Surface Modification of Polypropylene (PP) by Argon Ions and UV Photons

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The surface modification of polypropylene (PP) by monoenergetic argon ions and UV photons is evaluated in a particle beam experiment. Thereby, the polymer pre-treatment in a plasma process can be mimicked. The etching and chemical modification of the spin-coated PP thin films is monitored in real-time by in situ Fourier transform infrared spectroscopy (FTIR). It is shown that the initial exposure to the plasma ion source causes a modification of the film surface, which slows down the initially high etch rate. The separately measured UV-induced damage is more severe compared to the oxygen-containing polymer polyethylene terephthalate (PET).

1. Introduction

Plasma treatment of polymers is used in many industrial processes to improve barrier properties or enhance scratch resistance by depositing a thin film on top or by modifying the polymer surface. One prominent example is the plasma-induced change of hydrophobicity as a prerequisite for subsequent dying, gluing or printing processes. In all these applications, an inherent interface layer at the polymer surface is formed in the very first phase of plasma treatment, when ions from the plasma impinge onto the surface and release their energy by collisions and recombination reactions which leads to chemical modification and etching. The resulting interface layer is crucial for many applications, because film adhesion, contact angles, and stress evolution are extremely sensitive to its properties.

The effects of ion bombardment on polymers have been investigated by several groups.[1–9] At the onset of plasma treatment, a high initial etch rate (ER) is observed, which decreases afterwards reaching a lower steady state ER depending on pressure, ion energy and ion flux. This is explained by the particle bombardment promoting the generation of an interconnected carbon network at the beginning of the process, which causes the sputter yield to differ significantly from the sputter yield for the pristine sample. Such an interconnected carbon network is dehydrogenated and as a consequence cross-linked due to the plasma-induced formation of open bonds. Although these studies give a good insight into the interaction between ions and polymers, no absolute yields can be derived because absolute flux densities are often not given.

Recently, surface processes during argon ion sputtering and oxygen treatment of polyethylene terephthalate (PET) by exposing the polymer to quantified beams of particles...
were investigated. Beam experiments possess the advantage of an independent control of particle fluxes, and a prolonged time scale of the surface processes, which allows the isolation of the different stages of polymer etching. It could be shown that the PET sputtering exhibits almost no threshold behavior in the energy of the incident ions. The complicated interplay between ion-induced damage in the topmost polymer and sputtering has been modeled by a set of balance equations. Excellent agreement has been found.

In this paper, a particle beam experiment is used to study the etching of polypropylene (PP) in comparison to the etching of polyethylene terephthalate (PET). Both polymers are very different in their internal structure as well as their expected susceptibility to ion and UV radiation from a plasma:

- **Structure**: The monomer of PET contains a ring structure and a significant amount of oxygen. The unsaturated hydrocarbons invoke some steric hindrance for the mobility of the polymer chains. The monomer PP is much simpler in comparison and contains besides the CH₂ backbone a large number of CH₃ side groups. For illustration see Figure 1.

- **UV absorption**: PET shows a strong absorption in the UV region due to the unsaturated carbons in the monomer, whereas PP exhibits a smaller absorption coefficient. This comparison, however, might be not so significant, since any argon plasma contains a significant amount of excimers, which generate very energetic UV photons at a wavelength of 104.9 and 106.7 nm.

- **Resistance to sputtering**: In the case of PET, the monomer contains already a significant amount of oxygen which facilitates the formation of volatile CO or CO₂ during a collision cascade of the incident ions. This connection is the basis of the scaling of the etch rate of oxygen containing polymers with their oxygen content expressed as Onishi-parameter. In addition, the formation of CO and CO₂ as volatile products represents also the explanation for the absence of a real sputtering threshold in ion energy. This situation is completely different for the case of PP, where it is expected that the incident ions will preferentially displace bonded hydrogen in the film. The formation of volatile compounds such as CH₄ or C₂H₆ requires a significant rearrangement of the atoms in the collision cascade, which implies a lower yield. Therefore, an efficient removal of the CH₃ side groups and of hydrogen in the PP polymer and an intense cross-linking of the remaining PP polymer backbone is expected.

In this work, PP films are irradiated with beams of Ar ions and VUV photons emitted from the very same ion plasma source. The surface modification is monitored by means of in situ FTIR and the results are interpreted in the context of a surface coverage model. The points above illustrate that the etch resistance of PET and PP is expected to be very different. This hypothesis is tested and quantified by using the beam experiment in this paper.

## 2. Experiment

### 2.1. Particle Beam Experiment

Etching of PP is studied in a particle beam experiment employing a beam of argon ions impinging onto a spin-coated PP sample. A sketch of the experimental setup is shown in Figure 2. It consists of an ultra high vacuum (UHV) chamber, which contains the plasma ion source, and a load-lock chamber. The base pressure is 5 × 10⁻⁷ mbar in the UHV chamber.

The argon ion beam is produced using a commercial electron cyclotron resonance (ECR) plasma ion source. Ions are extracted from the plasma using a double-grid system. A gas flow of 1 sccm, a plasma grid bias of V_b = 0–800 V determining the ion energies, and an extraction voltage of V_ex = −50 V are used. The argon ion flux density at the sample is calibrated by means of a Faraday cup, yielding 0.5 to 4 × 10¹⁴ cm⁻² s⁻¹. The absolute photon flux, expressed as Onishi-parameter.

![Figure 1. Chemical structure of PP a) and of PET b).](image1)

![Figure 2. Particle beam experiment with substrate holder and attached Faraday cup (1) and ECR plasma ion source (2). The infrared beam passes the chamber via windows (3) and (4) and impinges onto the sample at an angle of incidence of 70°. (5) valve; (6) load lock; (7) transfer rod. The base pressure is 5 × 10⁻⁷ mbar.](image2)
2.2. Sample Preparation

Polypropylene thin films are deposited on oxidized silicon wafers (thickness of the thermal oxide 1 μm) by spin-coating. The backside of the wafer is coated with an aluminum layer (thickness 300 nm) by magnetron sputtering. The spin-coating is performed following a modified version of the procedure reported by Song et al. [17] 1.6 g syndiotactic polypropylene (average molecular weight 174 000, Aldrich) is dissolved in 400 ml xylene while constantly stirring at 95 °C for several hours. A reflux condenser is used to prevent solvent evaporation. Prepared solution is cooled down to 50 °C prior to deposition. A drop of 150 μl of this solution is placed on the sample. The spin-coating is then performed at 3 000 rpm (ramp 1 000 rpm s⁻¹) for 60 s. Using this procedure, homogeneous thin films with a thickness of 30 ± 5 nm and a roughness of the order of 2–3 nm are deposited, as verified using atomic force microscopy (AFM). Such thin films are necessary in order to apply the method of in situ FTIR, as explained in the following subsection. The fabrication of these films was only possible by means of spin-coating, while the attempt of a direct deposition of stretched thin polymer foils failed. The spin-coated films are, in contrast to industrially used polymers, non-crystalline, but can be used as model system to study elementary surface processes.

2.3. Infrared Spectroscopy

The exposure of PP to the particle beams is monitored in real-time using in situ Fourier transform infrared spectroscopy (FTIR) in reflection mode at an angle of incidence of 70°. A very high sensitivity of FTIR is required, because ions and neutrals affect the PP surface only within a penetration depth of the order of a few nanometers at most. Therefore, a so-called optical cavity substrate (OCS) is used as a substrate to enhance the sensitivity. [18] An OCS consists of an oxidized wafer with an aluminum backside coating. The thickness of the oxide layer is adjusted to 1 μm being resonant to the infrared wavelength of the probing light. Thereby, any absorption inside a PP layer on top of this OCS causes a damping of this optical resonance and thus relatively large absorption signals can be observed. The sensitivity of OCS is comparable to that of multiple internal reflection (MIR).

At first, a FTIR background spectrum \( R_0 \) is taken. Then, the FTIR spectra \( R \) are continuously sampled during exposure of PP to the particle beams with a time resolution of 30 s. Each sample spectrum is referenced to the initial background spectrum. The etching of the film becomes visible as an increase in reflectivity at specific wavelengths characteristic for the removal of the absorbing chemical groups in PP. The OCS method can resolve reflectivity changes of the order of \( \Delta R/R_0 \approx 10^{-6} \) corresponding to the removal of sub-monolayers of PP.

The FTIR spectra are also affected by interference fringes, which appear as a very weak modulation of the baseline. Their influence on the spectra is small, because the etched film thickness is only of the order of 30 nm, which is much smaller than the FTIR wavelengths of the order of 10 μm. Therefore, a simple baseline correction is used to normalize the spectra to unity by inspecting regions where no absorption peaks appear. A typical series of consecutive normalized spectra (the time period in between spectra is 30 s) is shown in Figure 3. After the onset of the ion beam, the reflectivity \( R/R_0 \) is increasing, indicating the removal of specific CH₃ groups: a change at 2 916 and at 2 841 cm⁻¹ corresponds to stretching modes of CH₃ groups, a change at 2 950 and at 2 867 cm⁻¹ corresponds to stretching modes of CH₂ groups, respectively. The bending vibrations are located at 1 465 cm⁻¹ for CH₂ groups, and at 1 375 cm⁻¹ for CH₃ groups [19].

The reduction of the PP film thickness \( d \) during exposure to the particle beams can be calculated from the peak heights by correlating the change in IR signal with the change in film thickness. This is realized in a calibration experiment by completely etching a film with known thickness, as being determined by an AFM scratching method. The complete removal of this film becomes visible in FTIR by a saturation of the absorption peaks after an extended exposure to the argon ion beam. This absolute change in \( R/R_0 \) can then be correlated to the film thickness \( d \) of this layer. This conversion was done by evaluating the strong CH₃ peak at 2 916 cm⁻¹ where a signal change of 1% corresponds to an etched thickness of 2.7 nm.

This monitoring of the etching process in situ and in real-time has the big advantage of being non-intrusive and that the infrared light probes the complete film. This is superior to the common method of ex situ depth profiling of plasma treated polymers by XPS, [7] because the ion bombardment inside the XPS setup modifies and destroys the plasma-modified polymer surface.

2.4. Modeling

The etch rate during the exposure of PP to the plasma ion source is modeled with a very simple rate equation model based on a balance between the particle-induced cross-linking of the pristine PP film surface, the particle-induced sputtering of this cross-linked surface, and the particle-induced sputtering of the pristine polymer. For details see Ref. [10]. This modeling is performed separately for the ion- and the photon-induced modification. A yield \( Y_{\text{activation}} = Y_a \) is used to describe cross-linking of the pristine polymer, and \( Y_{\text{cross}} \), the sputter yield of the cross-linked surface, and \( Y_{\text{pristine}} = Y_p \) of the pristine polymer, respectively. It is assumed that
The balance equation for the coverage \( \Theta_{\text{pristine}} = \Theta_p \) of the pristine surface during the simultaneous treatment with argon ions and UV photons is:

\[
\frac{d\Theta_p}{dt} = -j_i Y_{a,\text{ion}} \Theta_p + j_i Y_{c,\text{ion}} \Theta_c - j_{\text{ion}} Y_{a,\text{UV}} \Theta_p + j_{\text{ion}} Y_{c,\text{UV}} \Theta_c
\]

(1)

and for \( \Theta_{\text{cross-linked}} = \Theta_c \) of the cross-linked surface:

\[
\frac{d\Theta_c}{dt} = j_i Y_{a,\text{ion}} \Theta_p - j_i Y_{c,\text{ion}} \Theta_c + j_{\text{ion}} Y_{a,\text{UV}} \Theta_p - j_{\text{ion}} Y_{c,\text{UV}} \Theta_c
\]

(2)

where \( \Theta_p + \Theta_c = 1 \). The surface site density \( n_0 \) refers to the areal surface density of atoms in the first monolayer. \( j_i \) denotes the ion flux density while \( j_{\text{ion}} \) denotes the UV photon flux density.

An excellent agreement between this simple model and the data can be achieved by adjusting the sputtering yields \( Y_{a,\text{ion}}, Y_{p,\text{ion}}, Y_{c,\text{ion}}, Y_{a,\text{UV}}, Y_{p,\text{UV}}, \) and \( Y_{c,\text{UV}} \). Modeling of the data is performed in two steps. In a first step, the UV-induced etch rate \( \text{ER}_{\text{UV}} \) is determined by solving Equation (1) and (2) with the ion flux density \( j_i \) set to zero and fitting it to an experiment using UV exposure of the polymer only:

\[
\text{ER}_{\text{UV}} = j_i Y_{p,\text{UV}} \Theta_p + j_i Y_{c,\text{UV}} \Theta_c
\]

(3)

In a second step, the UV photon sputter yields \( Y_{p,\text{UV}}, Y_{c,\text{UV}}, \) and \( Y_{a,\text{UV}} \) obtained from this fitting procedure are used to fit the etch rate \( \text{ER}_{\text{plasma}} \):

\[
\text{ER}_{\text{plasma}} = j_i Y_{p,\text{ion}} \Theta_p + j_i Y_{c,\text{ion}} \Theta_c + j_{\text{ion}} Y_{p,\text{UV}} \Theta_p + j_{\text{ion}} Y_{c,\text{UV}} \Theta_c
\]

(4)

during the combined UV and ion bombardment from the plasma ion source in order to determine the argon ion sputter yields \( Y_{p,\text{ion}}, Y_{c,\text{ion}}, \) and \( Y_{a,\text{ion}} \).

The applied fitting procedure is unique, because \( Y_p \) and \( Y_c \) determine the ERs in the beginning and during steady state of argon ion or UV photon exposure, respectively. \( Y_a \) determines the ion/photon fluence, which has to be reached before the fast initial ER goes over into the small steady state ER. In addition, a transport and range of ions in matter simulation (TRIM) of argon ion sputtering of PP is performed, which mimics the etching of an amorphous network with a stoichiometry of C_3H_6.

3. Results

3.1. Investigation of UV Effects

Any observed change in IR absorption caused by incident ions and/or photons may correspond to an alteration or a removal of the material. Only the latter contributes to the mass loss and to etching. The impact of UV photons may cause bond scission in the polymer network within the complete film leading to etching and/or an enhanced cross-linking of the polymer. Any cross-linking leads to a hardening, which may be desired for certain applications, but may also impede the mechanical flexibility of the as-deposited polymer. The impact of reactive species from the plasma (ions, radicals, electrons) occurs within a penetration depth of the order of a few nanometer at most, even for ions at energies of 1 keV. Consequently, the interaction zone of UV radiation and of ions can be very different.

For a thorough understanding of the plasma treatment of polymers, it is, therefore, mandatory to separate ion from photon-induced effects. This is investigated experimentally by adjusting the grid voltages of the plasma source to completely suppress the ion current, as verified by the Faraday cup. In this configuration, only UV radiation from the ECR argon plasma may reach the sample. It has to be emphasized that synergistic effects of UV photons and ions...
may also play a role during the plasma treatment of PP. However, in order to isolate such synergism, it would be necessary to quantify and vary the photon flux independently from the ion flux, which is at present impossible in this experiment. Figure 4 shows the loss in CH₂ groups from infrared spectroscopy, converted into an etched thickness of PP. As a comparison, the loss in carbonyl groups at 1720 cm⁻¹ from infrared spectroscopy for the UV-induced removal of PET is converted into an etched thickness of PET. One can clearly see that the effect of UV photons is more severe in the case of a treatment of PP compared to the treatment of PET.

This signal in Figure 4 is modeled assuming a UV photon flux of the order 10¹³ cm⁻² s⁻¹, as measured by Ren et al.¹⁴ for a large volume ECR plasma. This results in values for Yc,UV of the order 0.1, whereas Yp,UV and Ya,UV are ranging from 1 to 10. The fundamental question, however, remains whether the signal change in the case of PP corresponds to a real etching or just a modification of the polymer. Any decrease in etch rate with fluence of the incident species can be explained by two effects, which may also overlap: (i) the formation of a cross-linked surface layer, which makes the film more resistant against etching, or (ii) just a modification due to preferential etching of specific groups, which are efficiently depleted during exposure.

The contribution of preferential etching is analyzed by monitoring the temporal evolution of the signal of individual groups in infrared spectroscopy. In case of PP, this comparison is based on the reflectivity ratio \( r_{\text{CH}_2/\text{CH}_3} \) for the loss of the CH₂ side groups \( (R/R_0)_{\text{CH}_2} \) at 2 950 cm⁻¹ with respect to the loss of CH₂ groups \( (R/R_0)_{\text{CH}_2} \) at 2 916 cm⁻¹ in the PP backbone

\[
r_{\text{CH}_2/\text{CH}_3} = \frac{R/R_0}_{\text{CH}_3} - 1 \quad \frac{R/R_0}_{\text{CH}_2} - 1
\]

Figure 5 shows the ratio \( r_{\text{CH}_2/\text{CH}_3} \) for a two step process consisting of an UV treatment of PP followed by an argon ion bombardment at 800 eV to completely remove the film by sputtering (solid squares). This is compared with the ratio \( r_{\text{CH}_3/\text{CH}_2} \) for an argon ion bombardment at 800 eV from the very beginning including the UV radiation from the ion plasma source (open circles). In the limit of long exposure times at the very end of both experiments, the ratio \( r_{\text{CH}_2/\text{CH}_3} \) should be identical since it corresponds to the loss of the complete film and \( r_{\text{CH}_3/\text{CH}_2} \) is only characteristic for bulk PP. This is consistent with the data indicating \( r_{\text{CH}_2/\text{CH}_3} = 1.2 \) for bulk PP. A ratio of 1 would be expected for PP given the structure in Figure 1, but it has to be kept in mind that in this work IR absorption signals are studied, which still depend on the oscillator strengths of the individual groups.

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**Figure 4.** UV-induced etching during exposure of a PP and PET thin film to the plasma ion source with suppressed ion extraction. Modeling of the UV etch rate was performed assuming a UV photon flux of \( 5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1} \) resulting in \( Y_{c,\text{UV}} = 0.1, Y_{p,\text{UV}} = 2.3 \), and \( Y_{a,\text{UV}} = 3.0 \).

**Figure 5.** Temporal evolution of \( r_{\text{CH}_2/\text{CH}_3} \) according to Equation (5) during exposure of PP to UV only (0–48 min) followed by an argon ion bombardment at 800 eV (>48 min, solid squares) and a simultaneous treatment of PP with argon ions at 800 eV and UV photons from the very beginning (open circles).
Figure 5 clearly shows a strong change of $r_{\text{CH}_2/\text{CH}_3}$ after the onset of UV treatment (solid squares), indicating a modification of the material within the penetration depth of the UV photons. If that modification would reach saturation, the ratio of $r_{\text{CH}_2/\text{CH}_3}$ has also to reach 1.2 during steady state etching, because the removal of a PP sample with a modified surface leads to an IR signal change of the underlying PP only. During the initial phase of UV exposure $r_{\text{CH}_2/\text{CH}_3}$ changes significantly and approaches a value of 1.3. At 48 min of exposure, an argon ion bombardment at 800 eV is switched on, leading to an intense sputtering of the PP sample, as described below. This very high etch rate removes apparently the UV modified layer at the PP surface and the value of 1.2 indicating bulk PP is quickly reached. The change of $r_{\text{CH}_2/\text{CH}_3}$ after the exposure of the pristine polymer directly to the argon ion bombardment at 800 eV (open squares) is very short indicating the fast formation of a modified surface. A steady state etching is quickly reached, indicated by $r_{\text{CH}_2/\text{CH}_3}$ values of 1.2.

The decrease of $r_{\text{CH}_2/\text{CH}_3}$ by UV treatment or by ion bombardment corresponds to either a loss of CH$_2$ groups and/or a gain in CH$_3$ groups. This behavior can most easily be explained by a photon- or ion-induced scission of the C–C bonds in PP. This bond breaking causes a reduction of the molecular weight of the polymer chain, which increases the number of end groups in the plasma exposed polymer: the density of CH$_3$ end groups increases and that of CH$_2$ groups decreases. The absolute change in $r_{\text{CH}_2/\text{CH}_3}$ depends now on the total volume at the film surface that is affected and the comparison between the sputter rate and the rate of modification: (i) in the case of UV treatment only, the modified volume at the polymer surface is large due to the large penetration depth of the UV photons. If in addition, the etch rate is small, a large deviation of $r_{\text{CH}_2/\text{CH}_3}$ from the bulk value of 1.2 is observed; (ii) in the case of 800 eV argon ion bombardment, the modified volume at the polymer surface is small due to the small penetration depth of the ions of a few nm only. However, the sputter rate is very high so that the deviation of $r_{\text{CH}_2/\text{CH}_3}$ from the bulk value remains small, because the removal rate is much faster than the modification rate. This is exactly observed in the experiment shown in Figure 5.

This complicated interplay between UV radiation and ion bombardment could be optimally analyzed by devising an experiment where the ion beam is clearly separated from the UV photon beam. Since the used plasma ion source is an inherent UV emitter, such a separation requires a complicated ion beam bending unit, which will be implemented in the future. Here, the experimental strategy is based on keeping the UV background constant in all experiments by adjusting always an identical plasma power and pressure and only varying the energy of the extracted ions. Based on this approach, the change in $r_{\text{CH}_2/\text{CH}_3}$ for ion energies between 20 and 800 eV (same data as in Figure 5) is analyzed, as shown in Figure 6.

One can clearly see different deviations of $r_{\text{CH}_2/\text{CH}_3}$ from 1.2 indicating a modification of the polymer surface, which however obeys different time constants for different ion energies:

- At 20 eV (Figure 6a): $r_{\text{CH}_2/\text{CH}_3}$ changes vary rapidly in the beginning until $r_{\text{CH}_2/\text{CH}_3}$ reaches 1.2 corresponding to the fast formation of the modified polymer surface. The absolute sputter rate is very small due to the low ion flux at 20 eV and the low steady state sputter yield of $Y_e = 0.03$, as discussed below. At 100 and 200 eV (Figure 6b and c): $r_{\text{CH}_2/\text{CH}_3}$ is initially very high, similar to the experiment at 20 eV, but it decreases much slower indicating that the modification does not reach saturation so quickly. This may be explained by the higher ion flux at 100 eV and 200 eV and the higher steady state sputter yield of $Y_e = 0.15$. If the sputter yield is high, the underlying pristine polymer is continuously exposed to the UV photon flux and the UV photons.
3.2. Sputtering of PP by Argon Ions

In the following, the sputter yields of etching of PP by the argon plasma ion source are evaluated. The investigation of the UV-induced effects showed that a careful separation of plasma-induced etch rate $ER_{\text{plasma}}$ given by Equation (4) from the purely UV-induced etch rate $ER_{\text{UV}}$ given by Equation (3) is necessary. Figure 7 shows the etched film thickness of the spin-coated PP layers as a function of argon ion fluence for different ion energies. The slope of the time dependence of the etched film thickness with particle fluence corresponds to the etch rate by the plasma ion source $ER_{\text{plasma}}$. One can clearly observe a transition from a fast initial $ER_{\text{plasma}}$ to a lower steady state $ER_{\text{plasma}}$ consistent with the findings in the literature.[4,8,9] In addition, all steady state $ER_{\text{plasma}}$ are rather similar, although the ion energy is varied from 20 to 800 eV. As a comparison, $ER_{\text{UV}}$ by UV photons, as extracted from the modeling in Figure 4, is shown as dashed lines in Figure 7, which exhibits different slopes because the exposure times are different for different ion energies. In the case of the 800 eV argon ion bombardment, for example, a fluence of $3 \times 10^{17}$ cm$^{-2}$ is rather quickly reached so that the total exposure time to UV photons of the plasma ion source is short, rendering $ER_{\text{UV}}$ small in comparison to $ER_{\text{plasma}}$. In the case of lower ion energies of 200 eV and below, however, $ER_{\text{UV}}$ becomes comparable to $ER_{\text{plasma}}$, indicating a very small ion-induced sputter yield. By regarding the slopes of the etched film thickness with ion fluence, one might even conclude that $ER_{\text{plasma}}$ is dominated by UV-photons-induced etching at ion energies below 200 eV. This is very different to the case of PET sputtering, where the influence of UV-induced etching was observed to be small, but nevertheless a high sputter yield was obtained at low ion energies.[10]

Since the UV treatment of PP induces a significant modification, the modeling of the measured $ER_{\text{plasma}}$ is performed in a consecutive two step approach: first $ER_{\text{UV}}$ is calculated from fitting the experiment for UV exposure only, shown as dashed lines in Figure 7. Second, by keeping these fitted parameters $Y_{a,\text{UV}}$, $Y_{c,\text{UV}}$, and $Y_{p,\text{UV}}$ fixed, $ER_{\text{plasma}}$ is fitted by varying $Y_{a,\text{ion}}$, $Y_{c,\text{ion}}$, and $Y_{p,\text{ion}}$. The dependence of the parameters on energy is shown in Figure 8b and the modeled change in film thicknesses are shown as solid lines in Figure 7. Such a two step approach is not possible for ion energies below 200 eV since $ER_{\text{UV}}$ and $ER_{\text{plasma}}$ are almost identical, which introduces a very large error in the determination of $Y_{a,\text{ion}}$, $Y_{c,\text{ion}}$, and $Y_{p,\text{ion}}$. The most simple explanation for this coincidence of $ER_{\text{UV}}$ and $ER_{\text{plasma}}$ at low energies is the hypothesis that PP etching is dominated by UV-photons at energies below 200 eV (regime I in Figure 8), whereas it is dominated by physical sputtering above 200 eV (regime II in Figure 8). Since all surface processes are based on momentum transfer, a comparable threshold for each process is reasonable. Figure 8a shows also an apparent sputter yield by relating the steady state etch rate to the flux of incident ions. Such an apparent sputter yield can be used to quantify any plasma induced damage of a PP surface, because the ion flux emerging from a plasma is proportional to the UV-photons flux.
The modeled yields $Y_{p,\text{ion}}$ and $Y_{a,\text{ion}}$ are one order of magnitude higher than for $Y_{c,\text{ion}}$. This difference is necessary to model the initial transition between the fast ER to the slow ER in the experiments. Additionally, this large difference is consistent with the results from molecular dynamics simulations by Végh et al.\textsuperscript{[9]} The effective sputtering converts from a high initial sputtering of the pristine polymer proportional to $Y_{p,\text{ion}}$ to the steady state sputtering of the cross-linked surface proportional to $Y_{c,\text{ion}}$. The modeled sputter yields $Y_{c,\text{ion}}$ for the cross-linked surface show reasonable agreement with the values for $Y_{\text{TRIM}}$ (see Figure 5b). The high values for the sputter yields $Y_p$ and $Y_a$ are expected, because the PP surface consists of weakly interconnected long polymer chains, whereas TRIM models an amorphous solid assuming a strongly interconnected carbon network. As a result, a single bond breaking event within a collision cascade may release large polymer fragments in case of PP, whereas the removal of only single C atoms is most likely during the sputtering of a strongly interconnected carbon network. Therefore, the dynamic process of cross-linking, which is described by the presented model using three different sputter yields, cannot be represented by TRIM.

The ion-induced effects are assessed by a TRIM simulation for the argon ion impact on to a stoichiometry C$_3$H$_6$ sample. The nuclear linear energy transfer (LET) is corresponding to the sum of the phonon energy transfer and the binding energy transfer and is shown in Figure 9. The values for average displacements per ion are 0.1 and 4.6 for and ion energy of 50 and 400 eV, respectively. The results show that for an ion energy of 400 eV target atoms are efficiently displaced within a depth of about 4 nm while there is no significant atom displacement and most energy is transferred to phonons for an ion energy of 50 eV. This underlines the importance of UV photon induced damage in the low energy regime. The comparison to TRIM is, however, only a very rough estimate, since TRIM regards only an amorphous solid. In addition, any reactions due to electron energy transfer and due to recombination of the incident ions are not accounted for in TRIM.

![Figure 8](image1.png)

Figure 8. Ion energy dependence of the sputtering yields of PP: a) apparent steady state sputter yield determined from measured ERs shown in Figure 7; b) argon ion sputter yield determined from the model described by Equation (1)–(4); $Y_{\text{TRIM}}$ as being modeled using the TRIM code for argon sputtering of an amorphous solid with the stoichiometry of PP. Regime I denotes an ER dominated by UV photons, regime II denotes an ER dominated by physical sputtering.

![Figure 9](image2.png)

Figure 9. TRIM simulation showing the nuclear linear energy transfer (LET) of argon ions impinging on to a stoichiometry C$_3$H$_6$ sample in dependence of the target depth.
4. Discussion

During the initial exposure of PP to the plasma ion source, a fast decrease of the ER by one order of magnitude is observed. The transition to the steady state is completed at a fluence of approximately $10^{17} \text{cm}^{-2}$ for an ion energy of 200 eV and above. This steady state is reached when a highly cross-linked surface layer is formed during the treatment. The results are in good agreement with molecular dynamic simulations of the sputtering of polystyrol (PS) by argon ions, which revealed a strong decrease of the H:C ratio from 1 to 0.1 after a fluence of the same order of magnitude.\(^{[9]}\)

In the high energy regime the measured steady state sputter yields ($Y_s$) are in good agreement with values predicted by TRIM. However, at ion energies below 200 eV, the effect of UV photons that are inherently emitted by the plasma ion source dominate the ER. In this energy regime, a quantification of the argon ion sputter yields is not possible with the presented simple model, because ion flux densities as well as the expected sputter yields predicted by TRIM are too low to compete with the UV effects. Figure 4 illustrates that a UV fluence of a few $10^{16} \text{cm}^{-2}$ is necessary to form a highly cross-linked surface, which is of the same order of magnitude as for ions.

Most striking is the difference of the UV effect on PP compared to PET, which has been analyzed in a previous study.\(^{[10]}\) Friedrich et al.\(^{[11]}\) showed that the effect of plasma UV radiation on PET does not play an important role due to the limitation of the extensive ring cracking to a depth of about 4 nm. This limitation is not present in the case of PP which leads to an extensive modification of the polymer. Consequently, volatile radicals are formed by UV-photon impact which finally results in the measured high etch rate. The effect of UV photons on the polymer modification might even be enhanced due to reflection of incident UV photons at the silicon oxide interface of the substrate. The dominant contribution of UV photons to PP etching at low ion energies can be considered characteristic for the intense ECR argon plasma source. Depending on the ratio between UV photons and ions, this might be different for other plasma generation methods.

The role of the ion bombardment during PP sputtering versus PET sputtering might be, however, very different: (i) in case of PET, a significant sputter yield at very low energies has been observed,\(^{[10]}\) which has been explained by the formation of volatile CO or CO$_2$. Due to the similar mass of carbon and oxygen, incident ions are not expected to cause preferential sputtering so that the formation of CO and CO$_2$ is not suppressed by any ion-induced change in surface stoichiometry; (ii) in case of PP, however, incident ions preferentially displace light hydrogen atoms in PP, which hinders the formation of volatile products such as CH$_4$ or C$_2$H$_6$. The high etch rate of a chemical sputtering regime can only be achieved, if this preferential loss of hydrogen is compensated by an external flux of H atoms towards the surface, as being demonstrated in the literature.\(^{[20]}\)

The formation of a high concentration of methyl groups as shown in Figure 6 and a higher degree of cross-linking (as postulated to explain the ion-induced formation of an etch resistant surface layer of PP of the polymer surface) might seem contradictory. However, PP might become easily more etch resistant by a few cross-linked sites despite an increasing number of methyl groups. This is especially important, if one regards our model system of spin coated PP with very long polymer chains. The growing percentage of CH$_3$ groups indicates chain scissions of the PP monomer and hydrogenation of terminal carbon atoms. Apparently, the chain scission together with the release of hydrogen from side groups generates a kind of internal hydrogen source that could account for this additional hydrogen supply.

The dissociation energies of isolated C—H bonds and of C—C bonds is 4.2 and 3.6 eV, respectively. As a consequence, one might conclude that C—C bonds are more efficiently broken than C—H bonds. However, the ion-induced displacement of hydrogen and carbon in the collision cascade is much more difficult to assess, because the efficiency of bond breaking of C—H versus C—C depends also on the surrounding chemical structure of PP with its high number of terminal hydrogen atoms and methyl groups. Consequently, a significant modification of the hydrogen rich methyl groups is expected. Nevertheless, Figure 6 indicates a stronger loss of CH$_2$ groups rather than methyl groups shielding the CH$_2$ backbone. This is surprising. One might speculate that the loss of methyl groups is overcompensated by the formation of new CH$_3$ groups as a result of the breaking of the CH$_2$ backbone.

Summarizing one can state, that PP is severely altered by UV impact in comparison to PET leading to bond scission of the PP polymer chain. This is overlapped by the sputtering of PP by ion impact, which is consistent with sputter yields from TRIM calculations for ion energies above 200 eV. At lower ion energies, PP etching is dominated by UV radiation, whereas the sputter yield by argon ions is expected to be much smaller than for PET.

5. Conclusion

PP has been exposed to a plasma ion source providing argon ions at various energies and fluences as well as inherently emitted UV photons. In the initial phase of the treatment the etch rate is very high, but decreases rapidly by one order of magnitude to a lower steady-state etch rate. This transition is explained by a gradual
transformation of the pristine polymer into an interconnected surface layer. For ion energies of 200 eV and above, the sputter yields decrease from the order of unity in the initial phase to the order of 0.1 in steady state. At lower ion energies the effect of UV photons is dominating the surface modification process which hinders a quantification of ion sputter yields. It could be shown that the UV influence on PP is significantly different compared to PET, which is attributed to its much simpler chemical structure.

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