

4. SIMS (Secondary Ion Mass Spectrometry)

4.1. Introduction

Secondary ion mass spectrometry, SIMS, is the mass spectrometry of ionized particles, which are emitted when a surface, usually a solid, is bombarded by energetic primary ions. The emitted or secondary particles will be electrons, neutral species atoms or molecules, atomic and cluster ions. For most materials the vast majority of species emitted are neutral. However, only the secondary ions can be detected and analyzed by a mass spectrometer. SIMS provides the mass spectrum of a surface and enables a detailed chemical analysis of a surface or solid to be performed.

4.2. Historical Development of static SIMS

Fundamental for SIMS is the work of Herzog and Viehboeck. In 1949 they developed the first instrument using an electron impact primary ion source. Some 10 years later the first complete SIMS instrument was designed by Honig, Bradley, Beske, and Werner. During the following years a rapid development took place both in instrument development and analytical application [68]

Static SIMS emerged as a technique of potential importance in surface science in the late 1960s, early 1970s as a consequence of the work of Benninghoven and his group in Münster [69]. The SIMS technique is basically destructive, but the Münster group demonstrated that by the use of a very low primary ion flux density ($<1\text{ nA/cm}^2$) spectral data could be generated in a time-scale, which is very short compared to the lifetime of the surface layer.

In mid-1970s, in the course of research focused to surface reactivity of solids Vickerman's group at UMIST (University of Manchester Institute of Science and Technology) saw the intriguing possibility that SSIMS could be developed into a surface mass spectrometry [70]. The research at UMIST using SSIMS to characterize organic surfaces, together with the extensive work by the Briggs group at ICI (Imperial Chemical Industries, PLC) in the field of characterization of polymer surfaces has shown, beyond all doubts, that static SIMS is a true surface mass spectrometry.

4.3. Fundamental of SIMS

4.3.1. The basic SIMS phenomenon

SIMS is a sputtering phenomenon. When high energy primary ions collide with a solid surface, energy is transferred from the primary particle to the atoms of the material to be analyzed. Some of the primary ions can be back scattered but most of them transfer their kinetic energy to the lattice through a collision sequence and are implemented into the target according to their energy, mass and impact angle. The final result is not only the emission of secondary ions but also the emission of low energy electrons, Auger electrons, photons (from visible to X-rays depending on the primary energy), neutral particles and excited clusters [68, 71]. As a matter of fact, secondary ions (mono and polyatomic) can be emitted from points well distant from the initial point of impact, as confirmed by their low energy compared to the primary ions [72].

4.3.2. The basic equation

The basic SIMS equation is

$$I_m = I_p Y_m \alpha \theta_m \eta \quad \text{Equation 4.1}$$

where I_m is the secondary ion current of species m , I_p is the primary ion flux, Y_m is the sputter yield, α is the ionization probability, θ_m is the fractional concentration of m in the surface layer and η is the transmission of the analysis system.

The two fundamental parameters are Y_m and α . Y_m is the total yield of sputtered particles of species m , neutral and ionic, per primary ion impact. It increases linearly with primary ion flux. It also increases with primary ion mass and energy although not linearly [73]. Y_m tends to maximize with energies at around 10 keV. Ionization occurs at, or close to, emission of sputtered particles with the consequence that the matrix participates in the electronic process. This means that the secondary ion yield is strongly influenced by the electronic state of the material being analyzed and it is very sensitive to the electronic state of the atom or the molecule to be ionized and to the matrix from which they are emitted. As a matter of fact, the secondary ion yield of different species (atoms or clusters) sputtered from the same matrix is a function of the ionization potential of the sputtered atom or cluster but it can be greatly enhanced by the presence of electronegative species, e.g. oxygen, at the surface. This is the well known matrix effect problem and it might bring significant complications when a quantification of SSIMS data is required [73].

4.3.3. Damage cross-section and static limit of SIMS

As a result of primary ion bombardment the sample surface is heavily modified not only by the loss of secondary particles but also by a variety of further radiation effects such as primary ion implantation, mixing of atoms, fragmentation of surface molecules or molecular structures. It is estimated that the impact of a keV primary ions leads to a damage in a region of several nm in diameter around its trajectory. This damage can be characterized by a damage cross-section (σ), describing the average size of the surface that is modified by a single ion impact (Figure 4.1). This area strongly depends on the surface composition and on the primary ion properties. Sicthermann and Benninghoven [74] obtained damage cross-section of around 10^{-14} cm² for amino acid and other small molecules on metal substrates.

To retain the molecular information in SIMS, it is essential that no primary ion strike again to an already damaged region. This is achieved by using the static SIMS mode, where an extremely low dose of primary ions is used, such that within the time scale of the experiment very much less than 1 % of the top surface layer constituents receive an ion impact. Under these conditions on a random impact basis no spot on the surface contributing to the spectrum should receive more than one primary ion strike. The secondary species generated arise also from a certain area remote from the next point of analytical impact. It is established that each impact physically influences an area of 10 nm². This implies that 10^{13} impacts/cm² influence all the atoms in the surface. Therefore, the static limit is defined to be $\leq 10^{13}$ ions/cm². Any primary ion dose lower than this value is accepted in the static regime of SIMS analysis.

The primary ion dose is calculated by using the following formula

$$\text{Primary ion dose} = \frac{I_p t}{A}, \quad \text{Equation 4.2}$$

where I_p is primary ion of flux (ions/s), t is the analysis time (s) and A (cm²) is the bombarded surface area.

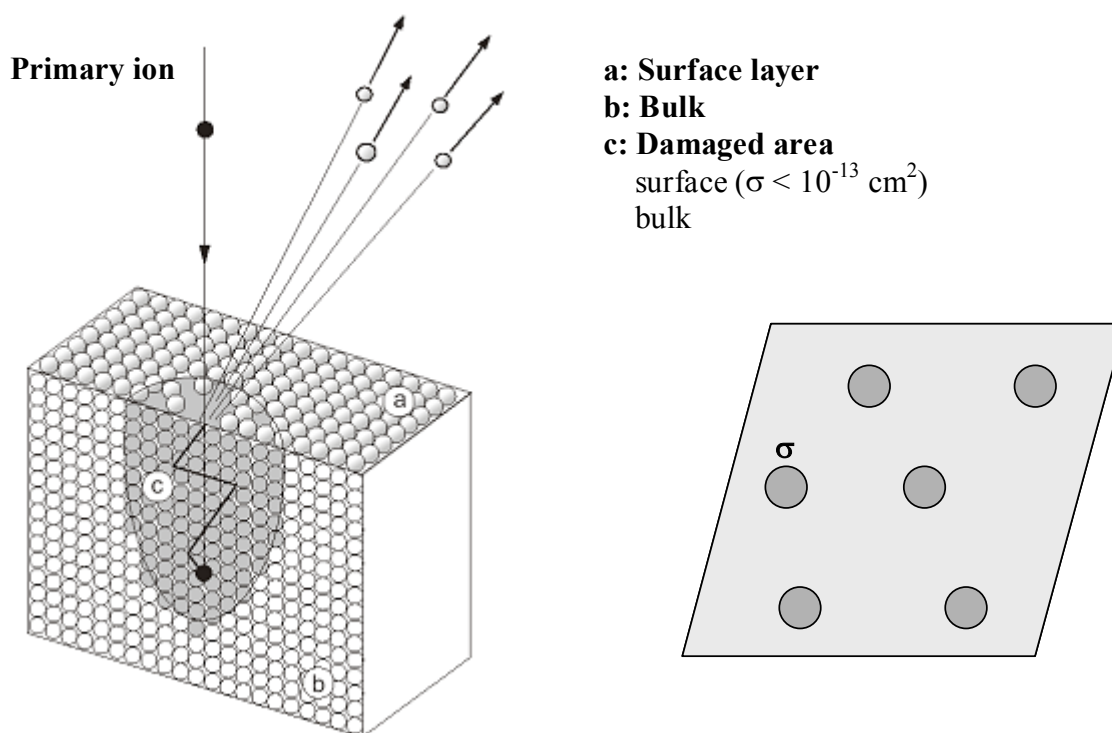


Figure 4.1. Concept of static SIMS. Primary ion impact on a solid surface results in surface damage and in the emission of atomic and molecular surface species, electrons and photons. The damaged surface area can be described by the damage cross section (σ). In static SIMS the total primary ion dose density is extremely low, and the probability of bombarding an already damaged surface area again can be neglected (adapted from Ref. [73]).

4.3.4. Anticipated mechanisms of secondary ion formation from organics

This section will give a brief survey on the major concepts and qualitative models to describe the process of secondary ion generation from molecular solids.

Cooks and Busch, [75] introduced the concept that desorption by vibrational excitation may be important in understanding the emission of cluster or molecular secondary ions from organic materials. They proposed the “desorption-ionization” model, which emphasizes that the processes of desorption and ionization can be considered separately. A wide variety of secondary ion emission processes is possible. One idea is based on the kick-off of preformed ions existing at the surface prior to primary ion bombardment. To generate other secondary ions, the model suggests that desorption is followed by subsequent reactions: i) in the gas phase of the selvedge ion-molecule reactions, ii) in the gas phase of the selvedge ionization of the released neutrals by the

emitted secondary electrons, iii) in the free vacuum unimolecular fragmentation occur, governed by the internal energy of the parent ion (or neutral) giving rise to fragmentation into ions.

To provide a better understanding of the process of secondary ion formation from polymers, a wide range of experiments has been undertaken by different groups. Rading et al. [76] investigated the sputtering of organic molecules deposited on metal substrates. Hearn and Briggs [77] studied the characteristics of polymer sputtering in terms of damage effects. Legget and Vickerman [78] used SIMS/MS techniques to probe the mechanisms of fragment formation from polymers. Here the parent ions produced in SIMS are further fragmented into daughter fragments in a collision cell and then analyzed by a MS. Delcorte and Bertrand [79-81] studied the kinetic energy distributions of secondary ions emitted from molecular and polymer materials. From these various approaches a consensus on the overall process has been reached. Figure 4.2 illustrates the different fragmentation processes of polymers at the surface are provoked by the primary particle impact. This model suggests that the primary ion energy is transformed into vibrational energy dissipated within the macromolecules [82].

In the region close to the point of impact, “impact region”, high energy events leading to the emission of atomic species and uncharacteristic small organic fragments are believed to prevail. Surrounding that area is a zone, “finger print region” with decreased energy density where structural rearrangements may take place, yielding e.g., polyaromatic moieties. Farther away from the impact point, there is the “monomer region”, where the energy available for rearrangements is low, and ejection of species minimally rearranged and species on the mass order of the monomers prevails. This gives rise to larger but structurally most informative fragments [82]. One may conclude that SSIMS is a relatively soft-ionization phenomenon [73].

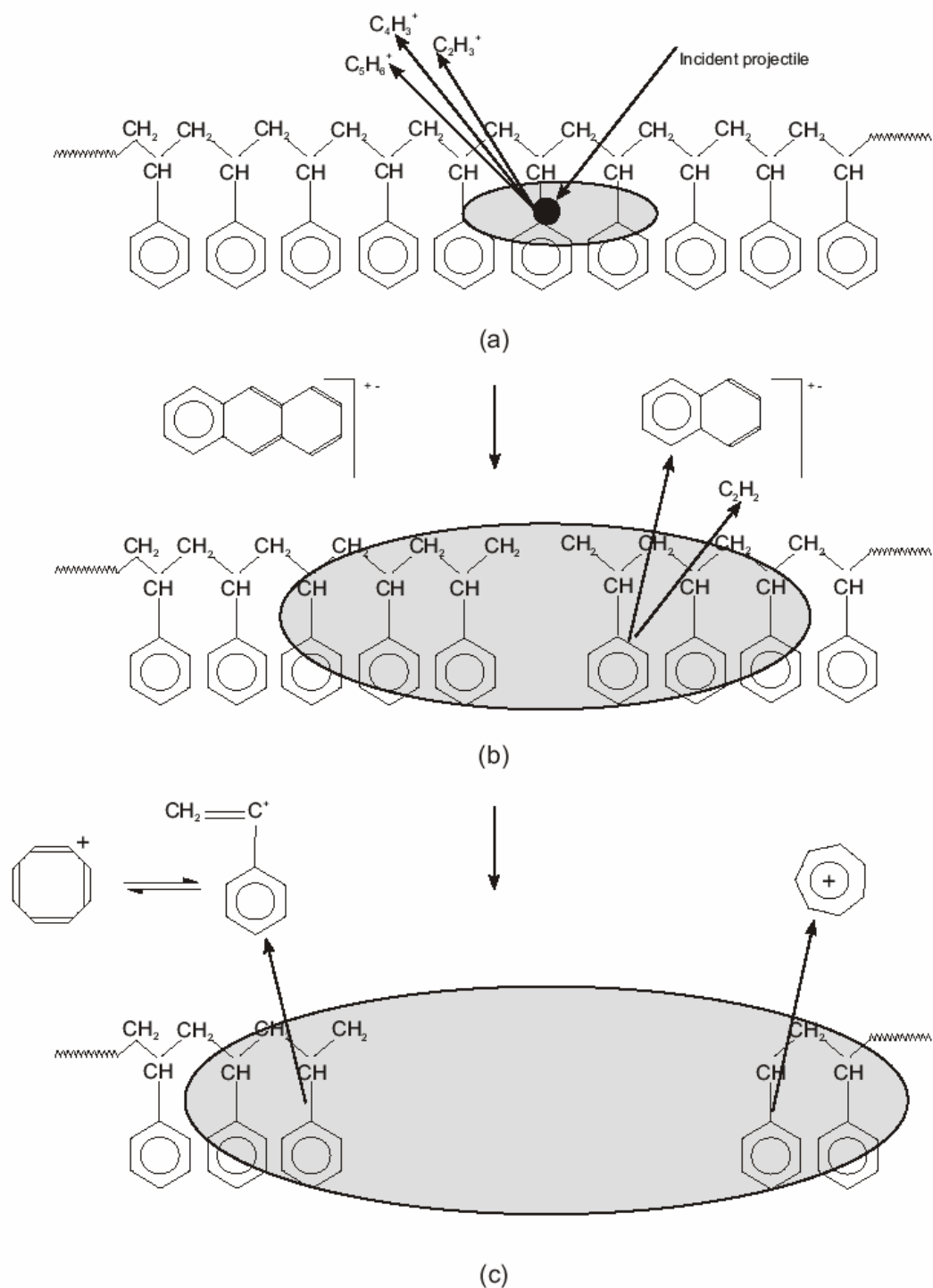


Figure 4.2. Model for ion formation of polymers in SSIMS involves the existence of three regions in which fragmentation on different levels occurs. (a) violent fragmentation in the “impact region”, (b) unzipping of larger fragments in the “fingerprint region” and (c) simple low-energy fragmentation into large sequences, e.g., monomer units of the macromolecules, in the “monomer region”. (adapted from Ref. [82]).

4.4. Interpretation of SSIMS data of organic materials

In the SSIMS spectra of organic materials three spectral regions can be discerned which provide information on their surface state. Each region potentially provides a different kind of information [70, 73, 83].

There is the “sub-monomer mass region”, below the molecular ion. This region usually provides information on the basic chemical structure of the components of the organic material, i.e., in the case of polymers, the monomer(s) and any contamination.

Then there is the “n-mer mass region” where ions and fragments are formed which are generated as a consequence of the bonding between two or more monomer units. This region may potentially contain valuable information about the macromolecular (polymer) structure. There is also evidence that branching and/or cross-linking of polymers can be followed by changes in the yields of n-mers [84].

Finally there is the “oligomer mass region” usually generated via metal cationization. In principle this region permits an estimation of the average molecular weight distribution. However, to generate spectra comprising the oligomer distribution information the sample preparation is crucial. The best results have been obtained when the polymer is deposited by evaporation or spin-casting to give a very thin patchy layer on specially prepared silver [84].

The information from SSIMS data is generally obtained from the “sub-monomer and n-mer mass regions”. For the sake of simplicity, “the finger print region” is defined as the combination of the sub-monomer and n-mer regions. It is generally defined as the low mass range from approximately 0 to 250 atomic mass units [amu]. It is a region of the total mass spectrum of an organic material where a large amount of chemical information about the sample can be found. Important information relating to chemical and structural aspects of the polymer material such as unsaturation, aromaticity, branching and cross-linking can be obtained.

It may often be difficult to extract quantitative values for particular polymer property such as the degree of unsaturation. However, by comparing the data of a new sample to a set of spectra of known reference samples the relative differences usually become apparent. In this way, for example, such particular properties of the plasma deposited films prepared at different plasma conditions by varying the external plasma parameters can be individually evaluated and compared to each other.

In the following paragraphs it will be shown how the relative degree of unsaturation, aromaticity, branching and/or cross linking in a given polymer can be deduced from SSIMS data. Additionally, the contribution of SSIMS to the semi-quantitative determination of surface functional group concentration of polymers will be discussed.

Unsaturation

The relative degree of the unsaturation in a given polymer can be deduced from the relative yields of the hydrocarbon secondary ions within a $C_nH_x^+$ cluster series. Generally, the pattern of yields within a $C_nH_x^+$ cluster series was found to be related to saturation: saturated polymers are characterized by cluster ions of higher mass, i.e., higher H content in $C_nH_x^+$ cluster series, relative to unsaturated polymers.

Considering the influence of saturation/unsaturation of aliphatics on their SSIMS spectra, Briggs [85] pointed out that the $C_3H_x^+$ cluster pattern of unsaturated polymers were distinctly different from those of saturated polymers. Going from saturated to unsaturated samples (polyethylene, polypropylene, poly(1-butene) and poly(4-methyl-1-pentene), poly(cis-butadiene) and poly(cis-isoprene)), the yield at m/z 43 ($C_3H_7^+$) increases and the yield at m/z 39 ($C_3H_3^+$) decreases. For negative SSIMS spectra Briggs [85] stated that the m/z 12/14 (C^-/CH_2^-) yield ratio was higher for unsaturated polymers. He found that the mean value for all aliphatic polymers studied was 1.2. The mean for the saturated aliphatic polymers was 1.0.

Another indication of unsaturation in the case of SSIMS of aliphatic polymers is the presence of aromatic secondary fragment ions. It is known that aromatic secondary fragment ions were observed in the SSIMS spectra of aliphatic hydrocarbons [85, 86]. At primary ion doses lower than the “static limit” aromatic secondary fragment ions were found exclusively in the positive SIMS of unsaturated polymers. At the “static limit” they are also obtained with saturated polymers. The presence of these ions in the positive SIMS of unsaturated aliphatic polymers is not necessarily correlated to the presence of aromatic moieties at the surface of the samples. In fact, they were results of the secondary ion formation process (c.f. section 4.3.4). Ions with aromatic structure are stabilized by resonance. They appeared in the $C_nH_x^+$ cluster series starting with six carbon atoms at m/z 77, 91, 105, 115, 128, 141, and 165. Briggs [85] has attributed the higher intensity of the aromatic fragments observed in the spectra of unsaturated aliphatic polymers to their

higher damage cross sections. Therefore, for analytical purposes, it is reasonable to use the sum of aromatic secondary fragment ion yields as a measure of unsaturation [59]. A parameter, Σ_{Arom} [59] can be defined, which is the sum of the yields of aromatic fragments at m/z 77, 91, 105, 115, 128, 141, and 165. It can be used to investigate the unsaturated character of plasma deposited ethylene, allylamine and allyl alcohol films.

Aromaticity

The presence of aromatic groups within a particular polymer is generally evident from the presence of secondary ions with aromatic character at m/z 77, 91, 105, 115, 128, 141, and 165 in the static SIMS spectrum. These secondary ions, especially the one at m/z 91, are observed at high yields in the positive ToF-SSIMS spectrum of polystyrene.

Petrat et al. [54] investigated the plasma modified polystyrene sample with ToF-SSIMS. They found that the integrity of the aromatic system could be monitored by using the intensity ratio of the secondary ions at m/z 91 (C_7H_7^+) and m/z 55 (C_4H_7^+). Due to its high stability the most intense peak in the positive secondary ion mass spectrum of polystyrene is the tropylium ion at m/z 91. This secondary ion is also generally observed at high yields in the SSIMS spectra of other aromatic polymers [83]. On the other hand, the secondary ion at m/z 55 (C_4H_7^+) is generally observed at high yields in the SSIMS spectra of aliphatic polymers [70, 83]. By taking these facts into consideration Petrat et al. [54] argued that the (C_7H_7^+) and (C_4H_7^+) secondary ions can be taken as key fragments for the aromatic and aliphatic systems, respectively.

Branching and/or cross-linking

Briggs [85] also investigated the aliphatic polymers in order to study the effect of branching. He observed that with an increasing length of the side chain there was a loss of relative yields for the C_4H_x^+ cluster ions.

The relative amount of the cross-linked character of the polymers can be investigated by taking the total secondary ion yield into consideration. It is well known that the emission probability of any secondary ion in SIMS depends on its environment (matrix effect, c.f. section 4.3.2), and, under the same conditions of SIMS analysis an increase in the cross-linked character should cause a decrease in the total secondary ion yield [73].

The effects of branching and/or cross-linking in a polymer are generally related to an increase in the ratio of high mass fragments to low mass fragments. Lianos et al. [84]

investigated the branching properties of selected aliphatic polymers and they found that the ratio of the total yield of $C_6H_x-C_8H_x$ hydrocarbon secondary ion clusters to the total yield of $C_2H_x-C_8H_x$ clusters $[\Sigma(C_6-C_8) / \Sigma(C_2-C_8)]$ could be used to monitor the branched character of the polymers. However, the $[\Sigma(C_6-C_8) / \Sigma(C_2-C_8)]$ parameter does not discriminate between branching and cross-linking, and its value was found to increase by increasing either of these properties.

It must be noted that branching and cross-linking generally cause similar variations in the SSIMS data of molecular surfaces. For this reason they are investigated in this study under the same headline as “branched and/or cross-linked character” in the case of the plasma deposited films.

Surface functional groups

Several classes of polymers consist of a hydrocarbon backbone with a functional group containing side chain. Some of these polymers have the general structure $(CH_2CHX)_n$, where X represents the side chain with a functional group. These polymers give secondary ion spectra again with hydrocarbon contributions from the backbone. On the other hand, fragmentation of X and fragmentations in the backbone result in secondary ions characterizing the presence of functional groups [73].

Table 4.1 presents a list of the different structures associated with the low mass oxygen or nitrogen containing secondary ions. It is clearly observed in Table 4.1 that for each functional group, there is more than one characteristic secondary ion, i.e., CH_3O^+ , $C_2H_3O^+$, $C_2H_5O^+$, $C_3H_5O^+$, and $C_3H_7O^+$ for the alcohol functional group. Moreover, one secondary ion can be a characteristic secondary ion for different functional groups, i.e., $C_2H_3O^+$ for both alcohol and carbonyl functional groups. However, there are some secondary ions corresponding to only one functional group, i.e., CH_3O^+ and CH_4N^+ for the alcohol and amino functional groups, respectively.

Table 4.1. Description of the structures proposed for the various series of low mass oxygen containing and nitrogen containing SIMS secondary ion (Adopted from Ref. [87]).

Secondary ion	Mass (amu)	Structure	
		Alcohol functional group	Ether functional group
CH_3O^+	31	$^+CH_2-OH$ $CH_2=O^+H$	
$C_2H_3O^+$	43	$CH_2=^+C-OH$ $^+CH=CH-OH$	
$C_2H_5O^+$	45	CH_3-^+CH-OH $^+CH_2-CH_2-OH$	$CH_3-O-CH_2^+$
$C_3H_5O^+$	57	$CH_2=CH-^+CH-OH$ $CH_2=C(OH)-CH_2^+$ $OH-C(CH_3)=CH^+$	$CH_2=^+C-O-CH_3$
$C_3H_7O^+$	59	$CH_3-CH_2-^+CH-OH$ $^+CH_2-C(CH_3)H-OH$ $^+C(CH_3)_2-OH$	$CH_3-^+CH-O-CH_3$ $CH_3-CH_2-O-CH_2^+$
		Carbonyl functional group	Acid and ester functional group
CHO^+	29	$CH\equiv O^+$	
$C_2H_3O^+$	43	$CH_3-C\equiv O^+$ $^+CH_2-C(=O)H$	
$C_3H_5O^+$	57	$CH_3-CH_2-C\equiv O^+$ $^+CH_2-CH_2-C(=O)H$	
CHO_2^+	45		$O=^+C-OH$
$C_2H_3O_2^+$	59		$^+O\equiv C-O-CH_3$
		Amino functional group	
CH_4N^+	30	$CH_2=NH_2^+$ (primary)	
$C_3H_6N^+$	56	$CH_2=CH-CH=NH_2^+$ (primary) $CH_2-CH-N^+H=CH_2$ (secondary)	
$C_4H_8N^+$	70	$CH_2=CH-CH_2-CH=NH_2^+$ (primary) $CH_2-CH-N^+H=CH-CH_3$ (secondary)	

Owing to fragmentation and reorganization reactions taking place during the SSIMS analysis (c.f. section 4.3.4.) quantification of such functional groups is rather difficult especially for the samples bearing several functional groups like plasma polymers or plasma modified polymers. However, in their work, Leonard et al. [87] indicated clearly the correspondence between secondary ions yields detected by ToF-SSIMS in positive mode and the functional groups that they characterize. They used ToF-SIMS as a semi-quantitative method for the determination of functional groups on the surface of post-discharge plasma modified high density polyethylene (HDPE) and hexatriacontane (HTC) samples. Similarly, Medard et al. [88] successfully applied ToF-SIMS in a semi-quantitative way to study chemical modifications of CO₂ plasma treated polypropylene (PP) and HDPE films. From the normalized yields of the secondary ion at m/z 45 (CHO₂⁺), they determined the relative concentration of carboxylic acid surface groups.

It can be concluded that principally relative concentrations of the functional groups present on the surface of plasma polymers can be determined from their respective ToF-SIMS spectra. Similar approaches will be used to investigate the concentration of the functional groups on the surface of plasma deposited films from allylamine and allyl alcohol in this study (c.f. sections 5.2.3 and 5.2.4).

4.5. ToF-SIMS Instrumentation and instrumental effects in Static SIMS

4.5.1 Operating principles of ToF-SSIMS

Before giving the description of the ToF-SIMS instrument presented in Figure 4.3, the relevant operating principles of the instrument are described.

A pulse of primary ions bombards the specimen and sputters it. This produces a cloud of atoms and molecules some of which are ionized species. The ionized particles of one polarity, atomic and molecular secondary ions, are accelerated by an electrostatic field to a unique energy into a reflectron type mass spectrometer. They travel two meters through a drift tube to arrive at the ion detection and counting system. However, because they all depart from the sample at the same time and were subjected to the same accelerating voltage, the lighter ones arrive at the detection system before the heavier ones.

All the secondary ions should be sputtered simultaneously or within a very short time intervals so that the spectral resolution is not degraded. This requires the primary ion pulse to be short as possible. Extremely short primary ion pulses with duration below 1 nanosecond are applied in high mass resolution analysis by ToF-SSIMS.

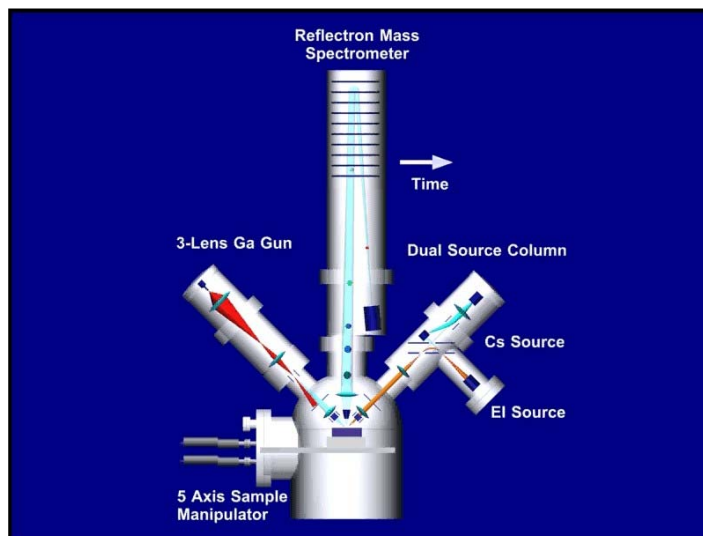


Figure 4.3. The instrumentation details of TOF-SIMS

4.5.2. Primary ion beam systems and effects of primary ion species and energy

The primary ion bombardment requires a beam of a suitable primary ion species, with a given energy, current density and diameter. ToF-SIMS IV, designed and manufactured by Ion-ToF GmbH, Münster, Germany, has three types of primary ion sources. These are the Gallium liquid metal ion gun, the surface ionization gun (Cs gun) and the electron ionization gun. Table 4.2 summarizes the characteristics of these ion guns.

Table 4.2. Properties of primary ion guns available at the ToF-SIMS IV instrument at BAM.

Type	Spot	Current density (Acm^{-2})	Energy (keV)
Electron ionization gun	50 μm – few mm	$< 10^{-3}$	1-10
Ga gun	> 30 nm	1	15-25
Cs gun	> 1 μm	10^{-1}	1-10

In static SIMS the relative secondary ion yields are strongly influenced by the primary ion mass and energy. In the early study performed by Briggs and Hearn [89] using He^+ , Ne^+ , Ar^+ , and Ga^+ ions with energies in the range 1 to 10 keV, it was found that any

increase in the primary ion energy increased the total secondary ion yield. On the other hand, increasing the primary ion mass, at constant energy, increased the total secondary ion yield ($\text{Xe} > \text{Ar} \sim \text{Ne} \gg \text{He}$) and increased the relative yields of the highest mass secondary ions. As a result, larger primary ions were seen as a promising way to improve the molecular information in static SIMS and much heavier primary ions, e.g. SF_5^+ , Cs, Au, CO_2 , C_2F_6 , are introduced to the static SIMS technique [73].

In this work a Cs primary ion beam was used to emphasize both the total secondary ion yield and the relative yields of the highest mass secondary ions.

4.5.3. Time-of-Flight (ToF) Mass Analyzer

The ToF analyzer accepts secondary ion packets, produced by a primary ion pulse. Secondary ions are accelerated to 2 keV over a very short distance. Over a flight path of 2 m the secondary ions are separated in mass because, for ions of constant energy, their flight time is proportional to $m^{-1/2}$.

The secondary ions travel upwards to an ion mirror where they are reflected downwards to the detection system. The single stage reflectron is created by a homogeneous electric field. It consists of a combination of drift regions with an ion mirror. The ion mirror utilizes an electrostatic field to reflect secondary ions in order to provide positive time dispersion, i.e. to increase the flight path of high-energy secondary ions with respect to the lower energy secondary ions. This allows easy compensation of the energy spread of the sputtered species and provides high mass resolution, ($m/\Delta m$). With a ToF mass analyzer $m/\Delta m$, above 10,000 can be achieved.

The major advantages of the ToF mass analyzer over quadrupole and magnetic sector type analyzers are the extremely high transmission, the parallel detection of all masses and the unlimited mass range [73].

4.5.4. Secondary Ion Detector

The detection system is a combination of a channel plate for ion to electron conversion, a scintillator for electron to photon conversion and a photomultiplier, combined with a very fast electronic pulse counting system. The electrons, emitted from the backside of the channelplate, are accelerated onto the scintillator. The scintillator is coated with a conducting Al film, which is penetrated by the keV electrons. The photons emitted out of the backside of the scintillator are detected by the photomultiplier.

Before striking the detection system the secondary ions pass through the post-acceleration optics, which improves the ion conversion probability by further accelerating the ions.

4.5.5. Surface charging and electron flood gun

The SIMS primary ion beam, secondary ion and electron fluxes produce a net electric charge at the sample surface. If the sample material conducts, the charge is compensated by the current flowing through the sample to the ground. However, insulating samples undergo a surface charge buildup. Sample charging can deflect the primary ion beam (especially when low energy primary ions are used) away from the region of interest. Also the emission of electrons and ions from the surface will be hindered. Surface potential variations affect the energy distribution of emitted secondary ions, which effects their transmission and detection by the mass spectrometer. Hence in case of insulating samples, charging compensation techniques must be used. Bombardment of the sample surface by low energy electrons is the most commonly applied technique for charge compensation. Electrons can easily compensate for the positive charge buildup [90].

The use of a electron flood gun to overcome charging problem in the case of insulating samples is well established. However, the effect of electron flood gun parameters i.e., electron energy, on SSIMS spectral data could be as important as the effect of primary ion species and energy [91-93]. Damage of polymers by flood gun electron beams has been recognized since early studies in this field [94].

In this work charge compensation was not required because the deposited films were obviously thin enough to allow a sample current to ground. This can also be due to the semi-conductive character of plasma deposited films. Indeed Retzko [95] reported that plasma polymers of ethylene, acetylene, butadiene and styrene were semi-conductive.

4.6. Normalization and repeatability of the ToF-SSIMS data

In order to get relative information about the differences between the properties of samples i.e., the degree of unsaturation, their SSIMS data must be compared. The absolute yields of secondary ions dependent on instrumental factors and for this reason, the use of absolute yields of the secondary ions for comparison require very good stability of all the spectrometer parts. To remove any absolute yield or beam current drift from spectrum to spectrum, yields of secondary ions should be normalized.

Normalization of each spectrum to the total ion yield of that spectrum is the commonly applied procedure [91, 96]. In this procedure, the yields of the different secondary ions, i , in spectrum, j , (I_{ij}) are multiplied by 100 and then divided by the total secondary ion yield of spectrum j , to get normalized yields of each secondary ion ($\overline{I_{ij}}$).

$$\overline{I_{ij}} = (100)I_{ij} / \sum_i I_{ij} \quad \text{Equation 4.3}$$

The repeatability of the SSIMS data is also rather important in terms of reliability of data. The repeatability of the SSIMS data produced at different laboratories is vital for a comparison of the analyzed data. In a recent inter-laboratory study, the repeatability of experiments was evaluated for 21 instruments [97]. Repeatabilities for some laboratories were as good as 1% but many were approximately 10 % and a few as poor as 80 %.

The repeatability was checked in this study by applying a procedure similar to the one described by [97]. In this procedure, the average of the normalized yield ($\overline{I_i}$) is obtained from;

$$\overline{I_i} = \sum_j \overline{I_{ij}} / j_0, \quad \text{Equation 4.4}$$

where j_0 is the total number of spectra.

This average of the normalized yields is now used to calculate the power, P_{ij} , for each secondary ion;

$$P_{ij} = \frac{\overline{I_{ij}}}{\overline{I_i}} \quad \text{Equation 4.5}$$

P_{ij} will be around unity for each secondary ion, i in each spectrum. The scatter in the relative yields of the secondary ions in the j th spectrum is now given by the standard deviation of the P_{ij} for any given secondary ion, i . If all of the spectra were identical in relative yields but merely changed in absolute magnitude, the P_{ij} would be identically unity. Also, the overall repeatability is given by the average standard deviation (σ_{ij}) of the P_{ij} values for selected secondary ion, i . That is

$$\sigma_{ij} = \sqrt{\frac{\sum_j (P_{ij} - 1)^2}{j_0 - 1}} \quad \text{Equation 4.6}$$

The repeatability was calculated by multiplying the average standard deviation with 100, i.e.,

$$\text{Repeatability of secondary ion, } i \text{ for each sample} = (100)\sigma_{ij} \quad \text{Equation 4.7}$$

Also the average repeatability for all secondary ions of one sample is calculated by taking the average of repeatability values of all secondary ions, i.e.,

$$\text{Average repeatability of all secondary ions} = \frac{\sum \sigma_{ij} (100)}{I_0} \quad \text{Equation 4.8}$$

The average repeatability values provide a reliable measure of the repeatability of data.

It should be noted that the repeatability values represents the absolute uncertainties, i.e., the statistical scatter of ToF-SSIMS yields. These scatters are used to calculate the error bars displayed in the reduced ToF-SSIMS data presented in Chapters 5-7.

In this work the repeatability of both the positive and negative spectra was checked by analysis of a polystyrene reference sample with a Cs primary ion beam. Four positive and negative ToF-SSIMS repeat spectra of polystyrene were acquired and the procedure described above was applied.

Values of P_{ij} of some selected secondary ions for four positive ToF-SSIMS repeat spectra of polystyrene are shown in Figure 4.4. The average repeatability in this example has an excellent value of 2.2 %. Detailed investigation of repeatability values showed that fluctuations were created mainly by the H^+ secondary ion yields and other secondary ions having very low yields. To understand their effects, repeatability values were calculated by excluding the H^+ secondary ion yield and the secondary ions of which yields were less than 0.1 % of total ion yields. This procedure provides, of course better, but more realistic repeatability values. The average repeatability value decreased to 1.6 %. The yields of the H^+ secondary ion are very sensitive to any kind of adsorbed species on the surface of the sample. Low-yield secondary ions are highly sensitive to instabilities of the instrument. Of course elimination of these secondary ions from the repeatability calculations improves the average repeatability value. However, it must be notified that all interpretations in this work were based on the investigation of characteristic secondary ions, of which yields are generally rather high.

Different from the positive spectra the average repeatability value of the negative spectra was calculated as 3.2 %. It decreased to 1.8 % when hydrogen was excluded from the repeatability calculation.

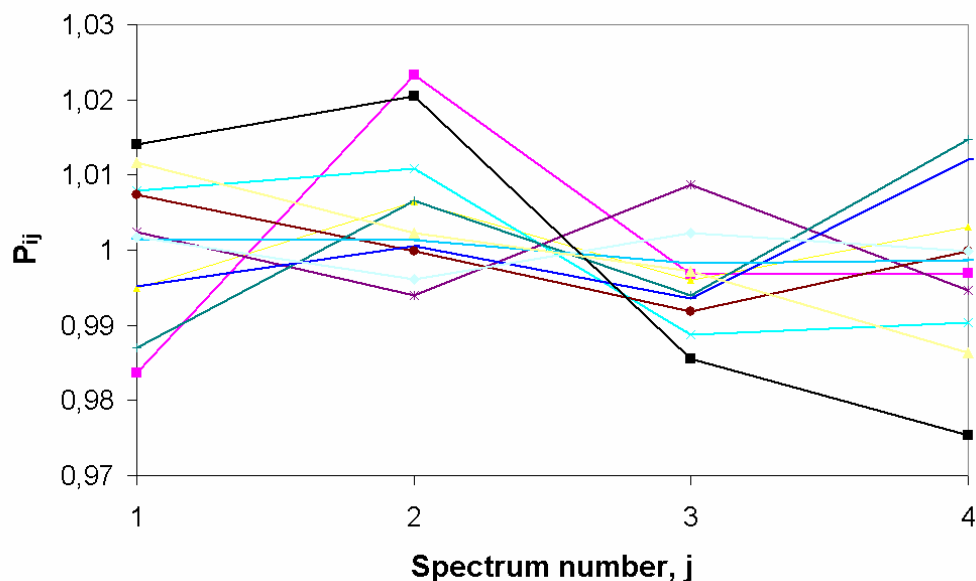


Figure 4.4. The P_{ij} repeatability values from four positive ToF-SSIMS repeat spectra of polystyrene. The average repeatability is 2.2 %.

4.7. Experimental parameters employed for the SSIMS analysis of plasma polymers

Targets were bombarded by a 10 keV Cs^+ primary ion beam with a pulsed primary ion current of 0.75 pA. For each analysis, the ion beam was digitally scanned with a 128 by 128 array over an analysis area of 200 μm by 200 μm . Spectra for each sample were taken from a square array with each analysis area separated by 1 mm. Two measurements at each adjacent area were performed by using the same experimental settings. Total acquisition times were fixed to 50 s. Thus the total ion dose was less than 6.0×10^{11} ions/ cm^2 , which was well below the so-called static limit of SIMS ($\sim 1.0 \times 10^{13}$ ions/ cm^2).

The mass resolution at m/z 28 (Si^+) was higher than 6000, which is good enough to resolve all peaks at low mass regions. For example, the peaks at m/z 43.05477 (C_2H_7^+) and 43.01838 ($\text{C}_2\text{H}_3\text{O}^+$) could be separated easily from each other.

ToF-SIMS analysis of the deposited films was performed immediately after their deposition *without* any exposure to air. In another experiment, the effect of exposure to air on the plasma deposited films was investigated by applying different exposure times.