

RESEARCH ARTICLE

Influence of Gallium Focused Ion Beam on Polyethylene: Study of Molecular Damage

Maciej Paśniewski^{1,2}  | Claude Poleunis³ | Arnaud Delcorte³  | Rachel Terry⁴ | David W. Abmayr⁴ | Anton-Jan Bons⁵  | Dominique Schryvers² 

¹ExxonMobil Petroleum & Chemical BV, European Technology Center, Machelen, Belgium | ²Electron Microscopy for Materials Science (EMAT), University of Antwerp, Antwerp, Belgium | ³Institute of Condensed Matter and Nanosciences, UCLouvain, Louvain-la-Neuve, Belgium | ⁴ExxonMobil Technology and Engineering Company, Baytown Technology and Engineering Center, Baytown, Texas, USA | ⁵Kessel Consultants VOF, Leuven, Belgium

Correspondence: Maciej Paśniewski (maciej.pasniewski@exxonmobil.com)

Received: 6 February 2025 | **Revised:** 24 June 2025 | **Accepted:** 6 July 2025

Review Editor: Paul Verkade

Keywords: FIB-SEM | ion implantation | molecular damage | polymers | polyolefins | ToF-SIMS

ABSTRACT

Focused ion beam-scanning electron microscopy (FIB-SEM) is a microscopy technique that can be used to investigate the quality and structural properties of industrial materials such as polyolefins. An understudied aspect and possible drawback of the technique could be the implantation of the impinging ions under the sample surface and damage to the molecular structure, hindering its use as a sample preparation tool for surface-sensitive techniques. We systematically investigated the damaging effects of gallium liquid metal focused ion beam under grazing incident beam angle and various accelerating voltages on polyethylene. Changes in molecular structure and ion implantation depth were analyzed with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) depth profiling and optical profilometry. Our results show that the gallium ion beam causes significant damage to the polyolefin structure, which is especially observed as dehydrogenation of the molecular structure of the (sub) surface. These molecular products are concentrated in distinct sub-surface zones, where damage is coupled to the presence of implanted gallium from the FIB etching.

1 | Introduction

Focused ion beam-scanning electron microscopy (FIB-SEM) is a technique combining methods of site-specific micromachining by FIB with high-resolution imaging with electrons by SEM, both down to the nanometer scale. It has become a well-established technique in materials and polymer research, widely employed for in situ (serial) cross-sectioning and high-resolution imaging. Additionally, it serves as a versatile sample preparation method for a range of advanced characterization techniques, including Transmission Electron Microscopy (TEM) (Bals et al. 2007), Atom Probe Tomography (APT) (Eder 2021; Schmidt et al. 2018), Atomic

Force Microscopy (AFM) (Virgilio et al. 2005), AFM-Infrared Spectroscopy (AFM-IR) (Baden 2015), and Secondary Ion Mass Spectrometry (SIMS) (Tiddia et al. 2019). Conventional FIBs, still constituting over 50% of the market, use a liquid metal ion source of gallium, while novel instruments use inductively coupled plasma technology, making a variety of ion species available, such as Xe (Smith 2006), O₂, N₂, and Ar (Gannon 2019). Initially developed for the semiconductor industry (Melngailis 1987), the technique has found its way to other materials research fields and is emerging in fields with “softer” materials, such as biomedical (Drobne et al. 2007; Kerstens 2020) and polymer research (Ohtake 2013). Despite its contributions (Akabori et al. 2009; Brostow et al. 2007; Guo

et al. 2023), the fundamental impact of the ion beam on the molecular structure of soft sample surfaces has not yet been studied extensively, especially for organic matter and specifically polymers.

Polymers are a crucial component of daily life produced at a scale of 10^{20} kg per year globally, out of which half of all industrial polymers are polyolefins, such as polyethylene, polypropylene, and associated rubber compounds (Plastics—the Facts 2022). Continuously improving technologies provide stronger materials, allowing down-gauging and light-weighting. The development of new materials with improved properties is guided by an in-depth understanding of the microstructure of the materials at a molecular and supra-molecular scale. An important question is whether the FIB-SEM ion beam, when used for, e.g., TEM or AFM sample preparation, will damage the surface to be imaged or analyzed, as this can change the original microstructure (García-Borquez 2023).

Previous studies on ion implantation and accompanying damage were mainly focused on plasma immersion of polymers and functionalization of those products. Various studies have analyzed implanted polymers using Ultraviolet-visible spectroscopy (UV-vis) (Chhokkar et al. 2021; Chawla et al. 2017), Raman Spectroscopy (Veres 2005), Attenuated Total Reflectance-Fourier-Transform Infrared Spectroscopy (ATR-FTIR) (Chhokkar et al. 2021), Electron Paramagnetic Resonance (EPR) (Popok et al. 2001), X-Ray Photoelectric Spectroscopy (XPS) (Popok et al. 2001), and X-Ray Diffraction (XRD) (Kondyurin and Bilek 2015), each showing in a different way that the material is altered at the surface and in the subsurface region.

The UV-vis studies show that changes in transmittance are due to ion implantation, even causing discoloration under high ion fluence (Chhokkar et al. 2021; Chawla et al. 2017). Raman spectra show graphitic peaks (Veres 2005), while infrared studies show attenuation of C-H vibrations and an increase in C=C bonds. Evidence from studies with EPR and XPS (Popok et al. 2001), and XRD (Kondyurin and Bilek 2015) show reduced crystallinity in ion irradiated species. As a result, ion beam treatment can influence the material's final mechanical properties (Sasuga et al. 1991), electrical conductivity (Irfan 2019), adhesion (Mesyats et al. 1996), and surface functionality (Švorčík et al. 1998).

The degradation of polyolefins has also been investigated using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), where the damage was dependent on the nature of the investigated polymer and the ion dose used for the investigation. A collision cascade caused by the ion beams results in ion collisions well below the surface, breaking bonds which rearrange during a pseudo-graphitization process. A fairly low dose of ion bombardment can thus cause a complete damage to the polyolefin structure (Delcorte et al. 1995; Gilmore and Seah 1996). While previous research has examined the general damage caused by the used ion beams, it did not investigate depth profiles of the identified species or their correlation with the implantation of the ion beam used.

Prior to Molecular Dynamics simulations (Duffour 2010; Delcorte et al. 2013) the interaction between ions and the crystal

structure in which they become embedded was not well understood. However, polyolefins are semi-crystalline materials that are challenging to model, and the used models consider either the crystalline or the amorphous part and are not fully representative of the entire material.

Moreover, the plasma studies described above were concentrated on the general effects of ion beams in polymer materials without considering any spatial resolution. Additionally, the typical ion dose (fluence) used in the FIB is 10^{19} ions/cm²—three to five orders of magnitude higher than in the aforementioned investigations (Delcorte et al. 1995).

This study evaluates the preparation of cross sections in Low-Density Polyethylene (LDPE) at various conditions, and subsequent in-depth analysis of their molecular nature with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and optical profilometry. To our knowledge, the effects of the focused ion beams in polymers have not been studied in such detail yet at the molecular level, and especially not with techniques such as ToF-SIMS. The goal of this study is to provide a fundamental understanding of the molecular changes at and near the surface of FIB-prepared cross sections, which is relevant to the interpretation of analytical data obtained from surfaces of beam-sensitive materials, such as polymers.

2 | Experimental Methods

2.1 | Sample Preparation

Plaques of low-density polyethylene (ExxonMobil LDPE LD 100.BW, ExxonMobil Chemical Europe LLC) were cryofaced using a cryo-ultramicrotome (Leica Ultracut UC7/FC7) to create a smooth and clean initial surface for FIB-milling. The samples were flash coated with a 5 nm layer of carbon in a Quorum Q150R ES plus sputter coater to make them conductive, thus reducing charging in the vacuum chamber of the FIB-SEM.

Traditionally, sample preparation with FIB is carried out under normal incidence of the ion beam with respect to the sample surface, as shown in Figure 1a. To produce a cross section, the bulk of the material is removed rapidly with a high energy ion beam (30 keV, 10–20 nA) creating a trench, followed by one or more steps using a lower energy beam (<5 keV, 200–700 pA) parallel to the surface of interest (Reyntjens and Puers 2001). To prepare a thin electron-transparent section for TEM analysis (Figure 1b), a second trench, adjacent to the first trench, is made and the resulting thin section is lifted out (Mayer et al. 2007).

For imaging a cross-section in SEM, including serial slice-and-view 3D imaging (Reyntjens and Giannuzzi 2007; Kizilyaprak 2014) the surface of interest forms one of the walls of the trench created by the FIB.

Because the goal of this study is to analyze the newly created surface by surface analysis techniques, we created sections by FIB under grazing incidence, where the ion beam is at 2° to the sample surface—i.e., (sub)parallel to the original surface of the sample (Figure 1c). We also made the sections wide enough to be compatible with the spatial resolution of the surface analysis

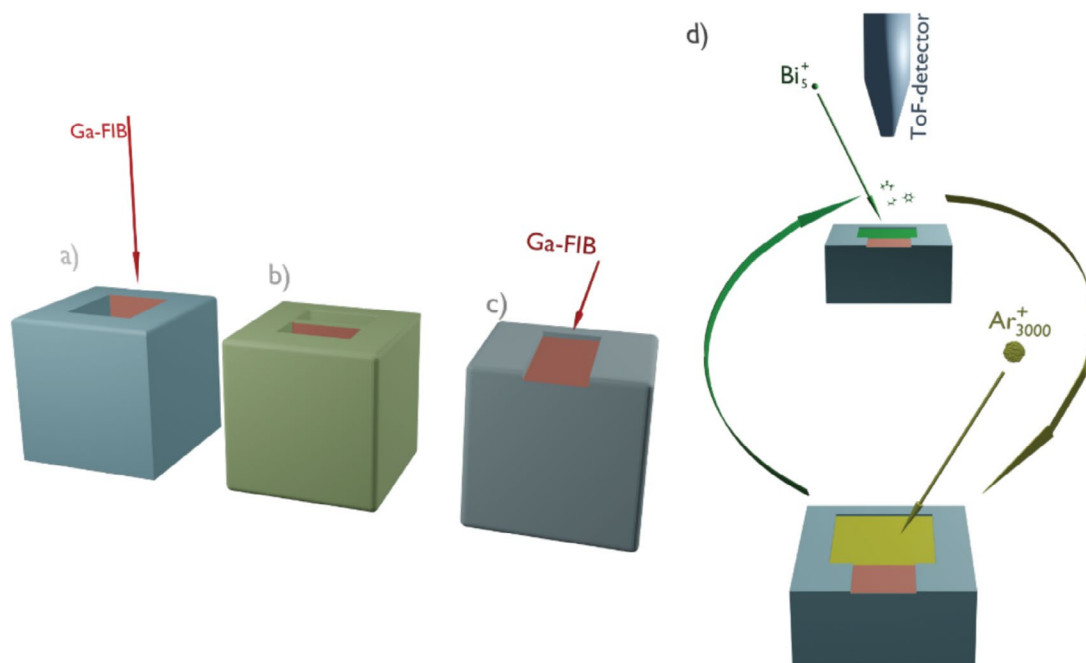


FIGURE 1 | (a) Schematic representation of the FIB geometry of a conventional cross section in the bulk of a sample, and (b) representation of a FIB trench for a TEM lamella. (c) To expose the surface of the cross section for further analysis, incident FIB angle is changed to a shallow grazing angle (2°). (d) Schematic representation of ToF-SIMS depth profiling experiment. The primary Bi_5^+ -beam creates secondary ions, captured by the ToF analyzer, alternated with sputtering Ar_{3000}^+ -beam which sputters the surface to expose the next layer.

TABLE 1 | Overview of Ga FIB milling conditions used.

Incident angle	Accelerating voltage	Beam current
2°	30 keV	21 nA
2°	16 keV	11 nA
2°	10 keV	6.5 nA
2°	5 keV	3.5 nA

technique (e.g., hundreds of micrometers wide, while a typical TEM section is in the order of 10 μm wide). This simulates the conventional cross-sectioning techniques mentioned above, where the ion beam is sub-parallel to the section surface in the FIB trench (Figure 1a).

FIB milled surfaces were prepared with a Helios NanoLab G3 UC DualBeam (Thermo Fisher Scientific Inc.) equipped with a gallium liquid metal ion source at conditions listed in Table 1.

2.2 | Analysis

2.2.1 | ToF-SIMS

The ToF-SIMS depth profiling measurements were performed with a TOF.SIMS 5 (IONTOF GmbH) instrument. The primary analytical beam used Bi_5^+ ions at 30 keV/0.04 pA, and the sputtering beam used Ar_{3000}^+ -clusters at 10 keV/3 nA, as shown in Figure 1d. Depth profiles were acquired in non-interlaced mode, employing a 3.28 s sputter and an 8.5 s pause. The analytical cycle

employed 1 shot/pixel/frame and 1 frame/cycle, set to 200 μs /cycle. The primary ion dose density (PID) for one cycle was 8.18×10^5 ions/ cm^2 , well below the static limit for organic polymers (McPhail 2006). The analytical beam used a random raster to avoid accumulation of charge and potential damage from the analytical beam (Cushman 2018). The sputtering process is presumed to be uniform, but roughness during analysis is always induced (Ekar and Kovač 2022). The Bi_5^+ analytical beam will create surface damage, but it has been established that the subsequent depth profiling step with the Ar_{3000}^+ Gas Cluster Ion Beam (GCIB) removes this damage layer before the next analytical cycle starts (Tiddia et al. 2019; Iida 2018). Spectra post-processing and peak identification were done with SurfaceLab 6 software (IONTOF GmbH). From all spectra, a list of representative secondary ions (molecular fragments and elements) was selected for all tested parameters.

2.2.2 | Optical Profilometry

During the depth profiling experiment, the response of the secondary ion signal is collected as a function of sputter time. Each datapoint is collected over a certain amount of time, dependent on ion fluence. To assess the final depth of the ToF-SIMS profiling crater, optical profilometry was used utilizing a Bruker ContourX-100 system (Bruker Nano GmbH). The step height between the unaltered surface of the sample and the bottom of the profiling crater was calculated using instrument software.

The calibration of the depth profiling is shown in Figure 2. The final depth of the ToF-SIMS depth profiling was extracted based on the step height measurement between the edge of the sputter crater and the bottom of the FIB trench.

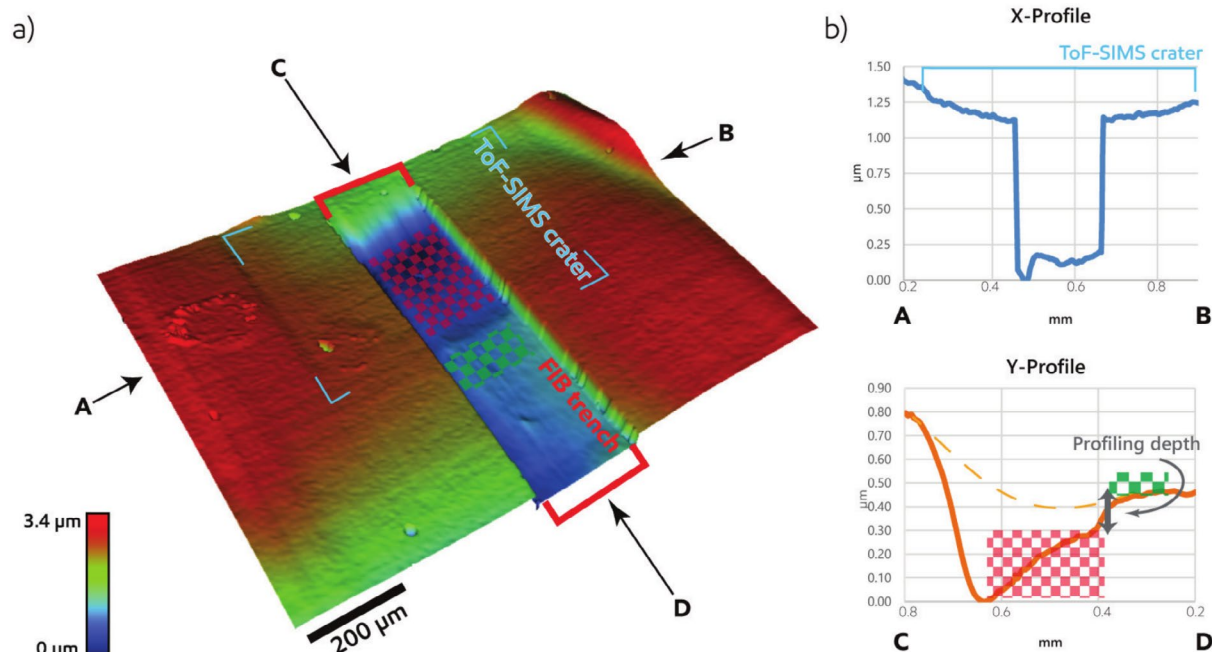


FIGURE 2 | Optical profilometry result: (a) the corners of the ToF-SIMS sputter crater are indicated with light blue lines and the FIB trench with red brackets. The dark blue area in the top part of the FIB trench is the SIMS crater where secondary ions were extracted for analysis. The X-profile is shown between arrows A and B, the Y-profile follows the FIB-trench between arrows C and D. The X- and Y-profiles in (b) are resulting from the indicated arrows at A, B, C and D on the image in (a). The FIB-trench is clearly visible in the center on the X-profile. Step height analysis was performed at the step between the red and green rectangle indicated in (a) and on the bottom graph in (b).

3 | Results

3.1 | Depth Calibration

The sputtering rate of the ToF-SIMS is calculated from optical profilometry, using the step height between the bottom of the FIB trench (the starting point) and the bottom of the ToF-SIMS crater (the final point of the SIMS depth profiling), divided by the total sputtering time and assuming a constant sputtering rate of the material. For the FIB-damaged LDPE used here, this yielded an average ToF-SIMS sputtering rate around $19 \text{ nm}^3/\text{ion}$, which is comparable to the values obtained in previously measured sputter yields in undamaged polymers (Cumpson et al. 2013; Seah 2013).

3.2 | Reference Spectra From Pristine LDPE

A reference mass spectrum was collected on a cryofaced block of pristine LDPE flash coated with 5 nm carbon to make it conductive. The trends of molecular fragmentation found in this material have been described before (Briggs 1982). LDPE can fragment in virtually all combinations of its basic components, i.e., C- and H-atoms, and the fragmentation behavior will depend on the macromolecular structure (molecular weight, chain branching), but also on settings of the analysis (Cole 1987; Kersting 2004). Most of the total signal collected can be assigned to a limited number of secondary ions, out of which the following fragments contribute to $\sim 50\%$ of the total signal: C_3H_5^+ , C_3H_7^+ , C_4H_7^+ , C_4H_9^+ , C_2H_5^+ , C_5H_7^+ and C_5H_9^+ . These dominant fragments for pristine LDPE measured with ToF-SIMS at the conditions described in 2.2 and shown in red on Figure 3 will

be referred to as *reference fragments* from this point on. The secondary ions from potential external hydrocarbon contamination and the applied conductive carbon coating were considered to be only affecting the first collected datapoint of the depth profile and were not taken into consideration in further analyses.

3.3 | Observations of Ga^+ FIB Damage

ToF-SIMS depth profiling was performed on samples of LDPE which were irradiated with gallium FIB at 5, 10, 16, and 30 keV under grazing incidence of 2° . Thanks to the typical geometry of a FIB-SEM, where the ion beam is at an angle to the electron beam, this still provides sufficient secondary electron yield for electron imaging and to a lesser extent for elemental analysis (e.g., using Energy Dispersive X-ray Spectroscopy (EDS)). However, the fact that the surface of interest is confined in the FIB trench is hampering other surface analysis techniques, such as AFM or SIMS, which need a wider unconfined surface.

In the spectrum of Figure 3 an example of the totally integrated spectrum over all depths of the 30 keV experiment is added in blue. The graphs presented in Figure 4 show ToF-SIMS depth profiles of selected elements and molecular fragments from LDPE after milling with a Ga FIB at various accelerating voltages. They are presented as the response signal of each secondary ion, normalized to the total signal, as a function of depth.

During the experiment, the intensity of reference fragments established in pristine LDPE was tracked over time. The depth profiling was stopped when a steady state was reached where no significant change in molecular products was observed and

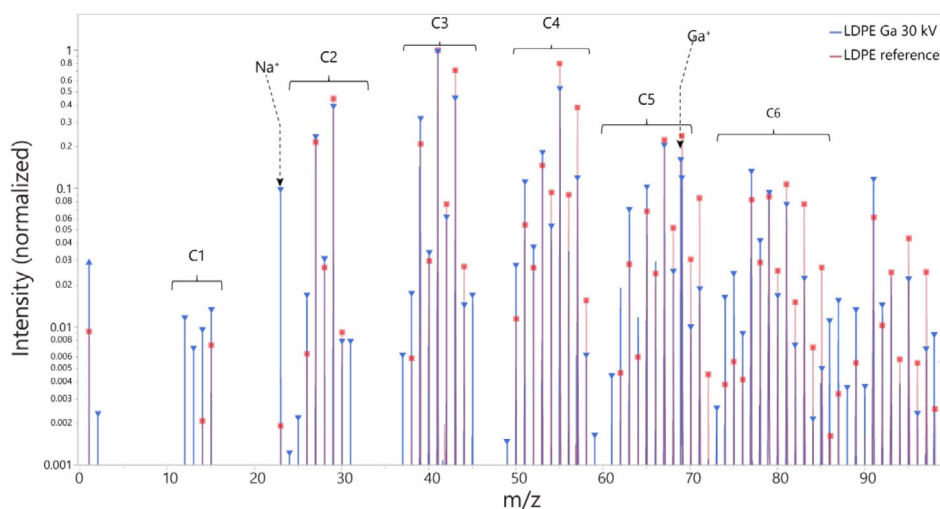


FIGURE 3 | Integrated ToF-SIMS spectrum of the reference pristine LDPE (red) and LDPE after irradiation with 30 keV FIB (blue). Intensity is displayed on a log scale to highlight the difference between relative intensities of hydrocarbon peaks before and after FIB irradiation. Some previously absent peaks appear in the post-irradiation spectrum, especially at the lower end of the spectrum (C1, C2-groups). The Ga^+ in the 30 keV spectrum originates from the FIB, Na^+ is an external contamination present in both samples.

only the reference fragments were detected, indicating that a depth had been reached where there was no more impact of the Ga beam.

Figure 4a presents the signal of gallium as a function of depth for all the FIB energies used. The measured implantation depth of gallium corresponds largely to simulations performed with Stopping Range of Ions in Matter (SRIM) software (see Supporting Information (SI, Figures S1 and S2)) (Ziegler et al. 2010). The increased presence of dehydrogenated carbon fragments (C^+ in Figure 4b) and reduced intensity of reference fragments (C_2H_5^+ shown as example in Figure 4c) correlate roughly with the Ga implantation.

Below the original sample surface, we observe an increase in intensity of fragments representative of polyaromatic hydrocarbons (PAHs), such as C_9H_7^+ (indene) (Figure 4d), $\text{C}_{10}\text{H}_8^+$ (naphthalene), $\text{C}_{13}\text{H}_9^+$ (phenalene) and $\text{C}_{14}\text{H}_{10}^+$ (anthracene/phenanthrene).

The ToF-SIMS mass spectra also show the presence of an oxygen-containing molecule fragment ($\text{C}_2\text{H}_5\text{O}^+$ in Figure 4e) in the intermediate zone behind the Ga implanted region.

There are works studying bombardment of polymer surfaces by ion beams and concurrent recovery of molecular signals with Gas-Cluster Ion Beams (GCIB) (Iida 2018; Mahoney 2023), but to our knowledge, this is the first time that detailed ToF-SIMS depth profiling of the molecular structure of focused-ion-bombarded LDPE surfaces is reported. Based on the observed ions and molecular fragments and the measured hydrogen-to-carbon (H/C) ratios, we distinguish three zones as a function of depth:

3.3.1 | Top Zone

Most gallium is implanted here.

Highly dehydrogenated fragments dominate (H/C ranging from 0 to 0.7).

Reference fragments from pristine LDPE are virtually absent.

3.3.2 | Intermediate Zone

Decline of highly dehydrogenated fragments (H/C < 0.7) and Ga.

Increase of the signal from partially dehydrogenated fragments (H/C around 1), representative of polyaromatic hydrocarbons ($\text{C}_9\text{-C}_{14}$).

Observation of oxygenated fragments ($\text{C}_2\text{H}_5\text{O}^+$).

Increase in reference fragments (H/C > 2, e.g., C_2H_5^+ to C_4H_9^+), indicative of pristine LDPE molecules.

3.3.3 | Bulk Zone

Ga and fragments with H/C < 1 are virtually absent.

Reference fragments (H/C > 2) are dominant and stable at levels observed in pristine LDPE, indicative of undamaged LDPE.

Implantation of gallium in the subsurface region and its dependence on accelerating voltage was expected, as was the accompanying effect of damage to the molecular structure of the polymer.

The effect of dehydrogenation of polyolefins after plasma beam treatment has been studied before (Delcorte et al. 1995; Gavrillov et al. 1998; Davenas and Thévenard 2003) and we observe it here as the presence of molecular signals such as C^+ , CH^+ , C_2H^+ etc. (see SI, Tables S1 and S2 for complete list). The damage products in the zone near the surface show a low hydrogen-to-carbon

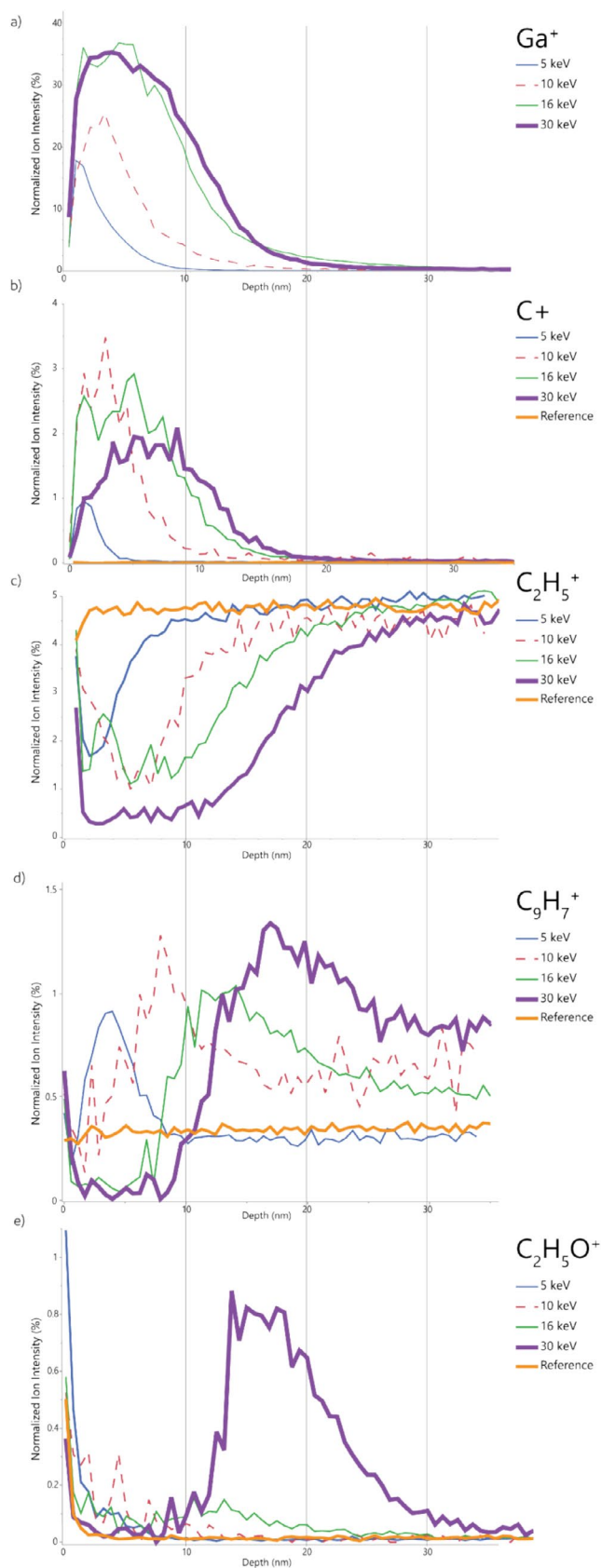


FIGURE 4 | Depth profiles of Ga^+ and selected molecular fragments at different Ga-beam energies. (a) Ga^+ ; (b) C^+ , completely dehydrogenated carbon; (c) C_2H_5^+ , representative of pristine LDPE; (d) C_9H_7^+ , representative of polyaromatic hydrocarbons; (e) $\text{C}_2\text{H}_5\text{O}^+$, i.e., an oxygenated compound.

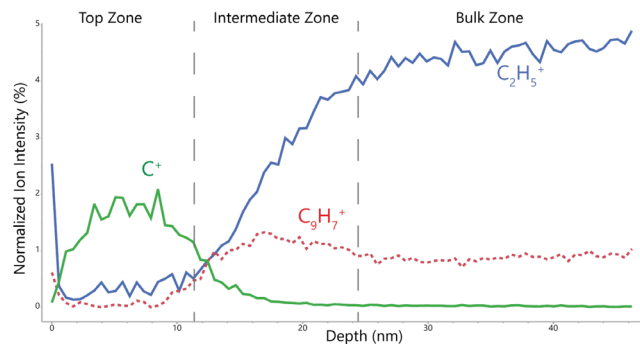


FIGURE 5 | Division of zones in LDPE with fragments indicative for the given regions: Top Zone represented by C^+ , Intermediate Zone by C_9H_7^+ (indene) and Bulk Zone by C_2H_5^+ .

ratio (H/C 0.7 and below). The ToF-SIMS response of these products is similar to that of graphitic carbon, such as carbon black (SI) (De Rosa et al. 2022).

In the Top and Intermediate zone, we also observe previously reported indicators of dehydrogenation and cross-linking, such as a decrease in total ion yield (Oran 2004) and increased signal of fragments above m/z 100 (Leggett et al. 1995; De Puydt et al. 1992).

Figure 5 illustrates the three depth zones using typical molecular fragments for each zone (data from 30 keV): C^+ ($\text{H}/\text{C} \approx 0$) for the Top Zone, C_9H_7^+ ($\text{H}/\text{C} \sim 1$) for the Intermediate Zone, and C_2H_5^+ ($\text{H}/\text{C} > 2$) for the Bulk Zone.

The thickness of each layer was determined by linking the final depth of the profiling crater by optical profilometry with each profiling point. The thickness of the top zone with maximum damage was determined by the strength of the C^+ -signal; the intermediate zone to the strength of the C_9H_7^+ -signal (aromatic indicator) and the bulk zone to the strength of the C_2H_5^+ -signal (reference LDPE fragment). The depth and thickness of the three zones are clearly dependent on the accelerating voltage of the Ga^+ ion beam, as is illustrated in Figure 6.

4 | Discussion

4.1 | Damage to Polyethylene Structure

As expected, gallium penetrates deeper into the material with increasing accelerating voltage. The goal of this study, however, is to understand the molecular structure of the damage products and their evolution with depth.

Polyethylene has a simple chemical formula, consisting of repeating $(\text{CH}_2-\text{CH}_2)$ units and a H/C ratio close to 2. The most prominent indicator of the damaged structure is the fully dehydrogenated secondary ion signal of C^+ , but also other secondary ions where the H/C ratio is smaller than 1 indicate damaged material. These molecular fragments are typical for a secondary ion spectrum of a low-hydrogen-containing material, such as carbon black (SI). This is consistent with previous observations from plasma bombardment of polyethylene (Gavrilov et al. 1998).

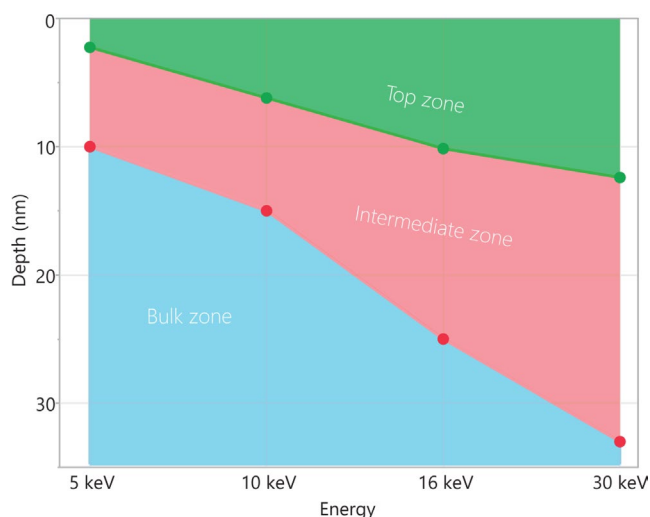


FIGURE 6 | Depth of different zones, depending on the maximum signal of indicative secondary ions for each zone as indicated in Figure 4.

We hypothesize that the incoming high-energy ions dissipate energy by breaking C–H and C–C bonds. This effect will be the strongest near the surface, where the incoming ions have not lost much of their energy yet. The number of broken bonds should be highest near the surface. As Ga undergoes inelastic collisions with C and H, there will be a collision cascade where energy is transferred to other atoms and dissipated within the material. The deeper into the material, the less energy the incoming ions have. Moreover, any resulting free hydrogen species will be able to escape into the vacuum. As a result, the surface zone will be formed by a high concentration of individual C* radicals and short carbon chain radicals, which will quickly recombine into a graphitic structure. This is supported by our observation that the ToF-SIMS mass spectrum in the Top Zone C₁–C₂ fragments ($m/z=10$ – 20) of similar intensity as carbon black (SI). This has also been observed in plasma treatment of polyethylene (Prošková et al. 2000; Popok et al. 1997).

The removal and displacement of hydrogen atoms/protons from polyethylene molecules is also consistent with molecular simulations of Cu⁺ bombardment (Duffour and Malfreyt 2004). The extent of this effect is dependent on the energy (accelerating voltage) and overlaps with the signal of implanted gallium ions.

4.2 | Composition of the Intermediate Layer

The presence of polyaromatic hydrocarbons (PAHs) can be explained by induced reactivity of LDPE after FIB milling. The active radicals are long-living and can interact with each other to form PAH (Prošková et al. 2000; Popok et al. 1997).

We hypothesize that at a deeper level into the material, the incoming ions will have lost part of their energy and fewer C–C and C–H bonds will be broken, leading to less dehydrogenation, longer chain fragments, and a lower concentration of free radicals. In addition, fewer of the free hydrogen species will be able to escape into the vacuum. These fragments will be able to recombine into (poly)cyclic hydrocarbons such as

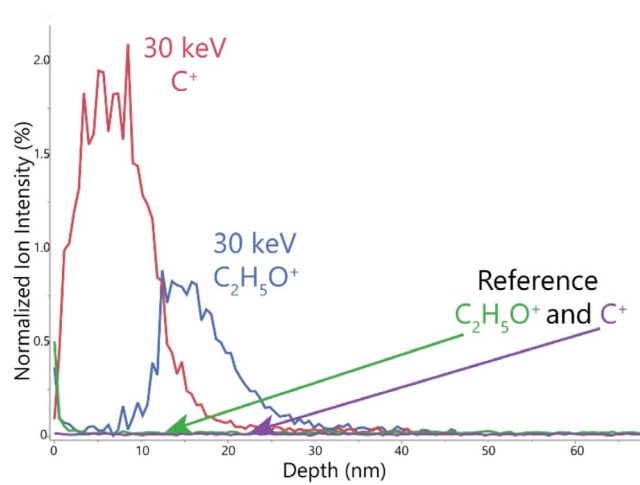


FIGURE 7 | Comparison of a depth profile of a reference and 30 keV LDPE. The signal of C₂H₅O⁺ increases in the Intermediate Zone around 16–20 nm below the surface, beyond the Top Zone.

naphthalene, indene, etc. by reaction of small radical molecules with cyclic precursor molecules leading to ring expansion (Zhao et al. 2019). This is consistent with the ToF-SIMS spectra from the Intermediate Zone in the ToF-SIMS depth profiles where fragments similar to indene, naphthalene, phenalene, and anthracene have been observed.

The observation of oxygen-containing fragments in the Intermediate Zone could be surprising at first sight, but has also been described before (Oran 2004; Leggett et al. 1995). As shown in Figure 7, such oxygen-containing compounds have only been found in the Intermediate Zone from which it is hypothesized that some radicals can remain active long after the interaction with the gallium, especially at some level below the surface, which was also observed in earlier plasma studies (Prošková et al. 2000; Popok et al. 1997). The level of the C₂H₅O⁺ fragment (up to 0.8% in 30 keV sample) cannot be explained solely by the additives included in polyethylene (up to 600 ppm of antioxidants, slip agents, catalyst residues etc.), consisting of oxygen-containing molecules which will also be broken down, ionized, and radicalized under the influence of the FIB. However, molecular oxygen from the atmosphere diffuses into the material (Kamal et al. 1984) and can react with the sub-surface free radicals, forming additional reaction products that will fragment into C₂H₅O⁺ as observed in the ToF-SIMS (Oran 2004).

4.3 | Role of the Carbon Coating

Please note that the original carbon coating, applied to the entire sample to mitigate charging, is not expected to significantly influence the ToF-SIMS data. Once the FIB trench begins to form, the carbon coating in that region is removed. The data presented in this paper were acquired from the bottom of the FIB trench—an area well beneath the original carbon-coated surface—ensuring that the analyzed surface is free of the initial coating.

Outside the trench, the carbon layer remains intact, continuing to provide conductivity and reduce overall charging by dissipating stray electrons and ions.

Simulations (see SI Figure S1) indicate that during the initial stage of FIB milling—when the carbon coating is still present—causes gallium (Ga) to deposit more shallowly than in its absence, as if the incoming Ga ions had less energy. Consequently, other molecular fragments may also form at shallower depths under these conditions. However, once the coating is removed, this effect ceases to be relevant.

We therefore hypothesize that the 5 nm carbon coating has a negligible impact on the ToF-SIMS results and, at most, may cause a slight broadening of the measured depth distributions.

5 | Conclusions

The effects of Ga FIB processing on polyethylene include dehydrogenation, bond breaking, radicalization, recombination, and post-processing oxidation of the sub-surface structure. These effects were investigated with ToF-SIMS depth profiling, the sputtering depth being calibrated with optical profilometry. The depth of the damage is dependent on the chosen accelerating voltage of the FIB and corresponds roughly to the depth of implanted gallium. Damage to the structure can be divided into distinct zones based on the products found at a certain depth. The Top Zone contains the most damaged structure, containing mostly dehydrogenated carbon next to implanted gallium. The Intermediate Zone shows polyaromatic hydrocarbon structures and oxygenated molecule fragments. The pristine structure is observed below the Top and Intermediate zones. Figure 6 summarizes the observed depth ranges as a function of ion beam energy.

Author Contributions

Maciej Paśniewski: conceptualization, methodology, data curation, investigation, validation, formal analysis, funding acquisition, visualization, project administration, writing – original draft, writing – review and editing, resources. **Claude Poleunis:** investigation. **Arnaud Delcorte:** investigation. **Rachel Terry:** investigation. **David W. Abmayr:** investigation. **Anton-Jan Bons:** conceptualization, methodology, validation, writing – review and editing, supervision, funding acquisition. **Dominique Schryvers:** conceptualization, supervision, writing – review and editing.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

Akabori, K., Y. Yamamoto, S. Kawahara, H. Jinnai, and H. Nishioka. 2009. "Field Emission Scanning Electron Microscopy Combined With Focused Ion Beam for Rubbery Material With Nano-Matrix Structure." *Journal of Physics: Conference Series* 184: 012027.

Baden, N. 2015. "New Method for Chemical Characterization of Polymer Materials in Industrial Devices: AFM-IR With FIB Sample Preparation." In *2015 IEEE 22nd International Symposium on the Physical and Failure Analysis of Integrated Circuits*. IEEE.

Bals, S., W. Tirry, R. Geurts, Z. Yang, and D. Schryvers. 2007. "High-Quality Sample Preparation by Low kV FIB Thinning for

Analytical TEM Measurements." *Microscopy and Microanalysis* 13, no. 2: 80–86.

Briggs, D. 1982. "Analysis of Polymer Surfaces by SIMS. 2—Fingerprint Spectra From Simple Polymer Films." *Surface and Interface Analysis* 4, no. 4: 151–155.

Brostow, W., B. P. Gorman, and O. Olea-Mejia. 2007. "Focused Ion Beam Milling and Scanning Electron Microscopy Characterization of Polymer+Metal Hybrids." *Materials Letters* 61, no. 6: 1333–1336.

Chawla, M., S. Aggarwal, and A. Sharma. 2017. "Rutherford Backscattering Spectrometry Studies of 100keV Nitrogen Ion Implanted Polypropylene Polymer." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 407: 125–131.

Chhokkar, P., V. Kumar, P. K. Goyal, et al. 2021. "Argon Ion Implanted CR-39 Polymer: Optical and Structural Characterization." *Optical Materials* 115: 111046.

Cole, R. B. 1987. "Effect of Primary Ion Beam Parameters on the Secondary Ion Emission of Biomolecules From Liquid Matrixes." *Analytical Chemistry* 59, no. 15: 1930–1937.

Cumpson, P. J., J. F. Portoles, and N. Sano. 2013. "Material Dependence of Argon Cluster Ion Sputter Yield in Polymers: Method and Measurements of Relative Sputter Yields for 19 Polymers." *Journal of Vacuum Science & Technology A* 31, no. 2: 020605.

Cushman, C. 2018. "Sample Charging in ToF-SIMS: How It Affects the Data That Are Collected and How to Reduce It." *Vacuum Technology, Coating* 19: 23–28.

Davenas, J., and P. Thévenard. 2003. "Models of the Hydrogen Release From Polymers Under Ion Beam Irradiation." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 208: 170–175.

De Puydt, Y., D. Léonard, and P. Bertrand. 1992. *A Static SIMS Study of the Chemical Modifications Induced by Plasma and Flame Treatments at the Surface of Polyolefins*, in *Metallized Plastics 3: Fundamental and Applied Aspects*, edited by K. L. Mittal, 225–241. Springer US.

De Rosa, S., P. Branchini, V. Spampinato, A. Franquet, G. Bussetti, and L. Tortora. 2022. "Effects of Cs⁺ and Ar⁺ Ion Bombardment on the Damage of Graphite Crystals." *Applied Surface Science* 585: 152756.

Delcorte, A., C. Leblanc, C. Poleunis, and K. Hamraoui. 2013. "Computer Simulations of the Sputtering of Metallic, Organic, and Metal-Organic Surfaces With bi-n and C-60 Projectiles." *Journal of Physical Chemistry C* 117, no. 6: 2740–2752.

Delcorte, A., L. T. Weng, and P. Bertrand. 1995. "Secondary Molecular Ion Emission From Aliphatic Polymers Bombarded With Low Energy Ions: Effects of the Molecular Structure and the Ion Beam Induced Surface Degradation." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 100, no. 2: 213–216.

Drobne, D., M. Milani, V. Leser, and F. Tatti. 2007. "Surface Damage Induced by FIB Milling and Imaging of Biological Samples Is Controllable." *Microscopy Research and Technique* 70, no. 10: 895–903.

Duffour, E. 2010. "Molecular Dynamic Simulations of the Collision Between Copper Ions, SF₆ Molecules and a Polyethylene Surface: A Study of Decomposition Products and an Evaluation of the Self-Diffusion Coefficients." 19, no. 2–3: 88–99.

Duffour, E., and P. Malfreyt. 2004. "MD Simulations of the Collision Between a Copper Ion and a Polyethylene Surface: An Application to the Plasma-Insulating Material Interaction." *Polymer* 45, no. 13: 4565–4575.

Eder, K. 2021. "A Multi-Ion Plasma FIB Study: Determining Ion Implantation Depths of Xe, N, O and Ar in Tungsten via Atom Probe Tomography." *Ultramicroscopy* 228: 113334.

Ekar, J., and J. Kovač. 2022. "AFM Study of Roughness Development During ToF-SIMS Depth Profiling of Multilayers With a Cs⁺ Ion Beam in a H₂ Atmosphere." *Langmuir* 38, no. 42: 12871–12880.

- Gannon, R. 2019. "Advances in Multi-Beam and Multi-Ion FIB-SEM for 3D Correlative Microscopy." *Microscopy and Microanalysis* 25, no. S2: 870–871.
- García-Borquez, A. 2023. "Surface Microstructure Changes Induced by Ion Beam Irradiation." In *Ion Beam Technology and Applications*, edited by O. Artun. IntechOpen.
- Gavrilov, N., D. Yakusheva, and A. Kondyurin. 1998. "Structure of Polyethylene After Pulse Ion Beam Treatment." *Journal of Applied Polymer Science* 69, no. 6: 1071–1077.
- Gilmore, I. S., and M. P. Seah. 1996. "Static SIMS: A Study of Damage Using Polymers." *Surface and Interface Analysis* 24, no. 11: 746–762.
- Guo, J., G. Wang, L. Xie, et al. 2023. "Three-Dimensional Analysis of Membrane Structures Associated With Tomato Spotted Wilt Virus Infection." *Plant, Cell & Environment* 46, no. 2: 650–664.
- Iida, S.-i. 2018. "Accurate and Reproducible In-Depth Observation of Organic-Inorganic Hybrid Materials Using FIB-TOF-SIMS." *Journal of Vacuum Science & Technology B* 36, no. 3: 20.
- Irfan, M. 2019. "Irradiation Effects of Cu Ions on the Electrical and Morphological Properties of Polypropylene." *Polymers and Polymer Composites* 27, no. 3: 103–107.
- Kamal, M. R., I. A. Jinnah, and L. A. Utracki. 1984. "Permeability of Oxygen and Water Vapor Through Polyethylene/Polyamide Films." *Polymer Engineering and Science* 24, no. 17: 1337–1347.
- Kerstens, W. 2020. "Three-Dimensional Visualization of APEX2-Tagged Erg11 in *Saccharomyces cerevisiae* Using Focused Ion Beam Scanning Electron Microscopy." *mSphere* 5, no. 1: 10–1128.
- Kersting, R. 2004. "Influence of Primary Ion Bombardment Conditions on the Emission of Molecular Secondary Ions." *Applied Surface Science* 231–232: 261–264.
- Kizilyaprak, C. 2014. "FIB-SEM Tomography in Biology." In *Electron Microscopy: Methods and Protocols*, edited by J. Kuo, 541–558. Humana Press.
- Kondyurin, A., and M. Bilek. 2015. "Structure of Polymers After Ion Beam Treatment." In *Ion Beam Treatment of Polymers*, edited by A. Kondyurin and M. Bilek, 69–127. Elsevier.
- Leggett, G. J., B. D. Ratner, and J. C. Vickerman. 1995. "Characterization of Plasma-Deposited Styrene Films by XPS and Static SIMS." *Surface and Interface Analysis* 23, no. 1: 22–28.
- Mahoney, C. M. 2023. "O₂ vs. Ar Gas Cluster Ion Beam Sources for ToF-SIMS Depth Profiling of Thick Polymer and Metal Film Samples." *Microscopy and Microanalysis* 29, no. Suppl 1: 751–752.
- Mayer, J., L. A. Giannuzzi, T. Kamino, and J. Michael. 2007. "TEM Sample Preparation and FIB-Induced Damage." *MRS Bulletin* 32, no. 5: 400–407.
- McPhail, D. S. 2006. "Applications of Secondary Ion Mass Spectrometry (SIMS) in Materials Science." *Journal of Materials Science* 41, no. 3: 873–903.
- Melngailis, J. 1987. "Focused Ion Beam Technology and Applications." *Journal of Vacuum Science & Technology, B: Microelectronics Processing and Phenomena* 5, no. 2: 469–495.
- Mesyats, G. A., Y. S. Klyachkin, N. V. Gavrilov, V. N. Mizgulin, R. M. Yakushev, and A. V. Kondyurin. 1996. "Ion Beam Modification of Polyethylene and Adhesion to Epoxy Adhesive." *Vacuum* 47, no. 9: 1085–1087.
- Ohtake, Y. 2013. "Degradation Profiles in Aged EPDM Water Seals Using Focused Ion Beam-Scanning Electron Microscopy." *Polymer Degradation and Stability* 98, no. 12: 2489–2496.
- Oran, U. 2004. "Surface Analysis of Plasma-Deposited Polymer Films." 1, no. 2: 123–133.
- . 2022. *Plastics—The Facts 2022*. Plastics Europe.
- Popok, V. N., I. I. Azarko, V. B. Odzhaev, A. Tóth, and R. I. Khaibullin. 2001. "High Fluence Ion Beam Modification of Polymer Surfaces: EPR and XPS Studies." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 178, no. 1: 305–310.
- Popok, V. N., V. B. Odzhaev, I. P. Kozlov, I. I. Azarko, I. A. Karpovich, and D. V. Sviridov. 1997. "Ion Beam Effects in Polymer Films: Structure Evolution of the Implanted Layer." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 129, no. 1: 60–64.
- Prošková, K., V. Švorčík, V. Rybka, and V. Hnatowicz. 2000. "Selected Degradation Reactions in Polyethylene Irradiated With Ar⁺ and Xe⁺ Ions." *Radiation Physics and Chemistry* 58, no. 2: 153–156.
- Reyntjens, S., and L. A. Giannuzzi. 2007. "Characterization Methods Using FIB/SEM DualBeam Instrumentation." In *Focused Ion Beam Systems: Basics and Applications*, edited by N. Yao, 126–145. Cambridge University Press.
- Reyntjens, S., and R. Puers. 2001. "A Review of Focused Ion Beam Applications in Microsystem Technology." *Journal of Micromechanics and Microengineering* 11, no. 4: 287–300.
- Sasuga, T., S. Kawanishi, M. Nishii, T. Seguchi, and I. Kohno. 1991. "Effects of Ion Irradiation on the Mechanical Properties of Several Polymers." *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry* 37, no. 1: 135–140.
- Schmidt, J. E., L. Peng, J. D. Poplawsky, and B. M. Weckhuysen. 2018. "Nanoscale Chemical Imaging of Zeolites Using Atom Probe Tomography." *Angewandte Chemie International Edition* 57, no. 33: 10422–10435.
- Seah, M. P. 2013. "Universal Equation for Argon Gas Cluster Sputtering Yields." *Journal of Physical Chemistry* 117, no. 24: 12622–12632.
- Smith, N. S. 2006. "High Brightness Inductively Coupled Plasma Source for High Current Focused Ion Beam Applications." *Journal of Vacuum Science & Technology B* 24, no. 6: 2902–2906.
- Švorčík, V., E. Arenholz, V. Hnatowicz, V. Rybka, R. Öchsner, and H. Ryssel. 1998. "AFM Surface Investigation of Polyethylene Modified by Ion Bombardment." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 142, no. 3: 349–354.
- Tiddia, M., I. Mihara, M. P. Seah, et al. 2019. "Chemical Imaging of Buried Interfaces in Organic-Inorganic Devices Using Focused Ion Beam-Time-Of-Flight-Secondary-Ion Mass Spectrometry." *ACS Applied Materials & Interfaces* 11, no. 4: 4500–4506.
- Veres, M. 2005. "Raman Scattering of Ultra-High Molecular Weight Polyethylene Treated by Plasma-Based Ion Implantation." *Thin Solid Films* 482, no. 1: 211–215.
- Virgilio, N., B. D. Favis, M.-F. Pépin, P. Desjardins, and G. L'Espérance. 2005. "High Contrast Imaging of Interphases in Ternary Polymer Blends Using Focused Ion Beam Preparation and Atomic Force Microscopy." *Macromolecules* 38, no. 6: 2368–2375.
- Zhao, L., R. I. Kaiser, W. Lu, et al. 2019. "Molecular Mass Growth Through Ring Expansion in Polycyclic Aromatic Hydrocarbons via Radical-Radical Reactions." *Nature Communications* 10, no. 1: 3689.
- Ziegler, J. F., M. D. Ziegler, and J. P. Biersack. 2010. "SRIM—The Stopping and Range of Ions in Matter." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 268, no. 11–12: 1818–1823.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.