one or two remaining bonds are formed with carbon or hydrogen.

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>Element</th>
<th>System</th>
<th>Associated structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>102.1</td>
<td>Si</td>
<td>2p</td>
<td>Si(-O)$_2$</td>
</tr>
<tr>
<td>102.8</td>
<td>Si</td>
<td>2p</td>
<td>Si(-O)$_3$</td>
</tr>
<tr>
<td>103.4</td>
<td>Si</td>
<td>2p</td>
<td>Si(-O)$_4$ = SiO$_2$</td>
</tr>
<tr>
<td>284.3</td>
<td>C</td>
<td>1s</td>
<td>C-Si</td>
</tr>
<tr>
<td>284.7</td>
<td>C</td>
<td>1s</td>
<td></td>
</tr>
<tr>
<td>286.6</td>
<td>C</td>
<td>1s</td>
<td>C-O-C; C-OH; C$^+$O--C</td>
</tr>
<tr>
<td>287.9</td>
<td>C</td>
<td>1s</td>
<td>C=O; O-C-O</td>
</tr>
<tr>
<td>289.0-289.3</td>
<td>C</td>
<td>1s</td>
<td>C$^+$O$^-$; HO--C--O</td>
</tr>
<tr>
<td>531.3</td>
<td>O</td>
<td>1s</td>
<td>O=C (aromatic)</td>
</tr>
<tr>
<td>532.2-532.3</td>
<td>O</td>
<td>1s</td>
<td>O=C=C; C=O (aliphatic)</td>
</tr>
<tr>
<td>532.6-532.9</td>
<td>O</td>
<td>1s</td>
<td>C-O-C; C-OH (aliphatic)</td>
</tr>
<tr>
<td>533.2-533.6</td>
<td>O</td>
<td>1s</td>
<td>O-C-O; C-OH (aromatic); O$^-$C--C</td>
</tr>
</tbody>
</table>

XPS is a surface sensitive technique. The inelastic mean free path (IMFP) of the photoelectrons depends on $E_k$ (and therewith on $E_b$) and the material through which the electron travels. Equations (3.20) and (3.21) give IMFP for photoelectrons with an energy $E_k > 150$ eV traveling through an inorganic and through an organic material, respectively [72].

$$IMFP[\text{nm}] = 0.096\sqrt{E_k[eV]}$$  \hspace{1cm} (3.20)
\[ IMFP[\text{nm}] = \frac{0.11\sqrt{E_k[\text{eV}]}}{\rho[\text{g cm}^{-3}]} \]  

(3.21)

where \( \rho \) is the density of the organic material \((1.36 \text{ g cm}^{-3} \text{ for PEN})\). The attenuation length \( \lambda \) is generally 10% smaller than \( IMFP \) and determines the depth of analysis, as the intensity \( I \) of photoelectrons originating from element \( X \) emitted in a direction normal to the surface from all depths greater than \( d \) is given by the Beer-Lambert relationship:

\[ I = I_o \exp(-d / \lambda_X) \]  

(3.22)

where \( I_o \) is the intensity for \( d = 0 \) and \( \lambda_X \) the attenuation length for photoelectrons from element \( X \). The sampling depth is defined as \( 3\lambda \), as, according to Equation (3.22), 95% of the photoelectrons escaping the material is generated at a depth \( d < 3\lambda \). Table 3.5 lists \( \lambda \) for photoelectrons originating from the relevant elements traveling through PEN and through an inorganic medium (SiO₂).

Table 3.5. The attenuation length \( \lambda \) of photoelectrons traveling through PEN and SiO₂ for the relevant elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>( E_k ) (eV)</th>
<th>( E_o ) (eV)</th>
<th>( \lambda ) (nm) in SiO₂</th>
<th>( \lambda ) (nm) in PEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si2p</td>
<td>103.4</td>
<td>1383.2</td>
<td>3.2</td>
<td>2.2</td>
</tr>
<tr>
<td>O1s</td>
<td>533</td>
<td>953.6</td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>C1s</td>
<td>284.7</td>
<td>1201.9</td>
<td>3.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure 3.19. The detected signal is the sum of the signal from overlayer \( A \) and the attenuated signal from substrate \( B \).

Equation (3.22) can also be used to calculate the thickness of a thin layer \( A \) on a substrate \( B \). This situation is schematized in Figure 3.19. The intensity of photoelectrons \( (I^A) \) from layer \( A \) is given by

\[ I^A = I_0^A \left(1 - \exp\left(-d / \lambda^A_X\right)\right) \]  

(3.23)

where \( d \) is the thickness of layer \( A \), \( \lambda^A_X(E_k) \) the attenuation length in \( A \) and \( I_0^A \) the intensity for \( d \gg \lambda^A_X \). Similarly, the detected intensity \( I^B \) of photoelectrons generated in a substrate \( B \) with an overlayer of \( A \) is given by:

\[ I^B = I_0^B \exp\left(-d / \lambda^B_X\right) \]  

(3.24)

where \( \lambda^B_X \) is the attenuation length of photoelectrons generated in \( B \) traveling through layer \( A \) and \( I_0^B \) the intensity for \( d = 0 \) (no overlayer). So, the thickness of \( A \) can be calculated either using Equation (3.23) and the intensity of the signal of an element present in \( A \) but not in \( B \), or by using Equation (3.24) and the attenuation of the signal of an element present in \( B \) but not in \( A \). It is important to stress that, due to the experimental error and the simplified assumption of a sharp boundary instead of an in this case more realistic graded transition, the calculated thickness is only indicative.
All XPS measurements are performed with an Axis Ultra XPS instrument from Kratos Analytical Ltd. with an Al Ka X-ray source ($h\nu = 1486.6$ eV). In order to remove any absorbed contaminants at the surface due to exposure to the ambient, the samples are sputtered for 15 seconds with 5 keV Ar ions, corresponding to a sputtering depth of 2-3 nm. Polymer samples without films are not sputtered, because preferential sputtering of oxygen with respect to carbon results in a distorted spectrum. As an example, the XPS spectrum of PEN is shown in Figure 5.4. It shows that peaks are separable if the difference in binding energy is larger than 2 eV. The contributions of the peaks are shown in Table 3.6 and correspond well to the theoretical values.

![Figure 3.20. The XPS spectrum of PEN. The three peaks in the C1s spectrum (left) correspond to O-C=O (289.0 eV), C-O (286.6 eV) and aromatic carbon (284.7 eV). The two peaks in the O1s spectrum (right) correspond to O-C (533.6 eV) and O=C (531.3 eV).](image)

Table 3.6. Quantification of the XPS spectrum of PEN as shown in Figure 5.4. The numbers refer to the numbered atoms in Figure 3.21.

<table>
<thead>
<tr>
<th>No.</th>
<th>Binding energy (eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theory</td>
</tr>
<tr>
<td>C1s</td>
<td>1 284.7</td>
<td>55.6</td>
</tr>
<tr>
<td>C1s</td>
<td>2 286.6</td>
<td>11.1</td>
</tr>
<tr>
<td>C1s</td>
<td>3 289.0</td>
<td>11.1</td>
</tr>
<tr>
<td>O1s</td>
<td>4 533.6</td>
<td>11.1</td>
</tr>
<tr>
<td>O1s</td>
<td>5 531.3</td>
<td>11.1</td>
</tr>
</tbody>
</table>

![Figure 3.21. The chemical structure of PEN. The numbers indicate different bond types, corresponding to different binding energies.](image)

$^1$ This is an estimation based on the known sputter rate of Ta$_2$O$_5$ in identical sputter conditions, which is 12 nm/min.
3.4.4 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is used to obtain morphological information about the samples, especially about the surface roughness. In this study, the AFM is used in the semi-contact mode. A small tip (radius of curvature < 10 nm) is approached to the sample surface to a distance within the range of atomic forces. As shown in Figure 3.22, this tip is located on a cantilever, which is driven with its eigenfrequency. The amplitude of the oscillation is monitored with a laser and a photodiode. The amplitude of the oscillation decreases due to the interaction with the sample surface. The height of the sample is continuously adjusted to keep the amplitude at a user-defined, constant level. This way, the distance between the tip and the sample surface is kept constant. By monitoring the height of the sample while scanning the surface, the topography of the sample is revealed.

![Figure 3.22. Left: schematic picture of the tip and the cantilever. Right: in the semi-contact mode, the cantilever is driven with its eigenfrequency.](image)

The AFM used in this study is a Solver Pro Scanning Probe Microscope from NT-MDT with NSG-11 tips (eigenfrequency 120-325 kHz, radius of curvature of the tip 10 nm). An area of 3.5x3.5 μm² was scanned with a frequency of 1 line per second. As Coulomb forces are much stronger than the Van der Waals-forces exploited with AFM, electrical charging of the samples must be eliminated. To this end, the samples are fixed with conductive tape onto a stainless steel, grounded sample holder.

3.4.5 Contact angle measurements

Contact angle measurements are performed in order to calculate the surface free energy of a material. A small volume drop (typically 5-20 µl) of a test liquid is put on the sample surface with a syringe. Next, the contact angle at the solid-liquid interface is measured. This is illustrated in Figure 3.23. During the measurement, the syringe is left in the liquid to make sure the so-called advancing contact angle is measured. If the syringe is removed, the total volume decreases, and a contact angle in between the value of the advancing (increasing drop volume) and the receding (decreasing drop volume) contact angle is measured.

![Figure 3.23. The contact angle ϕ depends on γ_s, γ_L and γ_SL.](image)

In equilibrium, the surface tension of the liquid γ_L, the surface free energy of the solid γ_s and the solid-liquid surface tension γ_SL are related by the Young equation [73]:

\[ γ_s = γ_SL + γ_L \cos ϕ \]  

(3.25)

If the contact angle is measured with at least two contact liquids, the surface energy can be calculated. The work of adhesion W_a is related to the contact angle ϕ and the surface tension of the test liquid γ_L [73]:

\[ W_a = γ_SL - γ_L \cos ϕ \]
In order to calculate $\gamma_S$, the work of adhesion has to be related to the surface free energy of the solid. The method of Owens-Wendt [74] is applicable for surfaces without acidic or basic groups and especially for the characterization of polymers. In this situation, $W_a$ is related to the surface free energy in the following way:

$$W_a = \gamma_S + \gamma_L - (\gamma_S - \gamma_L \cos \phi)$$

(3.26)

where $\gamma_S$ is related to the surface free energy in the following way:

$$W_a = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}$$

(3.27)

where a superscript $d$ refers to the dispersion component and a superscript $p$ to the polar component. If the dispersion and polar component of the test liquid are known, Equation (3.27) is an equation with two unknowns. Therefore, at least two test liquids are required to solve the surface energy of the solid.

Table 3.7. The surface tension of water and diiodomethane, the two test liquids used in this study.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_S^d$ (mN/m)</th>
<th>$\gamma_L^p$ (mN/m)</th>
<th>$\gamma_L^d$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>21.8</td>
<td>51.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>48.5</td>
<td>2.3</td>
<td>50.8</td>
</tr>
</tbody>
</table>

In this study, water and diiodomethane (CH$_2$I$_2$) are used as test liquids. Their surface tensions are listed in Table 3.7. Care is taken that the contact angle is independent of the drop size, meaning that the drop is large enough so that capillary forces between the liquid and the syringe do not affect the contact angle. To improve the accuracy of the measurement, the contact angle is measured on five spots for each sample and each test liquid. On each spot, the volume of the drop is increased twice, i.e. the contact angle is measured for three different drop sizes.

### 3.4.6 Determination of the Water Vapour Transmission Rate

The Water Vapour Transmission Rate of a sample can be determined with a so-called calcium test. By means of physical vapour deposition in vacuum a calcium film of 100 nm thick is deposited onto glass. The mass of the deposited calcium is monitored with a piezo-crystal. Next, the sample is glued to the piece of glass with Araldite 2012 epoxy glue in a nitrogen atmosphere. As shown in Figure 3.24, the calcium layer faces the barrier layer. Finally, when the glue has dried, the sample is transferred to the ambient, where the measurement is performed. The setup is represented in Figure 3.25.

![Figure 3.24. Schematic representation of the sample as it is prepared for a calcium test.](image)
Figure 3.25. The setup for the calcium test consists of a backlight and a CCD camera recording pictures of the sample. A computer calculates the light intensity transmitted by the sample from the pictures recorded by the camera.

The test is based on the following reaction of calcium with water:

\[
\begin{align*}
Ca + H_2O & \rightarrow CaO + H_2 \\
CaO + H_2O & \rightarrow Ca(OH)_2 \\
Ca + \frac{1}{2}O_2 & \rightarrow CaO
\end{align*}
\]

(reaction 1)  
(reaction 2)  
(reaction 3)

Calcium is metallic, but it becomes transparent when it is oxidized to calcium monoxide. Therefore, the light transmittance of the sample can be used as a measure for the amount of \( H_2O \) that has permeated the PEN + SiO\(_x\) barrier layer composite. It is assumed that no water vapour is transmitted by the glass or the glue and that reaction 1 is the only reaction that occurs. This assumption is valid because initially, there is no CaO yet, so reaction 2 has no contribution to the uptake of \( H_2O \). This leads to a slight underestimation of the WVTR, because this reaction does occur after reaction 1 has occurred. Reaction 3 has a negligible contribution: expressed in mol \( m^2 \) day\(^{-1}\), the OTR of PEN is a factor \( 3.3 \cdot 10^3 \) lower than the WVTR [2]. This factor has to be divided by 2 because only \( \frac{1}{2} \) \( O_2 \) molecule is involved in reaction 3, resulting in a difference of a factor of \( 1.6 \cdot 10^3 \), which is large enough to neglect the contribution of \( O_2 \).

The Beer-Lambert law relates the transmittance \( T \) to the thickness of the unoxidized calcium:

\[
\frac{T}{T_0} = \exp\left(-\frac{d_{Ca}}{d_0}\right)
\]  

(3.28)

The symbols are explained in Table 3.8. So, by measuring the transmittance \( T \) as a function of time, the oxidation rate of the calcium and thus the WVTR can be calculated:

\[
\begin{align*}
\Delta N_{Ca} & = \frac{\Delta (d_{Ca}) \cdot A_{Ca} \cdot \rho_{Ca}}{m_{Ca}} \\
\Delta N_{Ca} & = \Delta N_{H_2O} \\
WVTR & = \Delta N_{H_2O} \cdot \frac{m_{H_2O}}{A_{sample}}
\end{align*}
\]  

(3.29)
Table 3.8. Explanation of the symbols used in Equations (3.28) and (3.29).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>%</td>
<td>Transmittance</td>
</tr>
<tr>
<td>$t_g$</td>
<td>%</td>
<td>Transmittance without calcium</td>
</tr>
<tr>
<td>$d_{Ca}$</td>
<td>m</td>
<td>Thickness of the calcium</td>
</tr>
<tr>
<td>$d_0$</td>
<td>m</td>
<td>Extinction length of calcium</td>
</tr>
<tr>
<td>$t$</td>
<td>day</td>
<td>Time</td>
</tr>
<tr>
<td>$N_{Ca}$</td>
<td>mole</td>
<td>Number of unoxidized calcium atoms</td>
</tr>
<tr>
<td>$N_{H2O}$</td>
<td>mole</td>
<td>Number of transmitted water molecules</td>
</tr>
<tr>
<td>$A_{Ca}$</td>
<td>m²</td>
<td>Area covered with calcium</td>
</tr>
<tr>
<td>$A_{sample}$</td>
<td>m²</td>
<td>Area of the sample</td>
</tr>
<tr>
<td>$m_{Ca}$</td>
<td>g mole⁻¹</td>
<td>Mass of calcium</td>
</tr>
<tr>
<td>$m_{H2O}$</td>
<td>g mole⁻¹</td>
<td>Mass of water</td>
</tr>
<tr>
<td>$\rho_{Ca}$</td>
<td>g m⁻³</td>
<td>Density of unoxidized calcium</td>
</tr>
</tbody>
</table>

All samples used for the calcium test had a SiO₂ film thickness of $(1.0 \pm 0.2) \times 10^2$ nm. This is well beyond the critical thickness, which is approximately 30 nm in this case. All samples for the calcium test are on unscratched PEN substrates, otherwise the backlight of the calcium test setup is scattered and the transmittance cannot be monitored.
4 Comparison of the bulk properties of ETP- and rf plasma-deposited layers

In order to relate the present study to literature about plasma deposition of SiO₂-like films, the material properties of SiO₂-like films deposited in the remote Expanding Thermal Plasma are compared to SiO₂-like films deposited in the direct rf plasma, which is frequently used in literature [64, 75, 76]. The latter films are deposited in the presence of ion bombardment, which is, as explained in Section 3.2, absent during deposition in the ETP plasma. Because it is well known that ion bombardment [21] and the processing substrate temperature [77], which is limited by the use of polymer substrates, affect the film quality, it was investigated whether it is possible to deposit SiO₂-like barrier films on polymer in an Expanding Thermal Plasma with a quality similar to films deposited in direct plasmas. Furthermore, the bulk properties of the films have to be known in order to be able to identify an interphase as a region with properties that differ from the properties of the bulk SiO₂ as well as from the substrate.

The diagnostics here employed are FTIR and XPS, contact angle and AFM. The barrier properties of the films are determined by means of the calcium test. All films are deposited in the standard conditions as mentioned in the description of both plasma reactors (Table 3.1 and 3.2).

Figure 4.1 shows the FTIR spectra of thick SiO₂-like films on silicon substrates. These spectra clearly show that silicon dioxide-like films are obtained. As no carbon-related peaks are observed, it can be concluded that the C concentration is smaller than the technique's sensitivity and estimated to be less than 5%. Both spectra display the characteristic peaks of SiO₂ as listed in Table 3.3. Neither spectrum contains peaks associated with CH₄ or SiH₄. The SiOH stretch modes at $\approx 3450$ cm⁻¹ and $\approx 3650$ cm⁻¹ are more pronounced in the spectrum of the rf plasma-deposited layer than in the case of the ETP-deposited layer: the ratio of the SiOH intensity, represented by the SiOH¹ and SiOH² modes, and the SiOSi intensity, represented by the AS₁ and AS₂ modes, is about a factor of 6 larger for the rf plasma-deposited film than for the ETP-deposited film: $I_{\text{SiOH}} / I_{\text{SiOH}} = 5$ for the rf plasma-deposited film and $I_{\text{SiOSi}} / I_{\text{SiOH}} = 29$ for the ETP-deposited film. The summed bond density of the two SiOH stretch modes is $1.5 \cdot 10^{21}$ cm⁻³ for the ETP-deposited layer and $1.2 \cdot 10^{22}$ cm⁻³ for the rf plasma-deposited layer. The higher SiOH content of the rf plasma-deposited film indicates higher porosity [77] and suggests inferior barrier properties [30]. The larger OH content of the rf plasma-deposited film with respect to the ETP-deposited film is accompanied by the appearance of a peak at $930$ cm⁻¹ in the spectrum of the rf plasma-deposited film, which is absent in the spectrum of the ETP film. The higher SiOH content of the rf plasma-deposited film may be caused by the lower substrate processing temperature in the rf parallel plate reactor (20-40 °C) with respect to the ETP reactor (100 °C). This leads to the incorporation of more SiOH and the formation of a less dense layer, because condensation reaction (4.1), which reduces the SiOH content, is enhanced at higher substrate temperatures.

$$\text{SiOH} + \text{SiOH} \rightarrow \text{Si}_2\text{O} + \text{H}_2\text{O} \quad (4.1)$$

1 In a remote plasma, the plasma generation is separated from the plasma treatment/deposition region. In a direct plasma on the contrary, the plasma generation and deposition occur in the same region.
The results of XPS measurements of the deposited SiO₂-like films on PEN substrates are listed in Table 4.1; the spectra are reported in Appendix A. They confirm the conclusion of the FTIR measurements, namely that the silicon dioxide-like films from both plasmas are carbon-free within the detection limit of XPS (0.2 atomic %). XPS also points out to the larger OH content of the rf plasma-deposited films with respect to the ETP-deposited films, although hydrogen is not detected with XPS: the presence of OH-bonds is deduced from the larger O to Si-ratio (overstoichiometry) of the rf plasma-deposited layers.

Table 4.1. The chemical composition of the two SiO₂-like films on PEN as derived from XPS.

<table>
<thead>
<tr>
<th>SiO₂ thickness (nm)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETP</td>
<td>SiO₂₋₀.₁C₋₀.₀₁</td>
</tr>
<tr>
<td>rf plasma</td>
<td>SiO₂₋₀.₁C₋₀.₀₁</td>
</tr>
</tbody>
</table>

Table 4.2. The water vapour transmission rates of bare PEN and two SiO₂-like films on PEN. The film thickness is calculated from the known deposition rate.

<table>
<thead>
<tr>
<th>SiO₂ thickness (nm)</th>
<th>WVTR (g m⁻² day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare PEN</td>
<td>0</td>
</tr>
<tr>
<td>ETP (100 °C)</td>
<td>100</td>
</tr>
<tr>
<td>rf plasma</td>
<td>100</td>
</tr>
</tbody>
</table>

The barrier properties, which depend on the chemistry and the structure of the layers and the interphase, are evaluated by means of the calcium test. The results are displayed in Table 4.2. It is striking that the rf plasma-deposited layer yields a much better WVTR, in spite of the larger OH-content, which is associated with porosity [78] and thus with inferior barrier properties. This may be explained by degradation of the polymer due to the large heat load in the ETP reactor. This is caused by the large mass flux, resulting in both a high deposition rate and a large heat load. To test the hypothesis that the high temperature is responsible for the inferior barrier properties, a calcium test was performed on one sample deposited at 50 °C and another one deposited at a set temperature of only 20 °C. The effective substrate temperature during the deposition was most certainly higher due to the heat load effect from the plasma.

¹ No active temperature control was available in the rf plasma setup, so the depositions are carried out at room temperature. However, the substrate temperature is estimated to increase by 10 to 20 °C during the deposition.
Table 4.2 (continued).

<table>
<thead>
<tr>
<th>SiO\textsubscript{2} thickness (nm)</th>
<th>WVTR (g m\textsuperscript{-2} day\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETP, 50 °C</td>
<td>100</td>
</tr>
<tr>
<td>ETP, 20 °C</td>
<td>100</td>
</tr>
</tbody>
</table>

The WVTR of these samples is significantly smaller than at 100 °C and has reached a typical value for single layer barrier coatings for the film deposited at 20 °C, therewith demonstrating the influence of the temperature. However, the WVTR of the sample deposited at 50 °C is still a factor three higher than the WVTR of the rf plasma-deposited sample and a factor two higher than the WVTR of the sample deposited at 20 °C. As 50 °C is well below the glass transition temperature of PEN (121 °C), degradation of the polymer is excluded and cannot account for the inferior barrier properties at 50 °C. Therefore, it is concluded that the inferior barrier performance of the films deposited at 50 °C and 100 °C is probably caused by the formation of cracks under the influence of thermal stress in the film, when the sample is transferred from vacuum to ambient air and room temperature. The low silanol (SiOH) content may play a major role, as these groups decrease the stress in the film: the OH group is bonded to one silicon atom only, thus creating a break and relaxation in the matrix. Therefore, the inferior barrier properties of these ETP-deposited layers may be interpreted by the formation of small cracks. This hypothesis is investigated with AFM, but no indications for cracks are found. Figure 4.2 shows representative AFM pictures of both layers. The rf plasma-deposited film displays a smaller grain size than the ETP-deposited film (substrate temperature during deposition 100 °C). This may give rise to a higher defect density (e.g. due to geometric shadowing), which provides an easier pathway for oxygen and water vapour and thus decrease the barrier properties, in contrast to the observations of the calcium test.

Another reason for the difference in water vapour transmission rates between the ETP samples and the rf plasma-deposited samples may be found in the properties of the interphase region between the polymer and the SiO\textsubscript{2}-like film. As PECVD in general and, due to the low ion energy, ETP in particular are conformal deposition techniques, the interphase region also affects the growth and thus the structure and defect density of the bulk, thus affecting the barrier properties. Therefore, differences in interphase formation between the two types of plasma may lead to differences in barrier performance. Because the interphase also influences the adhesion [10, 19, 20], another very important issue for flexible applications, the interphase is a very important and interesting region. Therefore, the next chapters look into the interphase region in more detail. The interphase is expected to be more pronounced in the rf parallel plate reactor, where energetic ions can contribute to its formation, and where the growth rate is about a factor of 5 lower than in the ETP reactor, allowing more time for
plasma-polymer interaction. The central issue in the next chapter will be to detect and characterize the interphase. In Chapter 6, the causes for interphase formation are investigated. Chapter 7 concludes with a preliminary investigation of external substrate bias as a way to gain control over the interphase formation.
5 Identification and characterization of the interphase

The formation of an interphase between a polymer substrate and a SiO$_2$-like film is reported in literature in the case of direct plasmas [11, 13, 19], but, except for the work of Dennler et al. [13, 14], no study was found in literature that concerns the formation of an interphase in remote plasmas. Since the interphase can affect the barrier performance and the adhesion of the barrier layer [10, 19, 20], it is investigated in this section whether an interphase develops in the remote expanding thermal plasma and whether it is similar to the interphase that originates in the direct rf plasma. Because literature [14, 22, 23] shows that atomic oxygen and UV-radiation, both present in the expansion chamber of the ETP setup, play a major role in the etching and modification of the polymer, it is very likely that an interphase forms in the ETP plasma as well. In this framework, it is necessary to check whether the non-depositing radical flux (O, OH, H) can compete with the depositing flux present in the ETP setup. Furthermore, it is mentioned in literature [11] that energetic ions, absent in the case of ETP deposition, can contribute to this process as well.

Table 5.1 summarizes the results of XPS on SiO$_2$-like films of different thickness on PEN substrates. The thickness of the films is obtained with in situ (ETP) and ex situ (rf parallel plate reactor). It is important to note that this thickness is obtained using the single Cauchy model, and therefore it does not only comprise the bulk SiO$_2$, but the interphase as well, thus leading to an overestimation of the actual SiO$_2$ thickness. This is illustrated in Figure 5.1.

Table 5.1. The chemical composition of samples of various thickness as found with XPS. The original spectra of these measurements are found in Appendix A.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Substrate</th>
<th>Thickness from SE (nm)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Si (%)</th>
<th>Composition</th>
<th>Thickness from XPS (nm) (corrected for sputtering)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETP</td>
<td>PEN</td>
<td>14 ± 1</td>
<td>26.2</td>
<td>49.9</td>
<td>18.9 ± 4.9</td>
<td>SiO$<em>{2.10}$C$</em>{1.19}$</td>
<td>4.5 ± 1</td>
</tr>
<tr>
<td>ETP</td>
<td>PEN</td>
<td>21 ± 1</td>
<td>2.0</td>
<td>66.0</td>
<td>32.1</td>
<td>SiO$<em>{2.00}$C$</em>{0.06}$</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>ETP</td>
<td>PEN</td>
<td>60 ± 1</td>
<td>0.3</td>
<td>66.6</td>
<td>33.1</td>
<td>SiO$<em>{2.00}$C$</em>{&lt;0.01}$</td>
<td></td>
</tr>
<tr>
<td>ETP</td>
<td>PEN</td>
<td>116 ± 1</td>
<td>0.3</td>
<td>66.7</td>
<td>32.9</td>
<td>SiO$<em>{2.00}$C$</em>{&lt;0.01}$</td>
<td></td>
</tr>
<tr>
<td>rf</td>
<td>PEN</td>
<td>15 ± 2</td>
<td>2.2</td>
<td>67.0</td>
<td>30.9</td>
<td>SiO$<em>{2.17}$C$</em>{&lt;0.07}$</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>rf</td>
<td>PEN</td>
<td>19 ± 2</td>
<td>0.5</td>
<td>68.2</td>
<td>31.4</td>
<td>SiO$<em>{2.17}$C$</em>{&lt;0.15}$</td>
<td>&gt;15</td>
</tr>
<tr>
<td>rf</td>
<td>PEN</td>
<td>84 ± 2</td>
<td>0.2</td>
<td>68.1</td>
<td>31.7</td>
<td>SiO$<em>{2.15}$C$</em>{&lt;0.01}$</td>
<td></td>
</tr>
<tr>
<td>ETP</td>
<td>Si</td>
<td>14.0 ± 0.5</td>
<td>12.3</td>
<td>58.1</td>
<td>29.6</td>
<td>SiO$<em>{1.95}$C$</em>{0.42}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.1. The film thickness as obtained from SE modeling comprises both the interphase thickness and the thickness of the bulk SiO$_2$. The thickness as calculated from XPS measurements is only the thickness of the bulk SiO$_2$.

All XPS spectra corresponding to the samples listed in Table 5.1 are reported in Appendix A. The table shows that the thin ETP-deposited films (14 and 21 nm) contain carbon, in contrast to the thicker layers (60 and 116 nm). For the thin layers, the thickness is also calculated from XPS by means of Equation (3.23) and (3.24) under the assumption that a discrete continuous SiO$_2$ layer has been...
deposited on PEN. The calculated thickness is then increased by 1.5 nm to correct for the sputtering, assuming that 2.0 nm has been removed by the sputtering, from which 0.5 nm (corresponding to two monolayers) consisted of contamination. The SiO₂ thickness as calculated for the 14 nm thick ETP-deposited film is only 4.5 nm. Therefore, an interphase thickness of 8-9 nm is estimated. Furthermore, an equally thick film deposited on a silicon substrate contains less than half the carbon with respect to the deposition on PEN. Moreover, this carbon content partly originates from contamination present on the silicon substrate before the deposition occurred and is visible due to a too long sputtering time before the XPS analysis was performed: Figure 5.2, in fact, shows that a silicon peak is visible at 99.3 eV, corresponding to crystalline silicon [79] and therewith indicating that the substrate underneath is detected. Therefore, the plasma-polymer interaction and the formation of an interphase must be responsible for the extra carbon in the 14 nm-thick film deposited on PEN. Figure 5.3 shows the XPS spectrum of the latter sample. The C1s and O1s signals in Figure 5.3 are deconvoluted in order to determine the total peak area and the total contribution of carbon respectively oxygen. The peaks however cannot be resolved and thus cannot be assigned to specific bonds, like the peaks in the spectrum of PEN (see Figure 5.4). For example, the binding energy of aromatic carbon, originating from modified polymer, is 284.7 eV, whereas the binding energy of a C-Si bond, formed during the deposition, is only 0.4 eV lower.

Figure 5.2. The XPS spectrum of 14 nm SiO₂ on a silicon substrate. From left to right: the C1s, the O1s and the Si2p signal. The right peak in the Si2p signal represents Si-Si bonds.

1 This sample has been measured with a different XPS instrument and different sputter settings.
Figure 5.3. The XPS spectrum of 14 nm SiO$_2$ on PEN. From left to right: the C1s, the O1s and the Si2p signal. The right peak in the Si2p signal represents Si-C bonds.

Figure 5.4. The XPS spectrum of PEN. The three peaks in the C1s spectrum (left) correspond to O-C=O (289.0 eV), C-O (286.6 eV) and aromatic carbon (284.7 eV). The two peaks in the O1s spectrum (right) correspond to O-C (533.6 eV) and O=C (531.3 eV).

The presence of carbon in another sample, the 21 nm-thick film on PEN (see Figure 5.5), further witnesses the formation of an interphase, because the sampling depth of XPS is limited to 9.0 nm for photoelectrons originating from carbon traveling through SiO$_2$ (see Table 3.5) and only the top 1.5 nm is removed by sputtering. Thus, the total sampled thickness is 10.5 nm and much smaller than the thickness of the film as obtained from SE modeling. Furthermore, the C1s signal shows the peaks corresponding to PEN, implying that the PEN is detected underneath the SiO$_2$. This indicates that the thickness of the bulk SiO$_2$ is indeed smaller than the total film thickness as obtained from SE modeling, and therewith once again points out towards the detection of the interphase region between the (unmodified) bulk polymer and the SiO$_2$ bulk.
A detailed study of the Si2p deconvolution of the thin SiO₂ layer (14 nm) in Figure 5.3 shows the presence of a peak at a binding energy of 102.3 eV. This peak represents a partially oxidized silicon environment [71], suggesting that the silicon atom is bonded to carbon and/or hydrogen as well, and thus this peak points out to the formation of bonds between the polymer substrate and the deposited film, i.e. an interphase. As shown in Figure 5.6, this peak becomes negligible in the Si2p spectrum of thicker films. Figure 5.5 (21 nm) shows a peak at a lower binding energy as well. However, no conclusion can be drawn about the presence of partially oxidized silicon, because, contrary to the case of the 14 nm-thick sample, the area of this peak depends largely on the applied deconvolution settings, and a good fit is also obtained if this peak is left out completely.

Because the 60 and the 116 nm thick ETP layers have the same chemical composition, the interphase is certainly thinner than 50 nm. Based on the sampling depth of XPS, the estimated sputtered thickness and the difference in carbon content between the 14 and the 21 nm thick layers, the interphase thickness is estimated at 8-15 nm. As for the rf plasma-deposited layers (see Appendix A for the spectra), it can be argued on the presence of an interphase. The thinnest layer (15 nm) does contain 2.2% carbon, but this contribution is small enough to be explained by detection of the polymer.
substrate underneath the SiO$_2$-like film: 5% of the detected photoelectrons originates from $d>3\lambda$. The film thickness as calculated from XPS is $13 \pm 2$ nm. Therefore, if an interphase exists, it must be thinner than 5 nm and certainly thinner than the ETP interphase. Moreover, the 19 nm-thick rf plasma-deposited film contains significantly less carbon than the 21 nm-thick ETP film.

Contact angle measurements are performed in order to calculate the surface free energy, which depends on the chemical composition and the morphology of the surface. The surface free energy is plotted as a function of the film thickness in Figure 5.7. It points out towards the presence of an interphase of 4-15 nm for ETP-deposited films, supporting the conclusions drawn from XPS. The rf plasma-deposited layers on the contrary show a constant surface energy from the thinnest layer (3 nm) on. It supports the conclusions from XPS that the rf interphase, if it exists at all, is thinner than the ETP interphase. Care must be taken with the interpretation of these data, because not only the chemical composition, but also the surface roughness influences the contact angle and thus the calculated surface free energy. The small decrease in surface energy for thicker layers may be due to a change in surface roughness as well, as XPS showed that the chemical composition is nearly constant starting from a film thickness of 20 nm. The surface roughness measurements however are not accurate enough to verify this statement, as highlighted by the scattering of the roughness data in Figure 5.8. According to Müller et al. [80], the fact that the surface free energy is lower for the rf plasma-deposited layers than for the ETP-deposited layers, may be due to the higher surface roughness of the former layers (Figure 5.8). Other authors [81] however state that, due to capillary forces, a higher surface roughness leads to an increase instead of a decrease of the surface free energy.

![Figure 5.7. The total surface free energy $\gamma^{\text{tot}}$, as a function of thickness for SiO$_2$-like films on PEN deposited in the ETP reactor (■) and in the rf parallel plate reactor (▲). The dashed line indicates the surface free energy of 2 nm native SiO$_2$ on crystalline silicon.](image-url)
Figure 5.8. The root mean square (rms) roughness as a function of thickness for SiO$_2$-like films on PEN deposited in the ETP reactor (■) and in the rf parallel plate reactor (▲).

The rms roughness of the same thickness series is measured with the AFM. Some typical topographic pictures are shown in Figure 5.9. Figure 5.8 shows the rms roughness as a function of the thickness. The error of the data is estimated from different measurements on the same sample. It is estimated to be 0.6 nm and too large to draw conclusions about the development of the roughness with increasing thickness. It is, however, clear that the samples from the rf parallel plate reactor have a higher roughness than the samples from the expanding thermal plasma reactor (4.5 ± 0.6 nm and 3.3 ± 0.6 nm respectively). This higher roughness is likely to account for the differences in the surface energy as discussed above. Furthermore, the grain size is larger for the ETP-deposited films (100-200 nm) than for the rf plasma-deposited films (50-100 nm), as was the case for the thicker layers described in Chapter 4 (Figure 4.2).

Figure 5.9a. AFM pictures of SiO$_2$-like films on PEN. Left: a 19 nm thick rf plasma-deposited film (rms roughness = 4.4 nm). Right: a 14 nm thick ETP-deposited film (rms roughness = 3.0 nm).
Another possible explanation for the gradual increment of the surface free energy of the ETP-deposited films, besides of course the formation of an interphase, is that for thin films, the surface is not yet fully covered with SiO$_2$. This would be possible if the film growth occurs via island-coalescence (Volmer-Weber) growth and not in the layer-by-layer (Frank-Van der Merwe) mode. Literature about SiO$_2$-like deposition reports that in the case of PVD, the film growth occurs in the Volmer-Weber mode indeed, but the coalescence of the islands already occurs at a film thickness of 1 nm [14]. The growth of SiO$_2$-like films in rf plasma reactors was found to occur in the Frank-Van der Merwe mode [15]. Thus, it is very unlikely that the surface free energy of the ETP-films has not reached its bulk value at a thickness of 4.5 nm because the surface is not yet fully covered with SiO$_2$. However, one could argue that the relatively high deposition rate in the ETP-reactor leads to a larger minimum thickness for which a continuous film is formed. Therefore, in order to exclude this possibility, SEM pictures of bare PEN are compared with SEM pictures of a 3.7 nm thin ETP-deposited SiO$_2$-like film on PEN. As Figure 5.10 shows, both samples look very similar and no island-like structures are observed on the SiO$_2$ film. Therefore, it can be concluded that the formation of an interphase has to be responsible for the gradual increase in the surface free energy of the ETP-deposited films.

**Discussion**

XPS and contact angle measurements have demonstrated the existence of an interphase in the case of ETP-deposited layers, but not in the case of rf plasma-deposited films. From literature, it is known that plasma-polymer interaction can lead to modification and etching of the polymer [11, 14, 19, 22, 23]. Etching and re-deposition of etched products is considered to cause the formation of the interphase [11]. Radicals, UV light and ion bombardment can be responsible for etching and modification. So,
differences between plasmas, such as ion and radical densities, UV production and plasma sheath voltage result in differences in etch rates and modification and, thus, in the formation of an interphase. Differences in modification may also change the sticking coefficient of species from the plasma arriving at the substrate, thus changing the composition and morphology of the thin films. The result that the interphase in the rf plasma-deposited films is smaller than in the ETP-deposited films indicates that ion bombardment ($E_{\text{ion}} \approx 10$ eV) does not, or not significantly, contribute to the interphase formation at the ion flux present during the depositions in the rf parallel plate reactor. It is important to stress that the rf plasma is a low density-plasma, which means that energetic ions may very well contribute to the interphase formation if the ion flux is larger, e.g. when external rf bias is applied, leading to ion production, or in the Expanding Thermal Plasma, which is a high-density plasma. Since, however, no energetic ions were present during the depositions in the ETP setup, (V)UV photons and radicals must be responsible for the interphase formation. One explanation for the absence of an interphase in the rf plasma reactor may be the fact that the flux of active species (non-depositing radicals, (V)UV photons and energetic ions) is lower in the rf plasma reactor than in the ETP reactor. Another explanation is that, in the rf plasma, the SiO$_2$-like deposition starts once the plasma is ignited, immediately protecting the polymer from radicals and energetic ions. In the ETP setup on the other hand, the plasma is ignited for ten seconds before the shutter is removed and the deposition starts. During this time, radicals can modify the polymer without hindrance of a SiO$_2$-like film. But this explanation is in contrast with the results of Da Silva Sobrinho et al. [11] and Dennler et al. [13], who also used a direct plasma and nevertheless found an interphase width of 60 nm using PET substrates and an interphase width of 11 nm using polyimide substrates (see also Section 2.1). This mismatch may be due to a difference in stability between PEN and PET towards plasma treatment, which is known to be an important factor [23]. In the remote configuration, Dennler et al. found an interphase width of 16 nm, which is comparable to our results in the remote ETP (interphase width 8-15 nm).

Altogether, the radical density, the radical flux, the UV intensity and the stability of the polymer towards plasma treatment are likely to play a role in interphase formation. In the high density-Expanding Thermal Plasma, energetic ions are presumably important as well if an external substrate bias is applied. Differences in the mentioned properties would account for the observed differences in interphase formation. In the present chapter, the interphase formation and the modification have been studied mainly from a chemical point of view. To learn more about the modification of the substrate and to investigate whether it is responsible for the formation of an interphase, the modification and SiO$_2$-deposition are studied from an optical point of view in the next chapter. To facilitate this study, in situ spectroscopic ellipsometry (SE) is introduced besides the ex situ diagnostics used so far. SE is a non-intrusive technique and capable of detecting small changes not only in the top layer, but throughout the whole thickness of the polymer. The in situ availability of SE excludes the effects of ageing due to exposure to the ambient. Therefore, SE is expected to be a very appropriate tool for the study of interphase formation. Furthermore, the use of in situ SE for real-time monitoring of the sample is addressed briefly in the next chapter.
6 In situ study of interphase formation and modification of the PEN

This study of interphase formation and modification of the PEN focuses on samples deposited in the ETP reactor, because in situ SE is not available on the rf parallel plate setup. Therefore, all samples mentioned in this chapter are treated in the ETP reactor, unless stated otherwise.

6.1 Modeling of SE spectra of SiO₂ on silicon and on PEN

To start with, it is investigated whether the interphase can be detected by means of SE. SE modeling is started as simple as possible, i.e. using the single Cauchy model from Section 3.4.1 for SiO₂-like films on silicon substrates. Figure 6.1 shows that a good fit is obtained with a refractive index of 1.43.

![Figure 6.1. The real (<e₁>) and the imaginary (<e₂>) part of the complex pseudo-dielectric function <e> and the fit of 114 nm SiO₂ on silicon.](image)

The single Cauchy model also results in a good fit for PEN substrates, as shown for a 116 nm thick SiO₂ film on PEN in Figure 6.2a. Moreover, the model returns the same value for the refractive index (1.43) as SiO₂ deposited on silicon substrates in identical conditions (Figure 6.1). Problems arise however when thinner layers are studied: to obtain a good fit, the refractive index has to be substantially higher, i.e. at least 1.52. This is illustrated in Figure 6.2b (static measurements). A refractive index of 1.52 is not only higher than found for SiO₂-like films on silicon substrates, but also very high for carbon-free SiO₂ (fused silica: n = 1.457), and thus suggests the presence of carbon and the formation of a carbon-containing interphase. On silicon substrates on the contrary, the refractive index can be kept constant even for films as thin as 1.7 nm. Therefore, plasma-polymer interaction and the formation of an interphase must be responsible for the higher refractive index on PEN substrates. The interphase may consist of a region of mixed organic and inorganic material, and/or of a modified top layer of the PEN. The modified PEN may e.g. be cross-linked, contain new functional groups, or lose its anisotropy due to bond scission and the creation of new bonds. The latter was shown in Section 3.4.1 to influence the refractive index as obtained with SE modeling. As the refractive index approaches its bulk value of 1.43 from a film thickness of 20 nm onwards, it can be concluded that the interphase is less than 20 nm thick, confirming the results from the previous section as obtained from XPS analysis. Figure 6.2b also shows the results from real-time measurements of a SiO₂-like film deposited on a PEN substrate in identical conditions. The first data-points are lost due to a high noise level during the measurements. It is remarkable however that, for a film thickness between 40 and 60 nm, the obtained refractive index is significantly larger using the real-time scans than using the static scans of films deposited in identical conditions. This mismatch is attributed to the fact that the film changes while the spectrum is recorded; it grows by about 4 nm during the time needed to obtain one spectrum. In other words, the acquired spectrum is actually an average of 10-15 scans of different moments in the film growth, which introduces errors and decreases the accuracy of the measurements. Therefore, in order to use real-time scans to study the interphase formation and the film growth, the deposition rate should be small compared to the acquisition time. E.g., a deposition rate of 0.5 nm/s is
expected to be sufficiently low, as it corresponds to a film growth of 1 nm during the acquisition of one spectrum.

Figure 6.2a. The real ($\varepsilon_r$) and the imaginary ($\varepsilon_i$) part of the complex pseudo-dielectric function $\varepsilon$ and the fit of a 116 nm thick SiO$_2$-like film on PEN modeled with the single Cauchy model. Figure 6.2b. The refractive index of films of various thickness as obtained using the single Cauchy model and either static SE scans (w) or real-time SE scans (w).

In order to exclude the possibility that the higher refractive index of thin films is due to inadequacy of the biaxial model used to interpret the polymer optically (see Section 3.4.1), the experiment has been repeated in the much milder conditions as listed in Table 6.1. Mainly due to the higher oxygen and HMDSO flow rates, the ion and non-depositing radical flux and the (V)UV intensity are reduced significantly with respect to the standard conditions. For depositions performed in the mild plasma, the refractive index as found for thick layers (>50 nm) can be conserved for thinner layers, just as on silicon substrates. These results clearly demonstrate the importance of the ratio between the flux of modifying/etching species ((V)UV photons, non-depositing radicals and ions) and the depositing flux on the plasma-polymer interaction and the formation of the interphase. Therefore, it is very likely that a smaller flux of modifying/etching species is responsible for the thinner interphase of the films from the previous chapters that were deposited in the rf parallel plate reactor.

Table 6.1. The standard plasma conditions (see also Table 3.1) and the mild plasma conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard conditions</th>
<th>Mild conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current</td>
<td>75 A</td>
<td>75 A</td>
</tr>
<tr>
<td>Ar flow</td>
<td>100 sccs</td>
<td>30 sccs</td>
</tr>
<tr>
<td>O$_2$ flow</td>
<td>5.0 sccs</td>
<td>16.6 sccs</td>
</tr>
<tr>
<td>HMDSO flow</td>
<td>0.25 sccs</td>
<td>0.4 sccs</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>2 nm/s</td>
<td>3 nm/s</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.42</td>
<td>1.37</td>
</tr>
</tbody>
</table>

The interphase as observed with SE may not only form during the initial stages of film deposition, but also before the deposition starts, namely when the plasma is already ignited, but the shutter still closed. During those ten seconds, necessary to stabilize the plasma ignition, the sample is shielded from (V)UV radiation, but it may be exposed to long-life radicals like atomic oxygen (AO). Modification or etching during this time interval would change the optical properties of the top layer of the substrate, thus leading to the formation and detection of a region with properties different from both PEN and SiO$_2$: an interphase. Such modification or etching can also occur during the first stages of growth, when the substrate is not yet covered by the SiO$_2$-like film. Substrate modification may, furthermore, occur throughout the deposition by UV irradiation. The modification of the PEN by both the ETP and the rf plasma is characterized in the next sections. The modification is first studied from a chemical point of view with XPS (ETP and rf plasma reactor). The plasma-induced chemical changes of the PEN in the rf and ETP reactor are compared, in an attempt to further explain the difference in
interphase formation. Next, the modification is studied from an optical point of view with in situ SE (ETP reactor only), in order to elucidate the role of the (V)UV irradiation and the radicals.

6.2 Substrate modification and XPS

First, it is necessary to check if indeed no SiO$_2$ is deposited in the ETP reactor in the ten seconds between ignition of the plasma and the removal of the shutter. Such a pre-deposition would occur in conditions different from the conditions during bulk growth. The resulting thin film would have properties different from the bulk SiO$_2$, and thus define an interphase. However, no such pre-deposition is observed with SE on silicon: a silicon substrate is identical to SE both before and after 10 seconds of the standard Ar/O$_2$/HMDSO-plasma with the shutter closed (Figure 6.3).

![Figure 6.3](image)

Figure 6.3. The real ($\varepsilon_1$) and the imaginary ($\varepsilon_2$) part of the complex pseudo-dielectric function $\varepsilon$ of the silicon substrate before and after 10 seconds of plasma (shutter closed).

To fully exclude a pre-deposition on PEN substrates as well, XPS is performed on a PEN substrate that was shielded by the shutter while a standard Ar/O$_2$/HMDSO-plasma was ignited for 15 seconds. The spectrum is shown in Figure 6.4, next to the spectrum of pristine PEN. Both spectra only contain carbon and oxygen. No silicon was detected, confirming that no deposition has occurred on PEN either. Nevertheless, the spectrum of the shielded PEN clearly differs from the spectrum of pristine PEN, indicating modification of the polymer. At first sight, it is remarkable that no deposition occurs although the plasma has clearly interacted with the polymer. However, when considering the very high ratio of the atomic oxygen flux-to-depositing flux: $\Phi_{AO} : \Phi_{dep} \approx 750$ ([29]), it can be hypothesized that silicon-containing radicals are mainly lost at the walls and on the shutter, while the atomic oxygen density is high enough to cause significant modification and may show an enhanced reactivity at the polymer surface. A surface modification similar to the one in the ETP reactor was found for PEN exposed to a rf oxygen plasma for 5 seconds. The spectrum of this sample is reported in Appendix A. Since no shutter is installed on this reactor, the HMDSO was left out to prevent deposition. The O$_2$ flow was equal to 3.3 sccs. The results are quantified in Table 6.2 and visualized in Figure 6.5.
Figure 6.4. The XPS spectrum of pristine PEN (left) and PEN after 15 seconds of expanding thermal plasma, shielded by the shutter (right). The C1s signal is reported in the topmost spectra, the O1s signal by the bottom spectra.

Table 6.2. The contributions of C and O to the XPS spectrum for pristine PEN and PEN that is modified in the ETP and in the rf reactor. In order to reflect the different bond types, the C- and O-signals are split in three respectively two.

<table>
<thead>
<tr>
<th>No.</th>
<th>Bond type</th>
<th>Binding Energy (eV)</th>
<th>PEN theoretical (%)</th>
<th>Pristine PEN experimental (%)</th>
<th>ETP-modified PEN (%)</th>
<th>rf plasma-modified PEN (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C aromatic</td>
<td>284.7</td>
<td>55.6</td>
<td>56.8</td>
<td>40.1</td>
<td>42.7</td>
</tr>
<tr>
<td>2</td>
<td>C C-O</td>
<td>286.6</td>
<td>11.1</td>
<td>12.9</td>
<td>12.0</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td>C C=O</td>
<td>289.0</td>
<td>11.1</td>
<td>12.9</td>
<td>11.6</td>
<td>12.9</td>
</tr>
<tr>
<td>4</td>
<td>O O-C</td>
<td>533.4</td>
<td>11.1</td>
<td>9.1</td>
<td>10.5</td>
<td>7.7</td>
</tr>
<tr>
<td>5</td>
<td>O O=C</td>
<td>531.7</td>
<td>11.1</td>
<td>9.1</td>
<td>9.1</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>Total C</td>
<td></td>
<td></td>
<td></td>
<td>77.8</td>
<td>80.4</td>
</tr>
<tr>
<td></td>
<td>Total O</td>
<td></td>
<td></td>
<td></td>
<td>22.2</td>
<td>19.6</td>
</tr>
</tbody>
</table>
Figure 6.5. The contributions to the peaks in the XPS spectrum of untreated PEN (theoretical values), rf plasma-modified PEN and ETP-modified PEN.

As the plasma-treatment results in a modified top-layer of the PEN, a region is formed with properties different from the bulk of the substrate, i.e. an interphase is created. Therefore, during a standard deposition, the interphase partially forms before the deposition starts, namely during the first 10 seconds, when the substrate is shielded from the plasma. The interphase formation continues during the first moments of deposition. After all, from SE measurements and XPS analysis, an interphase width of 8-15 nm has been estimated (see Chapter 5). However, if the whole interphase were created before the start of the deposition, no samples with a smaller thickness should have been obtained from SE measurements. Figure 5.7 however shows that film thicknesses as small as 4 nm have been measured.

The modification by both plasmas is similar, again indicating that energetic ions ($E \leq 10$ eV) are of little importance in the rf plasma. They still may influence the reaction rates, but probably not the reaction routes. However, it is possible that the ions influence the etching rate, which would not be detected by means of XPS. The sample in the rf plasma is slightly less modified than in the ETP plasma, but it is very likely that the degree of modification increases if the sample is longer exposed to the plasma. However, when performing a normal deposition in the rf plasma reactor, the degree of modification will be much smaller because deposited $\text{SiO}_2$ will hinder the modification carried out by radicals and ions. Also, the plasma chemistry will be different when HMDSO is injected, leading to different reaction routes and rates, and possibly to a lower radical density due to the consumption of oxygen radicals by HMDSO. In the case of ETP deposition on the other hand, the degree of modification may be larger due to continued modification during the first stages of growth. This discussion leads to the conclusion that, during a typical deposition, the PEN is modified to a lesser degree in the rf plasma reactor than in the ETP reactor. Together with a lower flux of modifying/etching species, this can account for the fact that an interphase is observed in ETP-deposited films but not in rf plasma-deposited films.

The main change of the modified polymer with respect to the pristine PEN, not concerning etching as it cannot be detected with XPS, is the reduced contribution of aromatic carbon. At the same time, the contribution of the C-O bond increases in both the C- and the O-spectrum. Together, this suggests the insertion of functional groups (e.g., OH) in the aromatic rings. Many other reactions, like hydrolysis of the ester (which is the most susceptible point towards etching [82]) and opening of the aromatic rings possibly occur simultaneously. Figure 6.6 shows the structure of PEN and a suggestion of the structure of the modified PEN. These observations correspond with the results of Holländer et al. [22], who found that carbon oxides, vinyl groups and phenol groups are the main reaction products of PET due to VUV irradiation in an oxygen atmosphere.
Table 6.3 lists the depth of modification as calculated using the XPS signal of aromatic carbon (284.7 eV) and Equations (3.23) and (3.24), assuming a discrete transition from the pristine PEN substrate to the overlayer of modified PEN. It is assumed that in modified PEN, six phenol groups are inserted per monomer unit, i.e. as much as can be inserted without compromising the aromatic character of the polymer. Thus, in modified PEN, only four instead of ten carbon atoms per monomer unit contribute to the signal of aromatic carbon at 284.7 eV. These data show that atomic oxygen plays a major role in the modification: exposure to an Ar/O2 plasma leads to significant modification and the modification is smaller if HMDSO, which consumes ions and thus decreases the atomic oxygen density, is added to the plasma. Furthermore, the modification is observed to be more pronounced if the shutter is open, which is easily explained with the larger radical flux and the assistance of (V)UV radiation.

Table 6.4. The surface free energy of pristine PEN and PEN that is modified in the ETP and in the rf plasma reactor, as calculated from contact angle measurements.

<table>
<thead>
<tr>
<th>Plasma</th>
<th>Treatment</th>
<th>Thickness modified film (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rf plasma</td>
<td>5 s rf O2 plasma</td>
<td>1.2</td>
</tr>
<tr>
<td>ETP</td>
<td>15 s Ar/O2/HMDSO plasma, shutter closed</td>
<td>1.4</td>
</tr>
<tr>
<td>ETP</td>
<td>15 s Ar/O2 plasma, shutter closed</td>
<td>1.6</td>
</tr>
<tr>
<td>ETP</td>
<td>20 s Ar/O2 plasma, shutter open</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 6.4 shows, the dispersion component decreases slightly from 48 mN/m to 44 and 42 mN/m respectively. As with XPS, the modification of the rf plasma-modified sample appears to be similar but slightly smaller than the ETP-modified sample.

6.3 SE study of the modification mechanism

The previous sections have shown that an interphase is formed in the ETP plasma, but not in the rf plasma, and that this difference may be caused by a higher degree of modification of the polymer.
Because the interphase is likely to affect the properties of the composite, like the adhesion and the barrier properties, it is important to have control over this region. Knowledge about the modification mechanism and the influence of the modification on the film growth is essential in this context. The possible causes for modification of a polymer by plasmas are radicals, UV photons and energetic ions. The latter seems to be of little importance for ions with a relatively low energy (<10 eV) in the low density rf plasma, because an interphase is absent in the rf-deposited films but present in the ETP-deposited films and because the PEN is modified to a lesser extent by the rf plasma (sheath voltage = 10 V) than by the ETP plasma (sheath voltage ≈ 2 V). The two remaining species, UV photons and radicals, can be classified according to the energy of the photons and the type of radicals, respectively.

For example, Holländer et al. [22] demonstrated that the modification rates are much higher if \( \lambda_{\text{radiation}} < 310 \text{ nm} \) (i.e. \( E_{\text{radiation}} > 4 \text{ eV} \)), as such photons have sufficient energy to break chemical bonds. Furthermore, differences in reaction types were found between modification in an oxidizing and in a non-oxidizing environment, which indicates that the type of radical has a significant influence. As the atomic oxygen (AO) flux at the substrate in the ETP Ar/O\(_2\)/HMDSO plasma is high compared to the depositing flux (\( \Phi_{\text{dep}} = 4 \times 10^{19} \text{ m}^{-2} \text{s}^{-1} \); \( \Phi_{\text{AO}} = 3 \times 10^{22} \text{ m}^{-2} \text{s}^{-1} \) [29]), a significant contribution of modification and etching by AO may be expected. Holländer et al. and other authors [22, 23, 83] also reported about the importance of a synergistic effect of radicals and UV irradiation. In this section, the role of UV photons and radicals and the influence of modification on film growth are further investigated with SE in the ETP setup.

**Modification**

The modification can be adequately modeled with various SE models. The bottom layer of all three models is the biaxially modeled substrate as measured prior to modification. The modification can be modeled as a Cauchy layer, as a BEMA roughness layer consisting of 50% PEN and 50% voids or as a graded layer, which gradually changes from 100% PEN to 100% voids. All three models yield the same fit quality and so-called modification thickness, except that the single Cauchy model always results in about half the thickness with respect to the other two models. Since SE is not very sensitive to the refractive index of very thin films (\( d < 10 \text{ nm} \)), \( A_\varepsilon \) and \( B_\varepsilon \) are fixed at 1.40 and \( 10^{-3} \text{ \mu m}^2 \) respectively and only the thickness \( d \) is fitted. Although no indications for an increased surface roughness are found with AFM, the roughness model may still represent the true modification. After all, the BEMA layer does not necessarily represent a rough surface, but can also represent an increased micro-porosity, which would not be detected by AFM. The modification thicknesses mentioned in the remainder of this chapter are as obtained with the single Cauchy model.

First, the role of UV photons is investigated. The stainless steel shutter is replaced by a quartz shutter with less than 10% absorption in the 180-1000 nm range. To exclude any interaction with radicals or energetic ions, the PEN substrate was completely surrounded by aluminum foil and the quartz shutter. The standard Ar/O\(_2\)/HMDSO plasma was ignited for 50 seconds and, with a new substrate, for 5 minutes. For the latter sample, no HMDSO was injected to prevent considerable deposition on the reactor walls. The modification time of 50 seconds was chosen to approximate the amount of modification due to UV radiation during a standard deposition of 100 nm SiO\(_2\); because silicon oxide is transparent, UV photons can modify the polymer throughout the deposition. The modification thickness amounts to 1.3 nm after 50 seconds and 2.4 nm after 5 minutes. It is striking that the modification can be modeled with such a thin film with a lower refractive index than the substrate, because Bergeron *et al.* [19] report that SE shows an increase of 1-2 % over a depth of 40-200 nm in the refractive index due to plasma exposure. This is ascribed to cross-linking of the polymer (polycarbonate). In our case however, it is impossible to obtain a proper fit using a higher refractive index and/or a thicker film. Furthermore, it is remarkable that the UV photons, having a penetration depth of 30-200 nm in polymer [24], only modify such a thin layer. This apparent contradiction between literature and the expectation that UV photons modify the polymer throughout a depth of 30-200 nm on one side and our SE results on the other side may be explained with a synergistic process involving e.g. oxygen atoms or molecules at the surface. These may have been available due to incomplete vacuum and leaks in the enclosure of aluminum foil. In that case, the modification is caused by radicals rather than by UV photons, and therefore, the direct influence of UV photons has been negligible during these experiments. It is important to stress here that the influence of UV...
irradiation is likely to be larger than presented here, because photons with a wavelength smaller than 180 nm were not present in this experiment. Although photons with a larger wavelength are absorbed by and interact with PEN as well (see the absorption peaks the 240-350 nm range in Figure 3.17), photons with a lower wavelength correspond to a higher energy and may therefore be more important. The importance of VUV irradiation of polymers (λ <180 nm) is reported by Truica-Marasescu [24], who showed that it leads to bond scission and etching. Such photons are certainly generated by the Ar/HMDSO/O₂ plasma, as argon exhibits two strong resonance lines at 104.82 and 106.67 nm [84], and as hydrogen has a rich emission spectrum in the 125-175 nm region [85], although the latter emission band is quenched by the presence of oxygen [86]. Nevertheless, the influence of (V)UV radiation without the assistance of other species (e.g. oxygen) on the interphase formation appears to be limited, as Chapter 5 reports an interphase thickness of only 8-15 nm, which is much smaller than the penetration depth of (V)UV radiation.

To study the modification by different types of radicals, different plasmas have been ignited. At regular time intervals, the plasma is switched off to perform a SE measurement. In this way, the modification thickness from the fit with the single Cauchy model is monitored as a function of modification time. As the standard Ar/O₂/HMDSO plasma contains three types of non-depositing radicals (O, OH and H)¹, this experiment is performed with the various plasmas shown in Table 6.5. Each of these plasmas contains one or more types of those radicals. The oxygen and hydrogen flows in the O/OH/H plasma are optimized to maximize the ratio of the OH to O intensity as measured with Optical Emission Spectroscopy (OES).

Table 6.5. To investigate the role of the various radicals and UV photons, PEN substrates are modified in the plasmas listed in this table.

<table>
<thead>
<tr>
<th></th>
<th>Ar flow (scs)</th>
<th>O₂ flow (scs)</th>
<th>H₂ flow (scs)</th>
<th>HMDSO flow (scs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard HMDSO /O₂ plasma</td>
<td>100</td>
<td>5</td>
<td>-</td>
<td>0.25</td>
</tr>
<tr>
<td>O</td>
<td>100</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O, H, OH</td>
<td>100</td>
<td>1</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>100</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>UV only</td>
<td>100</td>
<td>5</td>
<td>-</td>
<td>0.25 (50 s) / - (5 min.)</td>
</tr>
</tbody>
</table>

Figure 6.7 shows the results of these modification experiments. One series has been carried out with the stainless steel shutter closed, so with the polymer exposed to long-life radicals only. The other series has been carried out with the shutter opened, i.e. with the sample exposed to both radicals and (V)UV radiation. The plasma is ignited with the shutter closed and after ten seconds, when the plasma is stable, the shutter is opened. Without HMDSO available to quench the plasma, the heat load is such that the samples cannot be exposed for more than a couple of seconds at a time. Therefore, this cycle was repeated a number of times for each of the substrates. Before starting a new cycle, the sample is cooled down to 50 °C for ten minutes.

¹ This is determined by Optical Emission Spectroscopy (OES). The OES spectrum is displayed in Appendix B.
Figure 6.7 shows that all plasmas modify the polymer faster than (V)UV irradiation alone, so both the H and the O radicals contribute to the modification of the polymer. The modification by the hydrogen plasma is very fast compared to the modification by the other plasmas. This high modification rate can be due not only to the action of H radicals, but, to a limited extent, also to a higher VUV intensity when no oxygen is present [86]. Nothing can be concluded regarding the role of the OH radical, since the O₂/H₂ plasma and the standard HMDSO plasma contain O and H radicals as well. The figure also shows that with the shutter closed, all plasmas yield a modification thickness in the 2.0-2.5 nm range after 10 s of plasma. This corresponds to the modification that, during a standard deposition, occurs before the shutter is opened and the deposition starts. With the shutter opened, the modification rate is much larger which is easily explained by the larger particle fluxes and the (V)UV irradiation. The initial modification rate by the Ar/H₂ plasma e.g. is about 0.5 nm/s. Since this is not negligibly small compared to the deposition rate of 2 nm/s, this indicates that modification can continue during the start of the deposition.

Finally, Figure 6.7 shows that after four minutes of hydrogen plasma and after ten minutes of oxygen plasma with the shutter closed, the modification thickness saturates at a thickness of 5 nm. With the shutter open, it appears that instead of reaching a saturation thickness, a constant modification rate of (0.030 ± 0.002) nm/s is reached in the case of the oxygen plasma. Since this modification rate is negligibly small compared to the SiO₂ deposition rate of 2 nm/s, no noticeable effect from this is expected on a possible subsequent deposition.

The fact that a saturation level is reached can imply two things. Either the modification is complete and stops, or equilibrium is reached between etching of the top layer and continued modification at larger depth. The former is very unlikely, since literature reports on the etching of polymers when exposed to oxygen radicals and/or (V)UV radiation [22-24]. Fozza et al. [23] report an etch rate of the order of 0.003-0.2 nm/s due to VUV exposure only (see also Figure 2.6), depending on the polymer, the VUV intensity and the VUV spectrum. A somewhat higher etch rate (0.01-0.3 nm/s) is found when the sample is placed in an oxygen environment, where it is exposed to both (V)UV radiation and radicals. As the upper limit of the etch rate is not negligible compared to R depos (2 nm/s), etching may indeed compete with deposition during the first stages of growth, especially in the view of the high ratio ΦAO : Φdep (~ 750) present in the plasma.

The saturation modification thickness \( d_{\text{mod}} \) is a measure for the depth of modification, i.e. the penetration depth of the radicals. \( d_{\text{mod}} = 5 \) nm is lower than the 15-40 nm (depending on the ion energy) reported by Logothetidis [82], who used SE for a study of the modification of PET by a Pulse DC N₂ plasma treatment. The difference can be attributed to the application of a negative bias voltage by Logothetidis. \( d_{\text{mod}} = 5 \) nm comes close to the modification thickness as obtained with SRIM.
simulations (8-20 nm, depending on the ion energy), although these simulations consider ions and not radicals. \( d_{\text{mod}} \) is also a measure for the time \( t_{\text{mod}} \) available for modification during a deposition, as radicals can modify the polymer only as long as their penetration depth is large enough to allow diffusion through the \( \text{SiO}_2 \) film. \( t_{\text{mod}} \) is estimated to be 2.5 s.

Table 6.6. Settings for the deposition of organosilicon-like films.

<table>
<thead>
<tr>
<th>Arc current</th>
<th>50 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon flow</td>
<td>25 sccs</td>
</tr>
<tr>
<td>HMDSO flow</td>
<td>0.25 sccs</td>
</tr>
<tr>
<td>Oxygen flow</td>
<td>0</td>
</tr>
<tr>
<td>Degree of ionization</td>
<td>6% [48]</td>
</tr>
<tr>
<td>( \Phi_{\text{AO}} )</td>
<td>(&lt; 2 (\pm 1) \cdot 10^{21} \text{ m}^{-2} \text{ s}^{-1} ) [29]</td>
</tr>
<tr>
<td>( \Phi_{\text{dep}} )</td>
<td>( 5 (\pm 1) \cdot 10^{19} \text{ m}^{-2} \text{ s}^{-1} )</td>
</tr>
</tbody>
</table>

This chapter concludes with an attempt to determine the penetration depth of radicals. To this end, the substrate is protected by first depositing a thin organosilicon-like (SiO\(_x\)C\(_y\)H\(_z\)) film with a very mild Ar/HMDSO plasma (see Table 6.6). No oxygen or hydrogen is required for such a deposition, so the atomic oxygen (AO) flux is much smaller \(< 2 (\pm 1) \cdot 10^{21} \text{ m}^{-2} \text{ s}^{-1} \) and thus the modification is expected to be much smaller. Moreover, no interphase formation has been detected with SE for depositions in the mild plasma conditions from Table 6.1 either (see Section 6.1), and during the organosilicon depositions the arc current will be lower, leading to the generation of less ions, thus decreasing the radical and ion densities and the UV intensity. Moreover, during the previous deposition experiments in the so-called mild conditions, the used oxygen flow was relatively high (16.6 sccs), and thus the AO flux was certainly higher than during deposition of organosilicon material using the parameters listed in Table 6.6. The organosilicon-like depositions are followed by an oxidation step using an Ar/\( \text{O}_2 \) plasma (shutter closed, conditions as in Table 6.5) in order to remove the carbon and hydrogen from the film. This way a \( \text{SiO}_2 \)-like film is obtained and it is ensured that, if subsequently an Ar/\( \text{O}_2 \)/HMDSO plasma is used to deposit a \( \text{SiO}_2 \)-like film, the optical properties of the sample change due to one process only, namely deposition. If oxidation would occur simultaneously with the deposition, interpretation of the data would be ambiguous, as both oxidation of the organosilicon-like film and growth of the \( \text{SiO}_2 \)-like film affect the SE spectrum.

Figure 6.8 shows the oxidation of a thin organosilicon film on a silicon substrate. The thickness remains 2.4 nm during the subsequent oxidation, but the refractive index decreases from 1.70 for the as-deposited film to 1.26 for the oxidized film. This is very low for silicon oxide, but this is assumed to be due to porosity, caused by the etching of carbon from the film. In contrast to the case on silicon substrates, on PEN it was not possible to keep the thickness of the organosilicon film constant during the oxidation, an indication for modification/etching of the polymer in spite of the organosilicon layer. Apparently, the penetration depth of the modifying/etching species exceeds the thickness of this organosilicon-like film (3.7 nm).

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\(^{1}\) This value is obtained in the same conditions as listed in Table 6.6, but with an additional oxygen flow of 1 sccs. The atomic oxygen flux is much smaller in the present study, where no oxygen is admixed.
Figure 6.8. Oxidation of the organosilicon-like layer on silicon (top) and on PEN (bottom). The bars indicate the film thickness; the refractive index is indicated with (m). The applied SE models are depicted next to the graphs.

Figure 6.9 shows the development of the refractive index of a thicker organosilicon-like film on PEN as a function of oxidation time. The film thickness (initially 14 nm) increases by only 1 nm during the oxidation, indicating that modification of the PEN during the oxidation is limited and is possibly induced by (V)UV radiation only. From this, the penetration depth of atomic oxygen is estimated at 10-15 nm, corresponding to the penetration depth of ions reported by Logothetidis [82]. The slow but steady decrease of the refractive index shows that the oxidizing species cannot reach the whole film immediately, like the case with the thin films from Figure 6.8, but that maybe the top has to be oxidized first, making it porous and providing access to larger depths. An alternative explanation is that the penetration depth of the oxidizing species is large enough to reach larger depths and maybe the PEN, but the volatile reaction products cannot emerge from the layer until the film porosity has increased.

Figure 6.9. Left: the refractive index and thickness of an initially 14 nm thick organosilicon layer on PEN as a function of the oxidation time. Right: the SE model used for the modeling of the refractive index.
A 106 nm thick SiO₂-like film (standard conditions) is deposited onto the oxidized organosilicon-like film from Figure 6.9. Figure 6.10 shows the results from a SE measurement. The fit quality is similar as for direct SiO₂ deposition on pristine PEN (Figure 6.2a). With 1.40 the refractive index is slightly lower than the one of SiO₂ on silicon (1.43), but this is attributed to a more porous growth of the film due to the porosity of the oxidized organosilicon film on which the SiO₂-like film was deposited. It is more important, that the refractive index of the film can be conserved for thin layers as well, contrary to the case of direct SiO₂ deposition on PEN. This is further proof for the protection provided by the organosilicon-like film, i.e. the penetration depth of the active species is indeed smaller than 15 nm, the thickness of the organosilicon-like film. It also provides another confirmation of the hypothesis that the higher refractive index of the thin film is caused by plasma-polymer interaction.

![Graph](image)

Figure 6.10. The real \(<\varepsilon_1>\) and the imaginary \(<\varepsilon_2>\) part of the complex pseudo-dielectric function \(<\varepsilon>\) of a 106 nm thick SiO₂-like film on 15 nm oxidized organosilicon (see Figure 6.9). The model used for the fitting is depicted to the right.
7 Influence of external substrate biasing

It is well known that external substrate biasing can be used as a tool to densify the silicon dioxide matrix [17, 18, 21]. In this chapter, its influence on the interphase is investigated, i.e. if biasing can be used as a tool to influence the interphase formation. Previous sections have shown that radicals, possibly assisted by (V)UV radiation, are more important than energetic ions, but that regarded ion with an energy \( E_{\text{ion}} \leq 10 \text{ eV} \). With biasing, ion energies up to 400 eV are used, which may be of much more importance. The biasing is likely to induce an increase in interphase width, because the energetic ions can penetrate deeper, initiate more reactions and break more bonds than unaccelerated ions. However, there is a chance as well that the interphase width decreases, because the ion bombardment densifies the film, thus providing a better protection for the polymer. Therefore, this chapter reports on a preliminary study of the effect of external substrate biasing on the interphase formation and the film properties.

The bulk is characterized first, so that an interphase can be identified as a region with properties different from both the SiO\(_2\)-like bulk and the PEN. Since no external bias system is available on the rf parallel plate reactor, all experiments with bias are carried out in the ETP setup. All depositions on PEN substrates in this section are carried out on substrates that were not deliberately modified prior to deposition. The modification prior to the deposition with and without bias is identical, because the biasing is not switched on until the shutter is removed and the deposition starts.

7.1 Rf bias

As rf biasing is the conventional way of applying an external substrate bias, the experiments are started with the rf bias. Figure 7.1 shows the refractive index of the SiO\(_2\)-like film on silicon substrates as a function of the rf bias power, as obtained with SE. The graph shows that the silicon dioxide has the highest refractive index and thus the densest matrix at a rf bias power of 5 W. This corresponds to a bias voltage of \(-50\text{ V}\) and is comparable with the optimum value reported by Martinu et al. [18]. According to Equation (3.9), the corresponding energy delivered by the ion bombardment is 60 eV per deposited SiO\(_2\) unit. For higher powers the negative effects of the ion bombardment (incorporation of hydrogen-rich species, high internal stress, sputtering) annul the beneficial effects (bond rearrangements, enhanced surface diffusion).

![Figure 7.1](image_url)

**Figure 7.1.** The refractive index of the SiO\(_2\)-like film (bars) and the bias voltage (\(U\)) as a function of the bias power. Note that the HMDSO flow is higher than in the standard conditions.

To investigate if the biasing indeed, like the increase of the refractive index suggests, has a positive influence on the barrier properties, the barrier properties of SiO\(_2\)-like layers on poly(ethyleneterephthalate) (PET) substrates deposited with various rf bias powers are determined. The results of these calcium tests are shown in Figure 7.2. The beneficial effect of the bias is confirmed: the barrier improvement factor (BIF), defined as \( \text{WVTR}_{\text{substrate}} \) divided by \( \text{WVTR}_{\text{substrate+barrier film}} \), increases from 2 without bias to 15 for a bias power of 8 W. A bias power of 8
W corresponds to a mean voltage of -70 V with a 20 V peak-to-peak oscillation. This optimal bias power of 8 W is higher than the 5 W that follows from the refractive index on silicon substrates. This is attributed to the voltage drop over the polymer substrate, which is a dielectric (Equation (3.6)). Due to this voltage drop, the actual bias voltage at the top of the substrate is smaller than the voltage measured at the substrate holder.

![Figure 7.2. The barrier improvement factor of SiO₂-like films on PET as a function of the bias power (bars) and the refractive index of SiO₂-like films deposited in identical conditions on silicon substrates (●), see also Figure 7.1.](image)

### 7.2 Ion Energy Selective bias

Rf bias results in a broad ion energy distribution function and ion production, so the influence of the ion energy is not separated from the influence of the increased ion flux. With Ion Energy Selective (IES) bias, the ion energy distribution function is much narrower and the ion production is much smaller (Figure 3.9). Thus, the dependence of the effect of the ion bombardment and ion energy on the film properties and interphase formation is studied with IES in a purer and more scientific way [61]. Biased and unbiased samples, deposited in the standard conditions, are characterized and compared with FTIR, SE, contact angle, AFM and XPS. First, thick films are characterized to obtain the bulk properties and subsequently thin films are analyzed to obtain information about the interphase.

**Bulk**

Figure 7.3 reports the refractive index of 200 nm thick SiO₂-like films deposited in standard conditions (see Table 3.1) on silicon substrates as a function of the bias voltage. A bias voltage of -60 V results in the optimal refractive index of 1.46, which corresponds to the refractive index of fused silica \((n = 1.457)\). This voltage is similar to the optimal bias voltage for rf biasing (-50 V, see Figure 7.1). In contrast to the results with rf biasing however, the refractive index continues to increase after it reaches its optimum value (1.457, the refractive index of fused silica) at a voltage of -60 V, indicating the formation of a highly stressed film. This different effect of large bias voltages is attributed to the fact that, due to plasma generation by the rf biasing (see also Figure 3.9), the ion flux is 4-10 times larger in the case of rf biasing than in the case of IES biasing. This large ion flux may cause damage rather than matrix densification.
Figure 7.3. The refractive index of 200 nm thick SiO$_2$-like films deposited in standard conditions on silicon substrates as a function of the IES bias voltage.

Figure 7.4 shows the bias signal of a -60 V bias. The slope of the ‘Difference’ graph amounts to -88V/ms. According to Equation (3.4) this corresponds to an ion flux of $5 \times 10^{19}$ s$^{-1}$m$^{-2}$. From the deposition rate a depositing flux of $4.4 \times 10^{19}$ s$^{-1}$m$^{-2}$ is calculated, resulting in an ion over SiO$_2$ flux of 1.2, which is somewhat higher than 0.78, the ideal value according to Martinu et al. [18]. Figure 7.5 shows the FTIR spectra of SiO$_2$-like films deposited in standard conditions on silicon substrates with and without IES biasing. No differences between the different bias voltages are observed. The SiOH bond densities are equal within the error of the fit procedure ($0.2 \times 10^{21}$ cm$^{-3}$; $1.5 \times 10^{21}$ cm$^{-3}$ for the unbiased film and $1.3 \times 10^{21}$ cm$^{-3}$ for the biased film (-60 V).

Figure 7.4. The voltage at the output of the amplifier and the voltage at the substrate holder.
Figure 7.5. The FTIR spectrum of a 350 nm thick SiO$_2$-like film on silicon deposited without bias and with a IES bias of -60 V.

Thick SiO$_2$-like films are deposited with IES bias on PEN as well. The bias voltage at the substrate holder was -60 V, but the voltage at the top of the substrate was smaller due to the voltage drop over the PEN. The voltage drop could have been calculated using Equation (3.6), had not an unknown constant been added to the signal of the output of the amplifier to display the signal more conveniently on the oscilloscope. However, SE shows the same increase in the refractive index as on silicon substrates: $n$ increases from 1.43 (no bias) to 1.46 (-60 V bias) for a film thickness of 113 nm, and thus indicates that the decrease in bias voltage due to the capacitance of the dielectric substrate is limited.

The surface free energy is calculated from contact angle measurements on 113-116 nm thick SiO$_2$-like films deposited onto PEN substrates with and without IES bias. As Table 7.1 shows, both the polar and the dispersion component are equal for both films. The surface roughness as measured with AFM is equal for the biased and the unbiased sample as well. With XPS no differences are detected either: both biased and unbiased samples are found to be stoichiometric and carbon-free (see Table 7.2). As it is observed that the bias increases the refractive index from 1.43 without bias to 1.46 at a bias voltage of -60V, it is concluded that the biasing densifies the matrix, but does not influence the chemical or morphological properties.

### Table 7.1. The roughness and surface energy of PEN and 113-116 nm SiO$_2$ on PEN.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>rms roughness (nm)</th>
<th>Polar</th>
<th>Dispersion</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEN</td>
<td>3.8</td>
<td>5</td>
<td>48</td>
<td>53</td>
</tr>
<tr>
<td>116 nm SiO$_2$, no bias</td>
<td>3.9</td>
<td>35</td>
<td>41</td>
<td>76</td>
</tr>
<tr>
<td>113 nm SiO$_2$, -60 V bias</td>
<td>3.5</td>
<td>36</td>
<td>40</td>
<td>76</td>
</tr>
</tbody>
</table>

### Table 7.2. The chemical composition of thick SiO$_2$-like films on PEN, with and without bias.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>SiO$<em>{2.00}$C$</em>{0.01}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No bias</td>
<td>116</td>
</tr>
<tr>
<td>-60 V bias</td>
<td>113</td>
</tr>
</tbody>
</table>

Thin films

Now that it is demonstrated that the bias affects the bulk properties, a closer look is taken at thin films and the effect of the bias voltage on the interphase. For this purpose, two thickness series are deposited on PEN: one without bias and one with an IES bias of -60 V. As Figure 7.6 shows, the roughness of both thickness series is similar. As the experimental error is estimated at 0.6 nm, the deviation of the
roughness of thin layers with respect to the roughness of the thicker layers is too small to draw conclusions about the development of the roughness.

Figure 7.6. The rms roughness as obtained from AFM measurements for biased and unbiased films.

Figure 7.7. The surface free energy of biased and unbiased samples as a function of the film thickness.

Figure 7.7 shows that the surface free energy of the biased thickness series reaches its bulk value at a thickness of 5.0 nm, whereas the unbiased thickness series has clearly not reached its final value at a thickness of 4.5 nm, suggesting that the interphase of the biased sample is thinner. However, insufficient data points are available in this critical region to reach an unambiguous conclusion. Therefore, XPS measurements are performed as well. The results are listed in Table 7.3. The results clearly confirm that the interphase is thinner for the biased thickness series: the biased 13 nm thick film contains only one third of the carbon of the slightly thicker 14 nm thick unbiased film. The biased 26 nm thick film still contains some carbon, so an interphase still forms. But apparently, the interphase is thinner for biased films than for unbiased films. The denser film may be responsible for this by quickly providing a good barrier for the radicals, thus protecting the polymer. These results confirm the hypothesis that ion bombardment not only influences the bulk properties of the film, but also the interphase formation, and thus ion bombardment can be used as a tool to control the interphase formation.
### Table 7.3. XPS results of biased and unbiased SiO₂-like films of various thickness.

<table>
<thead>
<tr>
<th>Thickness from SE (nm)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Si (%)</th>
<th>Composition</th>
<th>Thickness from XPS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no bias</td>
<td>14</td>
<td>26.2</td>
<td>49.9</td>
<td>SiOₓₓ₁₀Cₓ₀₁₀</td>
<td>4.5 ± 1.0</td>
</tr>
<tr>
<td>no bias</td>
<td>21</td>
<td>2.0</td>
<td>66.0</td>
<td>SiOₓₓ₁₅Cₓ₀₆</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>no bias</td>
<td>60</td>
<td>0.3</td>
<td>66.6</td>
<td>SiOₓₓ₀₁Cₓ₀₀₁</td>
<td></td>
</tr>
<tr>
<td>no bias</td>
<td>116</td>
<td>0.3</td>
<td>66.7</td>
<td>SiOₓₓ₃₁Cₓ₀₀₁</td>
<td></td>
</tr>
<tr>
<td>-60V bias</td>
<td>13</td>
<td>9.8</td>
<td>62.0</td>
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<td>0.6</td>
<td>66.1</td>
<td>SiOₓₓ₁₉Cₓ₀₂</td>
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<tr>
<td>-60V bias</td>
<td>113</td>
<td>0.3</td>
<td>66.5</td>
<td>SiOₓₓ₁₀Cₓ₉₀₁</td>
<td></td>
</tr>
</tbody>
</table>
8 Conclusions and recommendations

8.1 Conclusions

Silicon dioxide-like films have been deposited on PEN in an Expanding Thermal Plasma reactor and in an rf parallel plate plasma reactor. The presence of carbon and carbon-silicon bonds in thin ETP-deposited films, detected by means of XPS, has demonstrated the existence of an interphase of 10-15 nm thick. No conclusive evidence demonstrating the formation of an interphase in the rf plasma-deposited films is found and therefore, the interphase of films deposited by means of the rf plasma must be thinner than 5 nm. The difference in interphase formation can be rationalized by a lower ratio of the non-depositing radicals-to-depositing radicals flux and a lower (V)UV intensity in the rf plasma reactor. This decreases the relative importance of etching and/or modification with respect to deposition, resulting in a thinner interphase. Moreover, during ETP deposition sufficient time is left to long-life radicals to interact with the polymer before the deposition starts.

The plasma-induced modification of the polymer has been investigated from a chemical point of view by means of XPS. It was found that the modification in the ETP reactor and in the rf reactor is similar and leads to the insertion of oxygen-containing functional groups. In the ETP reactor, SE is used to investigate the modification from an optical point of view. Different plasmas are used to investigate the role of the different types of non-depositing radicals (O, OH, H) present in the Ar/HMDSO/O2 plasma. The modification thickness amounts to 2-2.5 nm after 10 s of plasma (shutter closed), demonstrating that significant modification occurs before the start of a deposition. Thus, the interphase development starts before the deposition due to the action of long-life radicals. The interphase further develops during the deposition due to the action of non-depositing radicals and (V)UV photons. With the shutter open, the modification rate is much higher due to the larger particle flux and the higher (V)UV intensity. In this case, the initial modification rate (0.5 nm/s) is not negligible compared to the deposition rate of 2 nm/s, indicating a competition between modification and possibly etching on one hand and deposition on the other hand during the early stages of film growth, which can lead to the formation of an interphase. Both with the shutter open and closed, the modification saturates at a thickness of 3.5-6 nm. This indicates either that the modification is complete or, more likely, that equilibrium is reached between etching and modification.

SE has been used in situ for the investigation of the plasma-polymer interaction and the formation of an interphase in the ETP reactor. For relatively thick (d > 30 nm) SiO2-like films on PEN, the refractive index n equals 1.43 and matches the refractive index found for SiO2 on a silicon substrate. For films thinner than 10 nm however, no adequate fit can be obtained for n < 1.52. This means that this region is different from the bulk SiO2 and suggests that it contains carbon. Therewith, it points out to the formation of an interphase. No such effect is observed for SiO2-like films that are deposited in milder plasma conditions, i.e. in conditions with a lower O flux and less (V)UV production. This result demonstrates the importance of the ratio of the non-depositing radical to depositing flux on the interphase formation. The penetration depth of oxidizing species has been estimated at 10-15 nm.

A preliminary study of the role of energetic ions during ETP deposition of SiO2-like films is performed by applying an external substrate bias (rf and Ion Energy Selective bias). Rf bias was found to influence both the refractive index and the barrier properties, with -50 - -70 V as optimal bias voltage. Using the IES bias setup, the refractive index was found to increase from 1.43 for unbiased samples to 1.46 at a bias of -60 V, both on silicon and on PEN substrates. With XPS, FTIR and contact angle measurements, it is found that the chemical composition and the surface free energy of thick unbiased and IES biased (-60V) samples are equal. XPS measurements on thin films show, contrary to what was expected, that the interphase is thinner for biased samples than for unbiased samples. This may be attributed to the denser matrix of the film, which protects the polymer better from active species from the plasma. These results point out to the fact that ion bombardment cannot only be used to obtain a denser matrix, but also as a tool to control the interphase.

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8.2 Recommendations

Much more research is needed to fully understand the plasma-polymer interaction, the formation of an interphase and its influence on the adhesion and barrier properties. In this section, a few recommendations for further research are given.

- Etching and re-deposition of etched fragments are presumably responsible for the interphase formation. To determine the relative importance of etching with respect to deposition, the etch rates should be determined, e.g. by using a quartz crystal microbalance coated with a thin film of PEN. In this framework, it would also be useful to measure the (V)UV intensity at the substrate, so as to determine the importance of (V)UV radiation and enable comparison with the work of Truica-Marasescu [24]. More information about the role of VUV radiation can be obtained using a window with a lower cutoff wavelength \( \lambda_c \) than the quartz window \( \lambda_c = 180 \) nm used in this work, e.g. a MgF\(_2\) \( \lambda_c = 112 \) nm or a CaF\(_2\) \( \lambda_c = 120 \) nm window.

- In this work, the influence of ion bombardment on the interphase was studied for one bias voltage only. More information about the role of energetic ions can be obtained if the interphase formation is studied as a function of the ion energy.

- The accurateness of SE would improve if information about the refractive index of the PEN is available for wavelengths smaller than 500 nm as well, so that the range used for modeling can be extended from 500-1000 nm to the full range of the ellipsometer, i.e. 247-1000 nm. In order to enable real-time monitoring of the film growth and interphase formation, the deposition rate has to be reduced, such that the status of the sample is nearly constant during the acquisition time of one measurement.

- With SE, the plasma-polymer interaction, the film growth and the interphase development are studied from an optical point of view. Using \textit{in situ} Attenuated Total Reflection FTIR (ATR-FTIR), these processes can be studied, possibly simultaneously with SE, from a chemical point of view. The combined information from both diagnostics would give much more information about the modification and interphase development.

- The chemical composition profile of the interphase can be determined by means of XPS, using thin films and angle resolved XPS instead of detection at a direction normal to the sample surface only, as used in this work. Changing the angle of detection changes the sampling depth, which is proportional to the cosine of the angle of incidence, and thus it can be determined whether an element is present mainly at the surface or more at larger depths. Such a measurement could elucidate whether the interphase consists of modified PEN with a more or less discrete transition to the deposit, or of a gradual transition from the substrate to the organic film.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Symbol</th>
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<td>AFM</td>
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<tr>
<td>d</td>
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</tr>
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<td>E_k</td>
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<td>e</td>
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<td>Poly(ethyleneterephthalate)</td>
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<tr>
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<tr>
<td>$\Psi$</td>
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A XPS spectra

The XPS spectra belonging to the Chapters 4 – 7 are displayed in this Appendix. Table A.1 gives an overview of the samples.

Table A.1. An overview of the samples of which the XPS spectrum is shown in this appendix.

<table>
<thead>
<tr>
<th>No.</th>
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<th>rf-modification</th>
<th>ETP-modification</th>
<th>rf</th>
<th>ETP, no bias</th>
<th>ETP, no bias</th>
<th>ETP, no bias</th>
<th>ETP, -60 V</th>
<th>ETP, -60 V</th>
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<tbody>
<tr>
<td></td>
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<td>Substrate</td>
<td>SiO₂ thickness (nm)</td>
<td>C (%)</td>
<td>O (%)</td>
<td>Si (%)</td>
<td>Composition</td>
<td>C (%)</td>
<td>O (%)</td>
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<td>PEN</td>
<td>-</td>
<td>80.4</td>
<td>19.6</td>
<td>-</td>
<td>CO₂₀.₄₁</td>
<td>30.9</td>
<td>67.0</td>
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<tr>
<td>2</td>
<td>rf-modification</td>
<td>PEN</td>
<td>-</td>
<td>72.7</td>
<td>27.3</td>
<td>-</td>
<td>CO₂₀.₃₇</td>
<td>31.4</td>
<td>68.2</td>
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<tr>
<td>3</td>
<td>ETP-modification</td>
<td>PEN</td>
<td>-</td>
<td>71.1</td>
<td>28.9</td>
<td>-</td>
<td>CO₂₀.₄₁</td>
<td>31.7</td>
<td>68.1</td>
</tr>
<tr>
<td>4</td>
<td>rf</td>
<td>PEN</td>
<td>15</td>
<td>2.2</td>
<td>67.0</td>
<td>30.9</td>
<td>SiO₂₁₇C₀.₀₇</td>
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<td>5</td>
<td>rf</td>
<td>PEN</td>
<td>19</td>
<td>0.5</td>
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<td>31.4</td>
<td>SiO₂₁₇C₀.₀₁₃</td>
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<td>66.0</td>
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<td>rf</td>
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<td>SiO₂₁₅C₀.₀₁</td>
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<td>66.7</td>
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<td>7</td>
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<td>26.2</td>
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<td>12</td>
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<td>ETP, no bias</td>
<td>Si</td>
<td>116</td>
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<td>66.7</td>
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<td>ETP, -60 V</td>
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<tr>
<td>14</td>
<td>ETP, -60 V</td>
<td>PEN</td>
<td>113</td>
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<td>66.5</td>
<td>33.2</td>
<td>SiO₂₁₀C₀.₃₅</td>
<td>-</td>
<td>28.1</td>
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Figure A.1. No. 1: untreated PEN.
Figure A.2. No. 2: PEN that has been modified in the rf parallel plate reactor.

Figure A.3. No. 3: PEN that has been modified in the ETP reactor.

Figure A.4. No. 4: 15 nm SiO$_2$ (rf parallel plate reactor).
Figure A.5. No. 5: 19 nm SiO$_2$ (rf parallel plate reactor).

Figure A.6. No. 6: 84 nm SiO$_2$ (rf parallel plate reactor).

Figure A.7. No. 7: 14 nm SiO$_2$ (ETP reactor).
Figure A.8. No. 8: 21 nm SiO₂ (ETP reactor, no bias).

Figure A.9. No. 9: 60 nm SiO₂ (ETP reactor, no bias).

Figure A.10. No. 10: 116 nm SiO₂ (ETP reactor, no bias).
Figure A.11. No. 11: 14 nm SiO$_2$ on a silicon substrate (ETP reactor, no bias).

Figure A.12. No. 12: 13 nm SiO$_2$ (ETP reactor, -60 V bias).

Figure A.13. No. 13: 26 nm SiO$_2$ (ETP reactor, -60 V bias).
Figure A.14. No. 14: 113 nm SiO₂ (ETP reactor, -60 V bias).
B OES spectrum

Figure B.1. OES spectrum of the Ar/O₂/HMDSO plasma used in this work.

Table B.1. Attribution of the peaks from Figure B.1 [1, 2].

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References
1. \textit{NIST webbook of science; NIST Atomic Spectra Database.}