The analysis of polymer interfaces: a combined approach

Citation for published version (APA):

DOI:
10.6100/IR562755

Document status and date:
Published: 01/01/2003

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
The analysis of polymer interfaces

A combined approach

Proefschrift

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van de
Rector Magnificus, prof.dr. R.A. van Santen, voor een
commissie aangewezen door het College voor
Promoties in het openbaar te verdedigen
op dinsdag 25 maart 2003 om 16.00 uur

door

Wouter Johan Hendrik van Gennip

geboren te Oss
Layout of thesis and cover: Angelica Goyenechea Jaramillo

Cover: Aurora Borealis (picture graciously provided by Matti Aladin). Aurora Borealis is caused when ions from the solar wind are trapped by the magnetic field of Earth, and subsequently impact with gases in the ionosphere. This impact causes these gases to emit visible light, characteristic of the elements involved. For example, oxygen atoms emit red and green light, depending on their altitude, whereas nitrogen atoms emit blue and violet light. This picture was taken on the night of the 25th of September 2001 between 23.00 and 02.00 local time. Photographical information: 28mm/F 2.8 Provia 400 or Sensia 400 II, 15-30 seconds exposure time. More pictures can be found at http://members.surfeu.fi/matti10/EIndex.htm, and the Finnish version contains even more pictures: http://members.surfeu.fi/matti10/

Picture of Aurora Borealis © Matti Aladin, Vuosaari, Helsinki, Finland

CIP-DATA LIBRARY TECHNISCHE UNIVERSITEIT EINDHOVEN

Gennip, Wouter J.H. van


Proefschrift. – ISBN 90-386-2894-3

NUR 913

Trefwoorden: polymeren: fysisch-chemische analyse / polymeeroppervlakken / grensvlak verschijnselen; diffusie / dunne lagen / massaspectrometrie; SIMS / foto-elektronspectroscopie; XPS / multivariate analyse

Subject headings: polymers; physicochemical analysis / polymer surfaces / interfacial phenomena; diffusion / thin films / mass spectrometry; SIMS / X-ray photoelectron spectroscopy; XPS / multivariate analysis

The work described in this thesis has been carried out with financial support from the Dutch Polymer Institute, project number 272

Printed at Universiteitsdrukkerij, Eindhoven University of Technology.
# Table of Contents

1. Scope of this thesis  
   1.1 Setting the stage .................................................. 1  
   1.2 Surface modified coatings ........................................ 2  
   1.3 Polymeric light emitting displays ............................... 2  
   1.4 Organic solar cell panels ....................................... 4  

2. Introduction to SIMS and XPS  
   2.1 Principle of SIMS .................................................. 7  
   2.2 SIMS operational modes .......................................... 9  
   2.3 Necessary SIMS equipment ....................................... 13  
   2.4 Sample preparation for SIMS .................................... 21  
   2.5 The principle of XPS .............................................. 23  
   2.6 Necessary XPS equipment ....................................... 27  
   2.7 Charge referencing ............................................... 30  

3. Depthprofiling of surface regions  
   3.1 Introduction ...................................................... 35  
   3.2 Experimental ..................................................... 37  
   3.3 Results and discussion ......................................... 38  
   3.4 Conclusions ...................................................... 44  

4. The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using the mixing-roughness-information depth model  
   4.1 Introduction ...................................................... 47  
   4.2 Experimental section ............................................ 53
1. Scope of this thesis

Abstract

This chapter describes the applicability of the surface science technique secondary ion mass spectrometry (SIMS) on polymer/organic surfaces without going into great detail. Mostly, some problems that can be encountered in applied surface science and that are described in this thesis will be discussed to provide a framework for the rest of the thesis.

1.1 Setting the stage

Although bulk properties determine the strength and durability of materials, the surface properties are often of greater importance for many sophisticated applications. The material at the outermost layer may be oxidized or contaminated with organic or inorganic compounds, which can have catastrophic results for the performance in the desired application. This is certainly the case for organic solar cells and light emitting devices, in which electron transfer across interfaces may be inhibited, or polymer degradation may occur. Close to the surface, material may have diffused into the polymer structure, which can have either a negative, or sometimes a positive influence on the device performance. Either way, it will be important for the scientist to know the chemical composition in the surface region in order to improve his understanding of the system.

An analytical technique that is capable of analyzing materials from the outermost atomic layer up to a depth of several micrometers is secondary ion mass spectrometry (SIMS), which will be discussed in detail in chapter 2. With SIMS, interface reactions, diffusion and segregation processes can be studied at an often remarkable depth resolution of only a few nanometers. However, this technique still has many limitations, especially for studying polymer and organic materials, which will be discussed in detail in later chap-
Scope of this thesis

ters. This chapter will only set the stage by discussing the background of the studies presented in this thesis, and the objectives of each study.

1.2 Surface modified coatings

Although many polymers have excellent bulk properties, their use in many applications is inhibited by their undesirable surface properties, such as poor wettability and abrasion or chemical resistance. Fortunately, there are many ways to modify the polymer surface so that it exhibits more preferable surface properties. The range in which this modification extends within the polymer layer may be limited to only a few nanometers, depending on the applied modification technique.

Although this depth scale is eminently suitable for application of SIMS in combination with depth profiling, in this range the SIMS signals are not very stable and any conclusions drawn from measurements within this unstable range have to be scrutinized with suspicion. Chapter 3 describes a technique with which this instability can be avoided in the range of interest.

1.3 Polymeric light emitting displays

Some polymers, such as polyacetylene (PA) that was the first such polymer reported, can act as a semiconductor because it is $p$-conjugated. This means that the molecular backbone, in the case of PA the whole polymer, consists of alternating single and double bonds. The $p$-electrons can be easily excited into delocalised molecular orbitals along the polymer chain, which causes semiconducting behavior.

After PA, many other $p$-conjugated polymers have been reported to act as a semiconductor. One of these polymers, poly(phenylenevinylene) or PPV, was used to construct the first polymer light emitting display. Fig. 1 shows a common design for such a device. It consists of the active layer, sandwiched between two electrodes, one of which obviously has to be transparent. The chemistry of the transparent electrode often damages the active layer, so that most often a protective conductive polymer is placed between the transparent electrode and the active polymer, also to prevent the transparent electrode to make direct contact with the opposite electrode, because the transparent electrode usually is very rough and the active polymer layer rather thin. By applying a sufficiently high bias voltage, holes and electrons are injected into the polymer from both electrodes. Because these holes and electrons move towards each other under the influence of the electrical field, they may recombine on a $p$-conjugated polymer chain to form excitons. Subsequent radiative decay of the excitons results in the emission of light.
The color of this light depends on the energy gap, also called band gap, between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the $\pi$-conjugated polymer. This means that the color can be tuned by making some changes to the chemical structure of the polymer. For example, PPV emits yellow-green light whereas alkoxy-substituted PPV derivates emit red light.

For optimal hole and electron injection the right electrode material has to be selected. For the hole injection electrode usually indium tin oxide (ITO) is used, because of its transparency and its availability from the liquid crystal display technology. However, ITO easily degrades PPV and its derivatives. To prevent this from happening, nowadays a conducting polymer layer, made of polystyrenesulfonate-doped polyethylene dioxythiophene (PEDOT:PSS) is added between the active and ITO layer, which increases the device lifetime by a factor of at least ten.

To study the effectiveness of this approach, the diffusion of indium can be studied by measuring the relative concentration profile of indium with SiMS. The diffusion of aluminum, that is sometimes used as low workfunction electrode, into the active layer, a process that some suspect happens during the thermal evaporation on top of the active layer, can also be studied. However, the depth resolution obtained in metal-polymer stacks such as organic light emitting displays can be extremely bad. Chapter 4 discusses some mea-
Scope of this thesis

Sures that can be taken to prevent some loss of depth resolution from happening, and a technique to improve the depth resolution post-hoc.

Many low workfunction metals have been tried as the electron injection electrode, such as Al, Mg and Ca. Their low workfunction ensures a good balance between the hole and electron injection, which in turn results in a higher number of photons emitted per injected charge carrier. However, these metals are susceptible to oxidation, especially at the interface, which can degrade their contact with the active polymer layer. The problem is to reach the interface with an analytical tool without perturbing the interface. However, by simulating the interface with a sub-nanometer layer of Ca on top of the polymer the oxidation mechanism at the interface could be studied and is reported in chapter 5 of this thesis.

The performance of these devices can be improved remarkably by the insertion of a 1 nm thin layer of LiF sandwiched between the low workfunction metal electrode and the active polymer layer. The precise mechanism of this improvement has been the subject of considerable debate, with two mechanisms being predominantly favored. By simulating the interface with sub-nanometer layers of LiF and Al, one of these mechanisms could be studied and disproved, which is described in detail in chapter 6 of this thesis.

1.4 Organic solar cell panels

In organic solar cells the reverse process of the polymer light emitting displays is used, so that the same basic design from the organic light emitting devices can be used. Light that falls on the solar cell results in an exciton, which relaxes through the production of a hole and electron. However, if the electron and hole are not quickly separated, they will recombine and no useful electricity will be produced by the solar cell. A molecule that can quickly adsorb and transport the electron has to be mixed with the active layer. Fullerenes are suitable as an electron acceptor, because the electron transfer from the active layer, the electron donor, has been measured to occur within fifty femtoseconds, while the reverse process takes milliseconds. The contact surface between active polymer and the electron-accepting molecule has to be as large as possible to facilitate the electron transfer.

However, fullerenes have the tendency to crystallise when blended with the electron donating polymer, for example PPV. The crystallisation of the fullerenes in the blend lowers the contact surface between the donor and acceptor, and hence is undesirable. To prevent crystallisation a fullerene derivative (PCBM) was developed with a reduced tendency to crystallise, and that is somewhat easier to dissolve in solvents used for spincoating. However, PCBM may still segregate into clusters within the polymer layer that adsorb preferentially at the surface of the polymer.
A depth profile of a PCBM:MDMO-PPV blend could possibly shed some light on this issue. However, the problem with applying SIMS on a blend of two organic molecules is that the raw data obtained with this technique is not particularly useful to distinguish between both molecules. Chapter 7 describes how two multivariate statistical analysis techniques, *canonical discriminant analysis* and *principal components analysis*, can be applied to distinguish between both molecules and even quantify their distribution in-depth, be it with some error.
Scope of this thesis
2. Introduction to SIMS and XPS

Abstract

This chapter will introduce the reader to the surface sensitive techniques Secondary Ion Mass Spectrometry (SIMS) and X-ray Photo-electron Spectroscopy (XPS). The physical background of the necessary components of the equipment is described, as well as the practical aspects of sample preparation and measurement procedures. Later chapters deal with sample degradation and behaviour under X-ray and ion beams.

Introduction

Secondary Ion Mass Spectrometry (SIMS) and X-ray Photo-electron Spectroscopy (XPS) are both versatile surface science techniques that can be successfully applied to a multitude of chemical, physical and material science related problems, especially when they are used together.1-7 For the sake of clarity this chapter deals with both techniques separately. First, the basic aspects of SIMS will be looked at, after which XPS will be discussed.

2.1 Principle of SIMS

Secondary Ion Mass Spectrometry, schematically explained in Figure 1, uses a focused primary ion beam targeted at the sample of interest. The primary ion energy is typically between 0.1 to 30 keV, depending on the type of experiment and ion source. A primary ion of this energy range that reaches the sample surface loses its energy by nuclear collision with the atoms of the sample material, transferring eventually all of its energy in the process.

The target atoms that have been hit by the primary ion also start to collide with neighbouring atoms, forming what is called a collisional cascade. Part of
this collisional cascade may reach the sample surface, from where atoms or molecular clusters can be emitted, as neutral or charged particles. Charged particles can be detected by a mass analyser, such as a quadrupole, hemispherical analyser or time-of-flight detector.

The final intensity of the detected ion signal depends on many parameters:

\[ I_s^\pm = I_p \cdot Y \cdot P^\pm \cdot C \cdot T \]  

with:

- \( I_s^\pm \): the ion signal intensity
- \( I_p \): the primary ion flux
- \( Y \): the sputter yield
- \( P^\pm \): the ionisation probability
- \( C \): the fractional concentration
- \( T \): the transmission of the used detector

In order to be detected, an atom or molecule needs to be present at the surface, expressed by the fractional concentration, \( C \). The sputter yield \( Y \), the number of particles sputtered per primary ion, determines the number of particles that can potentially exist as an ion, together with the primary ion flux \( I_p \). Every sputtered particle has a small chance of becoming ionised. This chance \( P^\pm \) is determined by the chemical surrounding of the departing particle, the so-called matrix effect, as well as by the ionisation potential or electron affinity, depending on the sign of the charge. Finally the percentage of the ionised particles that are able to reach the detector plate, the transmission \( T \) of the detector, influences the signal intensity.

The sputter yield \( Y \) depends on both the acceleration voltage of the primary ion and the angle of the primary ion beam from the surface normal. To dem-
SIMS operational modes

Demonstrate this, dynamic Monte Carlo simulations were performed of Ar, Ga and Xe ions colliding with a silicon substrate, using the SRIM 2000 program of Ziegler and Biersack. A thousand collisions were simulated for every calculation. Figure 2 shows that the sputter yield goes up with increasing acceleration voltage in the range measured, and with a larger angle from the surface normal. A higher acceleration voltage causes more energy to be deposited in the surface, which dissipates in the collisional cascade. At very high acceleration voltages the yield will go down again as most energy will be deposited in deep layers, which decreases the chance that the collisional cascade will reach the surface. A larger angle from the surface normal causes the collisional cascade to stay closer to the surface. What can also be noticed is that the highest sputter yield is associated with the largest, or heaviest, primary ion. However, a heavier ion transfers less of its energy than a lower-mass ion when hitting a low-mass target atom (neglecting possible binding energies of the target atoms).\(^9\)

\[
T_m = \frac{4M_1 M_2}{(M_1 + M_2)^2} E
\]  

(2)

With:
- \(T_m\) the maximum transferable energy
- \(M_1\) the mass of the primary ion
- \(M_2\) the mass of the target atom
- \(E\) the primary ion energy

When the interactions of Ar, Ga and Xe with Si are compared, the maximum transferable energy of each collision is 96.96%, 81.88% and 58.07%, respectively, using the natural abundance of each atom.

However, a heavier ion does not penetrate the target as deeply, so that in the end more energy is deposited in the near-surface region. The sputter yield scales linearly with the deposited energy in the near surface region, hence the yield goes up for the series Ar-Ga-Xe. These results correlate well with the findings of Kötter et al., who found that changing from Ar\(^+\) to Xe\(^+\) and to SF\(_5^+\) the sputter yield increased strongly.\(^10\)

2.2 SIMS operational modes

SIMS can be used in two distinctive modes. The main difference between both modes is the sputter speed. In the dynamic mode, referred to as
dynamic SIMS, many layers are removed per second, whereas in the static mode care is taken that all secondary ions are coming from a pristine surface. Both modes will be described in detail in this section.

2.2.1 Dynamic SIMS

Dynamic SIMS is a procedure during which, as opposed to static SIMS, many atomic layers are removed from the surface of the studied sample by sputtering them away. This way the composition of layers below the surface can be studied in sequence, so that relative concentration profiles can be constructed.

For dynamic SIMS the ion beam needs to be rastered over the surface of the sample. If an analogical scan unit is used, two sawtooth voltages are applied to scanning quadrupoles, a fast one to scan the beam in a line over the sample surface, the other slowly to reposition the beam slightly below the last line scanned before. At the end of every sweep of the surface the ion beam repositions itself to start the procedure anew. This way a kite-shaped crater is formed, as shown in Figure 3a.

A digital scan unit is capable of making square craters by using a stepped sawtooth for the slow scanning voltage, as shown in Figure 3b. The ideal result would be a square crater with sharp edges and vertical crater walls,

---

**Figure 2.** Dynamic Monte Carlo simulations show the dependence of the sputter yield \( Y \) on the acceleration voltage and the angle from the surface normal of the primary ion beam.
SIMS operational modes

Figure 3. (a) Kite shaped crater produced by rastering the MIG 102 Ga ion beam over a Si(100) surface with an analog raster unit,(b) Rectangular crater produced by rastering an Ar beam over the surface of a multilayered device. Note the slope of the wall. (measured at Philips CFT by Corrie Bulle-Lieuwma on an ION-TOF 4).

because otherwise the walls of the crater can also contribute to the signal, degrading the depth resolution, which is the accuracy of the determination of the depth from which the ions originate. To avoid this it is possible to use an electronic gate, which only allows data collected from the middle of the crater to contribute to the ion intensity signal. The width of the rastered area, assuming a square crater, should typically be about 2.5 times the width of the gated area5 and at least 5 times the beam diameter.5 The actual dimension of the crater is not only determined by the dimension of the raster, but also by the diameter of the primary ion beam.

A simple example of wall effects is shown in Figure 4. Here a depth profile was made of Si in Si(100) with an approximately 18 Å thick native oxide layer on top, as determined by XPS. The interface between the SiO2 layer and the Si(100) is usually very sharp, and the matrix effect (the enhancement of the Si+ intensity because of the presence of oxygen in the matrix) enabled the determination of the separate phases in an efficient manner. If no electronic gate is used the 'background' only decreases with approximately one order of magnitude. Gradually decreasing the electronic gate size reduces the contribution of the crater walls and thus also the Si+ ion intensity. Reducing the electronic gate size with more than 50 % of the total raster area only accomplishes the degradation of the signal to noise ratio. Increasing the raster size decreases the sputter rate at the same primary ion density, although of
Introduction to SIMS and XPS

2.2.2 Static SIMS

SIMS is in principle a damaging technique, as during the measurements surface layers, or at least parts thereof, are being removed from the sample, and layers below the surface are perturbed and altered by the collisional cascade. If, however, mass spectrometers of adequate sensitivity are employed it is possible to obtain a reasonable ion count rate at a very low sputter rate, e.g. one layer per several hours. Provided the measurement is short it is safe to assume that the secondary ion fragments measured originate from a pristine, i.e. unperturbed surface area. This can also be expressed in the amount of primary ions that have reached the surface per square centimetre, the so-called static limit above which deterioration of some ion intensities starts to

---

Figure 4. Concentration depth profile of Si in SiO$_2$/Si(100) measured with a 10 kV Ga beam at a current of 3 nA as a test of the functioning of the electronic gate. The Si ion intensity is initially high because of the presence of oxygen in the SiO$_2$ native oxide matrix. After the ion beam has sputtered through the SiO$_2$ native oxide phase the Si signal drops down to a lower level. However, the Si signal will not drop down to this ‘background’ level as long as wall effects are included in the ion signal. Making the electron gate size smaller than absolutely necessary only causes deterioration of the signal to noise ratio. The percentages denote the percentage of the area of the crater used in the analysis, centered on the middle of the crater, course not locally. Furthermore, increasing the raster size increases the chance that the surface of the bottom of the crater is sputtered away unevenly, deteriorating the depth resolution.
occur. This limit is quite low, especially for polymers, and is generally assumed to be around $10^{12}$ ions/cm².

Taking the static limit into account the surface can be studied this way, yielding qualitative information about the surface composition and chemical structure of compounds present. Although many attempts have been made to extract quantitative information, the feasibility of this is still a hotly debated issue.

2.3 Necessary SIMS equipment

The use of accelerated ions implies the necessity of an ultra-high vacuum (UHV) as the working environment. Indeed, SIMS is not a cheap technique and requires, besides obvious components such as an ion source and detector, expensive auxiliary equipment such as UHV pumps, valves and chamber. However, describing this auxiliary equipment is outside the scope of this dissertation, hence the reader is referred to some standard books about vacuum technology. Only the ion sources, quadrupole detector and electron flood gun will be described.

2.3.1 Ion sources

Several ion sources have been developed for SIMS and other applications over the years, such as the metal ion gun, the electron impact gun, duoplasmatron and surface ionisation gun. Table 1 shows the ions emitted from these sources, as well as their main application. Still in development in SIMS technology and hence not mentioned in Table 1, are cluster guns for sputtering with ions such as C₆⁺, (CsI)ₙCs⁺, C₆₀⁺ and clusters from e.g. Au, Nb, Al, Si, Cu, Ag, B and NaF. One notable exception is the use of SF₅⁺ clusters, which are readily made in electron impact and duoplasmatron sources equipped with filaments resistant against reactive gases, and their use has been reported numerous times. The main reason to use poly-atomic clusters is that these usually do not damage the near-surface region at the site of impact as much as atomic ions of the same kinetic energy, but still enhance the sputter yield with about one order of magnitude.

The VG Ionex as used in the present work is only equipped with a VG MIG-102 metal ion gun for dynamic and imaging SIMS, and the VG FAB-61 electron impact / fast atom bombardment gun for static SIMS. In the next few paragraphs the principle of these ion sources will be discussed.

2.3.1.1 Liquid metal ion gun

The working principle of a liquid metal ion gun (LMIG or MIG) is the field ion emission process. Very high electric fields in the order of $10^8$ Vcm⁻¹ modify
Introduction to SIMS and XPS

the surface potential barrier of a liquid metal film, causing electrons to tunnel more easily. If the right polarity of the field is chosen, the electrons will tunnel into the solid, thus generating ions at the surface. These ions will then desorb into the electric field (field evaporation).

To accomplish such a high field a very small emission substrate must be used, as demonstrated in Figure 5. A liquid metal, usually gallium, flows as a

<table>
<thead>
<tr>
<th></th>
<th>Metal ion</th>
<th>Electron impact</th>
<th>Duoplasmatron</th>
<th>Surface ionisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron emission current range [μA]</td>
<td>NA</td>
<td>$10^{-4}$ - $10^{4}$</td>
<td>$10^{3}$ - $5 \times 10^{5}$</td>
<td>NA</td>
</tr>
<tr>
<td>Source pressure [mbar]</td>
<td>$5 \times 10^{-8}$ (max)</td>
<td>$10^{-7}$ - $5 \times 10^{-4}$</td>
<td>$10^{-3}$ - $10^{-2}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Ion energy spread [eV]</td>
<td>5</td>
<td>10</td>
<td>10 - 20</td>
<td>0.2</td>
</tr>
<tr>
<td>Ion energy [keV]</td>
<td>$0.1 - 30$ (^1)</td>
<td>$0.1 - 5$</td>
<td>10</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Spot size range [μm]</td>
<td>$\geq 0.2$</td>
<td>100 - 2000</td>
<td>5 - 100</td>
<td>$\geq 0.2$</td>
</tr>
<tr>
<td>Ion current range [nA]</td>
<td>0.1 - 300</td>
<td>$800 \times 10^{4}$</td>
<td>$5 - 2 \times 10^{4}$</td>
<td>$\geq 1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Current density [mA cm(^{-2})]</td>
<td>$10^{3}$</td>
<td>4</td>
<td>20 - 100</td>
<td>100</td>
</tr>
<tr>
<td>Beam brightness [A cm(^{-2}) sr(^{-1})]</td>
<td>$10^{6}$</td>
<td>0.01</td>
<td>100 - 200</td>
<td>50 - 500</td>
</tr>
<tr>
<td>Neutrals content (maximum)</td>
<td>0 %</td>
<td>2 - 4 %</td>
<td>0 % (^3)</td>
<td>0 %</td>
</tr>
<tr>
<td>Elements/gases used</td>
<td>Ga, In, Au</td>
<td>Ar, Ne, Xe, (O(_2), N(_2), SF(_6))^2 (^2)</td>
<td>Ar, Ne, Xe, (O(_2), N(_2), SF(_6))^2 (^2)</td>
<td>Cs</td>
</tr>
<tr>
<td>Main application</td>
<td>all</td>
<td>static</td>
<td>dynamic</td>
<td>dynamic</td>
</tr>
</tbody>
</table>

\(^1\) Typically metal ion guns have an energy range between 1 to 30 keV, but for some applications (ultra-shallow junction depthprofiling) it is necessary to retard a pre-focussed beam to an energy as low as possible. \(^2\) Only possible if the ion source has been fitted with an inert filament, e.g. thorium coated. \(^3\) This value assumes the presence of a bend in the optical column.

Table 1. Comparison of the typical operation parameters of the most commonly used ion sources in SIMS. Adapted from Briggs and Seah.\(^7\)
thin film over a tungsten needle with a tip sharpened to a radius of 1-10 µm (needle/filament type) or out of a capillary nozzle (nozzle type), thus forming an emission substrate. The electrical field forces the metal film into a conical shape at the apex of the needle, known as the Taylor cone, with the half-angle determined by the opposing forces of the electrical field and the surface tension of the metal. From the end of this cone an even smaller ‘wisp’ of liquid metal is pulled, at the tip of which the actual field evaporation takes place. The radius of this tip is approximately 2 nanometers.

The amount of metal ions emitted must be replenished from a reservoir. In the case of the MIG-102, the needle is spotwelded onto a tungsten heating filament and stands in the middle of a gallium slab that is heated carefully by the filament/needle to ensure enough gallium is present, although care must be taken to avoid flooding of the needle, which would result in unstable current characteristics of the gun. Another consideration is that evaporation will take place if the gallium becomes too hot, severely reducing the reservoir’s lifetime.

The optical column of the MIG-102 ion source is based on the Köhler illumination principle,20 demonstrated in Figure 6. The condenser lens images the source (d_o) to the objective lens aperture, while the objective lens images the condenser lens aperture (d_a) to the sample surface. The minimum spot size (d_g) is determined by the objective lens aperture.
Introduction to SIMS and XPS

Because the imaging ratio from the source to the objective lens is chosen such that the resulting image \( (d_i) \) is larger than the lens aperture, only a portion of the beam is utilised, which can be set by several criteria. A consequence of this is that larger spot sizes equal higher current on the sample, as demonstrated in Figure 7. Using only a portion of the image on the objective lens aperture \( (d_o) \) to the sample surface. Because the imaging ratio from the source to the objective lens is chosen such that the resulting image \( (d_i) \) is larger than the lens aperture, only a portion of the beam is utilised. This way the spot on the sample surface will not move when the source experiences lateral drift.

Beside the lenses, two other optical features have been added to the MIG-102, as Figure 4 shows. With the stigmator quadrupole rods, chromatic aberrations to the shape of the spot, caused by the ion energy spread, may be corrected by either elongating or compressing the spot in the direction of the \( x \) or \( y \) axis. The scanning quadrupoles are used to scan the ion beam over the sample surface in the same manner as an electron beam is scanned over the fluorescent screen of a television set or monitor.

---

**Figure 6.** The MIG-102 ion optics column makes use of the Köhler illumination principle. The condenser lens images the source \( (d_o) \) to the objective lens aperture, while the objective lens images the condenser lens aperture \( (d_g) \) to the sample surface. Because the imaging ratio from the source to the objective lens is chosen such that the resulting image \( (d_i) \) is larger than the lens aperture, only a portion of the beam is utilised. This way the spot on the sample surface will not move when the source experiences lateral drift.

Because the imaging ratio from the source to the objective lens is chosen such that the resulting image \( (d_i) \) is larger than the lens aperture, only a portion of the beam is utilised, which can be set by several criteria. A consequence of this is that larger spot sizes equal higher current on the sample, as demonstrated in Figure 7. Using only a portion of the image on the objective lens \( (d_i) \) has several advantages. Neither the shape nor the size of the source can influence the size of the final spot. Also, if lateral drift occurs in the source, the beam spot will not move on the sample surface but on the objective aperture, although the current may fluctuate because the beam intensity is usually not entirely radially uniform. Finally, for some applications a steep edge to the ion beam intensity profile may be required. Choosing a flat part of the beam can easily be accomplished in this manner. Sputtering of both apertures may be a disadvantage, because this will slowly deteriorate the shape of the ion beam.

Beside the lenses, two other optical features have been added to the MIG-102, as Figure 4 shows. With the stigmator quadrupole rods, chromatic aberrations to the shape of the spot, caused by the ion energy spread, may be corrected by either elongating or compressing the spot in the direction of the \( x \) or \( y \) axis. The scanning quadrupoles are used to scan the ion beam over the sample surface in the same manner as an electron beam is scanned over the fluorescent screen of a television set or monitor.
2.3.1.2 Electron impact gun

When a gas atom or molecule is bombarded with electrons it may ionise upon impact or when an electron passes close by, resulting in a positively or negatively charged ion, depending on whether the gas atom or molecule lost or gained an electron.\textsuperscript{23,24} Except in special cases, only the positive ions are used for analysis. The electron impact gun makes use of this principle, as demonstrated schematically in Figure 8a. A heated filament generates the necessary electrons, which are attracted towards an electron trap through a gas chamber, possibly ionising the gas on the way to the electron trap. The current to the electron trap is measured and used in a feedback loop to control the filament temperature to maintain the electron emission at the desired level. An efficient design is the cylindrical symmetry source, shown in Figure 8b and present in the VG FAB 61. In such a source the electrons make multiple passes through the cylindrical grid area, increasing the chance of the gas ionisation per electron and hence the sensitivity of the ion source. After ionisation the ions are drawn and focussed into the quadrupole filter by an ion focus electrode.

The electron impact gun is the most commonly used ion source, because it is very versatile in its use. Changing the gas pressure within the ionisation
chamber or the ionisation current can alter the ion current up to six orders of magnitude. The spot it can potentially produce ranges from centimeters to microns in diameter. Altering these settings makes it possible to record static SIMS mass spectra, sputter large areas of surfaces clean, sputter large surfaces at higher ion current for XPS depthprofiling, or to use it for SIMS depth-profiling.

The sputtering characteristics of the source are also depending on the gas used for ionisation. Typically noble gases are used, such as Ar and Xe, but if the source is equipped with an inert filament (e.g. zirconia or thoria coated iridium), reactive gases such as O₂, N₂ or SF₆ can also be used. Noble gases usually penetrate more deeply than molecular gases, causing more damage to the sample. This does not mean that atomic gases yield more particles per incoming ion, because most of the energy will be deposited in deep layers and will not result in sputtered particles at all. Although molecular gases get the same energy in the ion source as the noble gas ions, upon impact on the surface of the sample these molecules split up, dividing the energy over the constituent atoms in the molecular ion according to their mass ratio, so that at the same initial energy molecular ions do not penetrate as deeply as similar mass noble gas ions, causing much more energy to be deposited near the surface. Oxygen also enhances the ion yield by locally oxidising the surface, inducing an altered matrix effect.

2.3.2 Quadrupole Mass spectrometer

A quadrupole mass analyser filters ions based on their m/z ratio, with m the mass of the ion and z its charge. It essentially consists of four parallel, molybdenum rods or electrodes, located in a square array. Opposite electrodes are connected together. A potential of \( \Phi = U + V \cos(2\pi ft) \) is applied to one pair, with U a D.C. voltage with opposite sign to the secondary ion and V.
the peak amplitude of a radio frequency voltage of frequency \( f \), larger than \( U \). The other electrode pair carries a potential of \( \Phi = U - V \cos(2 \pi ft) \).

If an ion enters the quadrupole assembly, shown schematically in Figure 9, parallel to the z-axis, it will be either attracted or rejected by the electrode pair in the xz plane, and hence will be excited into an oscillatory motion by the RF field. The higher the mass of the ion, the higher the amplitude of this oscillation will be and hence it will more readily neutralise against the electrode pair, which in other words acts as a low mass pass filter.

While the ion is rejected by the first electrode pair, it will be rapidly attracted towards the second electrode pair in the yz plane. However, the RF field gradients between the electrode pairs exert an average focussing force on the ion. This effect increases with the mass of the ion, hence this part of the quadrupole assembly acts as a high mass pass filter.

If the low and high mass pass filters almost overlap, then the quadrupole assembly will act as a band pass filter. The position and width of this band are controlled by \( V \) and \( V/U \), respectively. The mass that a particular filter is tuned to is:

\[
M = \frac{V}{7.2f^2/r_0^2} \tag{3}
\]

---

**Figure 9.** Schematic representation of a quadrupole mass filter.

Potential on x-rods = \( U + V \cos(2 \pi ft) \)
Potential on y-rods = \( U - V \cos(2 \pi ft) \)
with

\[
\begin{align*}
M & \quad \text{mass [a.m.u]} \\
V & \quad \text{peak amplitude [V]} \\
f & \quad \text{radio frequency [MHz]} \\
r_0 & \quad \text{radius of the cavity between the quadrupole rods [cm]}
\end{align*}
\]

At a ratio of V:U of 6:1 the stable range is approximately only 1 a.m.u., enough resolution for a SIMS experiment.

Finally, the hyperbolic rod assembly is not used in practice. Instead, circular rods of radius \( r \) are used that approximate the exact quadrupole field.

### 2.3.3 Low energy electron charge neutralisation gun

During sputtering, positive primary ions are introduced into the surface area of the sample and secondary electrons are emitted. When the sample is an insulator this will lead to a build-up of a positive charge at the surface. This charge will deflect the primary ions from the intended point of impact. In the case of depth profiling and imaging SIMS this will result in a distorted crater shape. Even worse, the secondary ions coming from the surface will either get a boost in kinetic energy if positively charged, or will be retarded if negatively charged, possibly pushing the secondary ions out of the energy acceptance window of the quadrupole mass analyser, resulting in loss of signal intensity. To counteract charging, the surface is usually gently sprayed with low energy electrons when dealing with insulating samples. The usual procedure is to optimise the ion source, energy window and electron flood-gun simultaneously.

However, using an electron charge neutralisation gun can induce damage in the studied polymer, by C-C and C-H scission, radical production, crosslinking and hydrogen abstraction,\textsuperscript{25} and the emission of secondary ion emission not related to secondary ion emission from the primary ion sputter cascade, called electron stimulated ion emission. This damage is mostly caused by the secondary low energy electrons emitted.\textsuperscript{26} The VG Ionex unfortunately employs 500 eV electrons, which is close to the optimum energy for secondary electron emission at 1000 eV. As the electron beam is typically much broader than the utilised ion beam, the area from which electron stimulated ions originate is much larger than the area sputtered by ions. In the case of imaging SIMS the lateral resolution, or image contrast, will be adversely affected, whereas during depth profiling the depth resolution will deteriorate. In both cases this is caused by ions from outside the area of analysis. The procedure to check for ESIE is to switch off (to blank) the ion beam. If ions are still being detected then ESIE is occurring. In any case the electron current should never exceed 10 mA/m\textsuperscript{2}.\textsuperscript{27}
Often it will be enough to just reduce the electron emission current. The fraction of secondary ions emitted by ESIE can be lowered by changing the target potential bias, i.e. by changing the velocity of the secondary ions, pushing the secondary ions formed by ESIE out of the energy acceptance window of the quadrupole analyser. This is possible because the velocity distribution of the secondary ions formed by ESIE is different from the normal secondary ion velocity distribution. A drawback is that also the intensity of the normal secondary ions will be reduced.

2.4 Sample preparation for SIMS

Because of the sensitivity of SIMS to contamination on the surface, strict cleaning and storage procedures should be observed. An excellent review of these procedures has been given by D.F. Reich. Here, only the most important points of his review will be discussed together with two often neglected, but related subjects.

2.4.1 Cleaning and storage of samples

The importance of the package material choice is something that is usually woefully underestimated by the average “client”. Normal plastic boxes or bags are covered with polydimethylsiloxane (PDMS), which is a mould-release agent. PDMS is a liquid polymer that can creep over a sample surface, hiding it from sight as far as static SIMS is concerned. Obviously, PDMS-free packaging material should be used, as otherwise the whole measurement is going to be pointless. There are two good solutions. The cleanest packaging material is in use in the semiconductor industry: boxes made from polypropylene to contain any size wafers. A much cheaper and nearly as good a solution is to use kitchen aluminium foil, which is surprisingly clean on both sides as long as it is not touched, and can be used to store samples for up to several months.

All kinds of organic samples will be measured in time in any SIMS equipment. Contamination of the sample stubs by the samples is inevitable. To avoid cross contamination, the sample stubs should be cleaned prior to use by submersion in an ultrasonic bath. The same holds of course for the tweezers used to handle the samples. The following sequence is recommended:

1. Ultrasonic rinse in methylene chloride to remove various fatty acids, oils and contaminants such as DOP (a plasticizer)
2. Ultrasonic rinse in hexane to remove PDMS contamination
3. Ultrasonic rinse in acetone
A less drastic cleaning procedure can be used when depth profiling will be performed. Usually a rinse in acetone or alcohol will suffice. A check whether diffusion of contaminants over the surface is still a problem during depth profiling is to enlarge the sputter raster. Because the sputter rate changes quadratically in relation to the size of the raster, and the distance linearly, any diffusion of contaminants during the measurements should be visible by the change of the shape of the depth profile of ions characteristic of the contaminant.

Kleenex tissue paper to dry the stubs should come from a carton box from which the plastic slit has been removed: the plastic transfers some of the PDMS on its surface to the paper, which in turn contaminates the stub and sample!

Most generic double-sided tape contains high amounts of PDMS. Because of the high mobility of PDMS, which can move to the sampling side of the sample with obvious effects, special PDMS tape should be used to attach the sample to the sample stub. “Scotch” and “Highland” tape from 3M are recommended.

2.4.2 Pros and cons of thick or thin layers

In polymer research, authors often use thin, spincoast polymer films when studying the polymers with static SIMS. They claim it provides the advantages of not having to use an electron flood gun for charge neutralisation, and a clean surface. This is true when using freshly prepared polymer without any additives.

However, if commercial polymers are dissolved and spincoast, it is unrealistic to claim that this results in clean surfaces. Commercial polymers contain large amounts of low-molecular weight plasticizers and release agents, not to mention fillers such as soot. These will gather at the surface of the thin, spincoast film, masking the polymer, which results in an altered static SIMS spectrum.

Another problem is that the maximum film thickness of the polymer up to which charge correction by an electron flood gun is not necessary is usually 20 nanometers or less. The formation of pinholes in the polymer film at this thickness is inevitable, exposing the substrate to the ion beam, which in turn results in signal from the substrate.

Thick layers or sheets of polymers do not have these problems. Clean bulk polymer can be easily achieved by removing the top layer mechanically with e.g. a scalpel, having rinsed the scalpel with ‘pro analysis’ quality solvent to remove any possible contamination. Charge compensation by electron flood gun does not have to be a problem, as will be shown in later chapters.
2.4.3 Sacrificial top layer for depth profiling

A steady state between the substrate and the ions from the primary ion beam slowly forms upon initiation of a depth profile. The relative concentration depth profiles are not reliable before this steady state is reached. This can be very inconvenient, especially when the study involves modified top layers of polymers, which are per definition very thin, and might well be sputtered through before the steady state has been reached, with the loss of all relevant information.

To avoid this, a sacrificial layer may easily be applied to the studied material. It is important to use a material of approximately the same density as the layer of interest, because otherwise the process of reaching a steady state may be initiated again, making the whole procedure useless. Another prerequisite is that the layer must be deposited in very thin layers. If thick layers are used, depth resolution will be less than optimal once the region of interest is reached.

A very practical material is polystyrene (PS), as it easily dissolves in toluene and can be spin coated in very thin layers on top of most other polymers without de-wetting. Most polymers have more or less the same density, hence PS can be used for all (thermo)hardening polymers. A procedure that can be followed when dewetting occurs is described in chapter 3.

2.5 The principle of XPS

When a sample is irradiated with light of sufficiently high energy, electrons are emitted with characteristic kinetic energies, which is the photoelectric effect shown in Figure 10. In the case of XPS, an X-ray source is used for this excitation. The XPS analyser measures the kinetic energy of the emitted electrons. Because the energy of the exciting X-ray is known, the difference between this energy and the kinetic energy of the electron should be the binding energy the electron had to overcome to leave the core level. However, a small correction should be made. Because the spectrometer and the sample are in electrical contact, their Fermi levels are lined up. However, their work functions are not the same, resulting in a potential field between the sample and the spectrometer. Hence, the electron is either accelerated or decelerated on its way to the analyser. The measured kinetic energy of the electron is thus different from the kinetic energy of the electron leaving the sample. Taking this into account, the binding energy can be calculated using:

\[ E_b = h\nu - E_{k,\text{spec}} - \phi_{\text{spec}} \]  

(4)
with

- \( E_b \) the binding energy with respect to the Fermi level
- \( h\nu \) the energy of the absorbed photon
- \( E_{k,\text{spec}} \) the kinetic energy of the photoelectron measured in the spectrometer
- \( \phi_{\text{spec}} \) the work function of the spectrometer, obtained by calibration using the binding energy of a known compound.

A spectrum is obtained by plotting the intensity of the photoelectrons as a function of the binding energy \( E_b \), usually expressed in eV. Several types of peaks are observed in XPS spectra. Some are fundamental to the technique and are always observed. Others are dependent upon the exact physical and chemical nature of the sample or are the result of instrumental effects. The various spectral features that are likely to be encountered are:

Photoelectron lines: These are the most intense photoelectron lines. They are relatively symmetrical and are typically the narrowest lines observed in the spectra. With these lines the elemental composition of the sample, the oxidation state of the elements and the effect of surrounding ligands can be determined.

Auger lines: These are groups of lines in rather complex patterns. Because Auger lines have kinetic energies which are independent of the ionising radiation, on a binding energy plot they appear to be in different positions when different x-ray sources are used.

X-ray Satellites: The X-ray emission spectrum from non-monochromatic sources exhibits not only the characteristic X-ray but also some minor X-ray

![Schematic representation of the photoemission and Auger process.](image-url)

**Figure 10.** Schematic representation of the photoemission and Auger process.
components at higher photon energies. For each photoelectron peak that results from the routinely used Mg and Al K$\alpha$ X-ray photons, there is a family of minor peaks at lower binding energies, with intensity and spacing characteristic of the X-ray anode material. Table 2 shows the pattern of these satellites for Mg and Al.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{1,2}$</th>
<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>displacement [eV]</td>
<td>0</td>
<td>8.4</td>
<td>10.1</td>
</tr>
<tr>
<td>relative height</td>
<td>100</td>
<td>8.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>displacement [eV]</td>
<td>0</td>
<td>9.8</td>
<td>11.8</td>
</tr>
<tr>
<td>relative height</td>
<td>100</td>
<td>6.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 2. X-ray satellite energies and intensities

### 2.5.1 Angle-resolved XPS

Usually, XPS measurements are performed with the sample surface perpendicular to the XPS analyser axis. Because the information depth of XPS is limited to approximately three times the inelastic mean free path (approximately 95% of the total signal originated from this surface volume), turning away the surface normal from the axis of the analyzer results in the measurement becoming more surface sensitive. Figure 11 shows this principle. The relationship between the angle from the surface normal $\alpha$, the inelastic mean free path $\lambda$, and the information depth $d$, is $d = 3\lambda \cos \alpha$.

The value of the inelastic mean free path $\lambda$ can be estimated with an empirical formula from Tanuma, Penn and Powell, dubbed the TPP-2M formula$^{30}$ which has been adapted for use with polymer materials:

$$\lambda = \frac{E}{E_p^2 \left[ \beta \ln(\gamma E) - (C/E) + (D/E^2) \right]}$$

$$\beta = -0.01 + 0.944 \left( \frac{E_p^2 + E_g^2}{E_p} \right)^{-1/2} + 0.069 \rho^{0.1}$$

$$\gamma = 0.191 \rho^{-0.50}$$

$$C = 1.97 - 0.91U$$

$$D = 53.4 - 20.8U$$

$$U = N_p \rho / M = \frac{E_p^2}{829.4}$$

(5)
with:

- $E_p$  the free-electron plasmon energy (20.52 eV)
- $E_g$  the bandgap
- $N_v$  the number of valence electrons per atom or molecule
- $E$  the kinetic energy [eV]
- $r$  the density

From the data measured at different angles, it is theoretically possible to reconstruct a depth profile. However, the influence of errors in the data on the shape of the reconstructed depth profile can be considerable, and there are about twenty methods in use to reconstruct depth profiles from AR-XPS measurements.\textsuperscript{31,32} Nearly all of these methods depend on the following assumptions:

1. The specimen is amorphous or finely poly-crystalline
2. The surface of the sample is smooth at the atomic scale
3. No phase separation has occurred within the sampled surface
4. Elastic scattering can be neglected
5. Refraction of electrons on leaving the specimen surface is negligible
6. The attenuation length of the detected electron is independent of the material through which it has passed
7. The acceptance angle of the analyser is very small

The first three assumptions suggest that the analyst has prior knowledge about the sample structure, for example from atomic force microscopy or X-

![Figure 11](image-url)

**Figure 11.** When the analyser is placed in line with the surface normal, a surface volume with depth $d_1$ is measured. This depth equals three times the inelastic mean free path of the electrons travelling through the sample. Turning the surface normal away from the analyser axis makes the measurement more surface sensitive.
ray diffraction analysis. Assumption 4 is only true for angles equal to or smaller than 70 degrees from the surface normal for weakly elastic scattering specimen such as polymers. Assumption 5 is always valid at the energies that XPS is usually carried out with. Although assumption 6 is always false, it can be accounted for by rescaling the depth scale afterwards. Assumption 7 is true for all modern XPS analysers.

In most samples the expected build-up of samples is as follows. The first, outermost layer is an adsorbed or surface segregated monolayer, often hydrocarbons adsorbed from the air. The second region is the region where usually the gradients are found. The third region is where the concentrations of the present species approach their bulk value. All three regions can contribute to the overall signal intensity when present. However, each region has its own optimal side constraint for deconvolution. Using the wrong constraint can cause misinterpretation of the true depth profile.33

2.6 Necessary XPS equipment

For XPS only an X-ray source of appropriate energy and a photo-electron detector with auxiliary control electronics are necessary, apart from an UHV environment. Only the types employed on our modified VG Ionex system will be discussed.

2.6.1 The X-ray source

X-rays are generated by focussing electrons of sufficient energy on a surface, most commonly of Mg or Al. To obtain the highest possible sensitivity for the measurement, the photon flux on the surface of the sample should be maximised. To achieve this the electron current on the surface of the anode should be as high as the anode will tolerate. Because Mg and Al do not conduct heat particularly well, they are coated as a thin layer on top of a thick copper plate. The anode is usually cooled with forced-flowing water at 4 bar pressure. Because the photon flux on the surface of the sample is related inversely to the square of the distance, the sample should be as close to the X-ray source as possible.

In some measurements Auger peaks will obscure regions of interest. This can be solved by using another anode material, which has an excitation energy somewhat removed from the original anode material. To this end most X-ray sources are equipped with a dual anode as shown in Figure 12. By carefully shielding and focussing the electron beam it is possible to only irradiate one anode material. By simply switching from filament 1 to 2 or vice versa either anode can be chosen. Switching usually takes only a few minutes. The aluminium window is used to protect the sample surface from stray primary electrons, heat and any contamination originating in the source. Fur-
Introduction to SIMS and XPS

Therefore it acts as a band-pass filter, which suppresses the Bremsstrahlung produced together with the X-ray $K\alpha$ line. Finally, the low energy secondary electrons produced in the aluminium window by the X-rays neutralise the positive charge buildup, caused by the leaving photo-electrons, at the surface of isolators.

2.6.2 The concentric hemispherical analyser

Figure 13 shows the VG Clam II concentric hemispherical analyser used on the modified VG Ionex. It consists of three parts: the lens system that focuses the electrons, the analyser that selects the electrons by their energy, and the channeltron detector.

The electrostatic lens acts as a rough energy filter. In XPS mode both lenses $N$ and $R$ are at equal potential and project an image of the sample surface onto the entrance slit, enabling better sample handling because the analyser can be situated further from the sample.

The analyser acts as a narrow band filter. Electrons with too high an energy will strike the outer hemisphere, while electrons with too low an energy are attracted towards the inner hemisphere. Both hemisphere surfaces are coated to minimise the secondary electron emission. Before an electron enters the spherical electrostatic field of the analyser it is retarded to a constant energy, called the pass energy $E_p$, at the entrance slit $W_1$. This is done to keep the absolute resolution of the instrument under the natural line width of the unmonochromatised X-ray sources, 0.70 eV for Mg $K\alpha$ and 0.85 eV for Al $K\alpha$, without having to construct excessively large analysers. The pass energy is usually set between 5 to 200 eV, with a lower pass energy resulting in a better resolution but a lower signal intensity.

![Diagram of X-ray source](image)

Figure 12. A typical X-ray source. Switching from filament enables the operator to choose the X-ray energy by changing the irradiated anode material.
The analyser consists of two concentrically positioned hemispheres of radii $R_1$ and $R_2$. Potentials $-V_1$ and $-V_2$ are applied to the inner and outer hemisphere, respectively, with $V_2$ greater than $V_1$. With respect to $E_p$, $V_1$ is positive and $V_2$ negative. The relation between the hemisphere radii, potentials and the energy of the electrons injected with the right energy and tangentially to the median equipotential surface is described by:

$$E = e\frac{R_2^2 - R_1^2}{R_1 R_2} = k e \Delta V$$

(6)

with $k$ the spectrometer constant. If an electron is injected at a $\Delta E$ difference in energy $E$ and at an angle $\delta \alpha$ from the ideal path, the shift $\Delta R$ along the radial axis can then described by:

$$\Delta R = 2R_0 \left[ \frac{\Delta E}{E} - (\delta \alpha)^2 \right]$$

(7)

from which the base resolution, the base width of a peak, follows:

$$\frac{\Delta E_b}{E} = \frac{W_1 + W_2}{2R_0^2} + (\delta \alpha)^2$$

(8)
The signal intensity will be proportional to the entrance slit, because the source is spread uniformly over the sample surface. Because in the CLAM II the entrance slit $W_1$ is equal to exit slit $W_2$ ($W_1=W_2=W$), the optimum condition is reached when:

$$\frac{W}{R_0} = (\delta a)^2$$

(9)

### 2.7 Charge referencing

An integral part of XPS measurements is that electrons leave the sample. If these electrons are not replenished in the target material, i.e. if the target material is not conductive, then the surface of the sample will become positively charged. The result of this is that subsequent electrons attempting to leave the surface will be retarded by the opposite charge at the surface. These electrons will hence be detected as having a lower kinetic energy, or a higher binding energy than they ought to have.

Because the level of charging is not easily predicted, usually the binding energy scale is adjusted after the measurements so that at least one peak matches a calibration line obtained from a sample with a well-defined physical and chemical state on the instrumental binding-energy scale, usually taken from literature. Some common methods are:

- **Adsorbed pure element**: A thin layer of a pure, non-reactive element, most commonly gold, can be deposited and measured together with the other regions of interest. In the case of gold, the Au 4f$_{7/2}$ binding energy is assumed to be 84.0 eV. The disadvantage is that electrons from the underlying layer of interest become attenuated, resulting in loss of signal.

- **Adventitious carbon**: On samples containing no carbon, the presence of adventitious hydrocarbon on the specimen surface can be used for referencing. The C 1s line is assumed to have a binding energy of 284.8 eV. The disadvantage is that these adventitious hydrocarbons, because they are a mix of various compounds, do not give very sharp photo-electron lines, which makes the calibration not very precise.

- **Co-condensed hydrocarbon**: A hydrocarbon is adsorbed on top of the layer of interest and can be used as the charge reference with an assumed binding energy of 284.8 eV. The advantage over the adventitious carbon method is that the resulting photo-electron line is much sharper. Hence, the calibration is more precise.
• **Argon implanting:** Implanted Ar can be used with the Ar 2p line as the charge reference. An Ar 2p binding energy of 242.5 eV is assumed on a typical insulator. The disadvantage is that sputter damage may change the surface, which would make the measurement useless.

A more active approach is to balance the accumulation of charge at the surface by using a low energy electron floodgun to supply an external current. Better surface charge compensation is possible by using a low energy ion flood gun at <5 eV as a partner to the electron flood gun. A more advanced concept is the use of the electrostatic/mirror electron source within a magnetic snorkel lens. The mirror reflects all electrons that are not admitted into the analyser lens back onto the surface, following the field lines the photo-electron initially took away from the surface. This way, local charge compensation is almost perfectly achieved.

2.7.1 Sample preparation for XPS

XPS is much less sensitive to contamination than SIMS, since the surface sensitivity of XPS is much smaller than that of SIMS. Hence, the same procedures as used in SIMS methodology are not called for in XPS practice. However, to prevent unnecessary surprises basic ‘good laboratory practice’ should always be adhered to.

References

Charge referencing


Introduction to SIMS and XPS
3. Depth profiling of surface regions

Abstract
In this chapter a fluorinated epoxy/amine coating was investigated by XPS and ARXPS to establish that a fluorine gradient existed close to the surface of the coating. The length scale of this gradient was found to be within the range of the information depth of the XPS measurements. The pre-equilibrium phase was found to severely distort the fluorine signal of the SIMS depth profile. The addition of a 77 nm thick PS sacrificial layer removed this distortion, because equilibration between the ion beam and the polymer material took place in the sacrificial PS layer, and not in the fluorinated coating. The best depth resolution obtainable in this way was 4.9 nm according to the IUPAC definition, and was shown to be dependent of the acceleration voltage, due to atomic mixing. The quantification by SIMS of the amount of fluorine proved to be questionable, because of possible matrix effects and of the atomic mixing.

3.1 Introduction
The main problem when performing dynamic SIMS on samples that contain the sought-after information in the near-surface region is that the measured intensities near the surface are unreliable. During the initial sputtering, called the pre-equilibrium phase, more primary ions are implanted than removed again by sputtering. Hence the matrix of each subsequently sputtered layer is different regardless of actual compositional differences, resulting in a changing intensity. Equilibrium between primary ions and sputtered material is reached around the layer where the first primary ions were implanted. The implantation depth, i.e. the depth from where a reliable signal can be measured, can be manipulated by altering the acceleration voltage.

For some polymers there is another cause for the pre-equilibrium phase. These polymers are transformed into amorphous carbon because the hydro-
gen that they contain is sputtered away preferentially, causing radical reactions after the hydrogen loss. The change of the matrix not only influences the ionization chance, but also the sputter speed through the polymer layer. Because usually a uniform sputter speed is assumed when calibrating the depth scale, this also causes a distortion of the measured depth profile. At some point this process can also enter a steady state.

To study a possible solution to prevent both distortions, a surface-modified coating was chosen which surface properties could be easily and reproducibly modified. It was first described by van de Grampel, who adapted a strategy from Torstensson et al. These researchers introduced small photo-polymerizable perfluorinated surfactants into a photo-crosslinkable matrix to ensure a permanent surface modification, as in multi-component systems the component with the lowest surface tension, the fluorinated component, will adsorb preferentially at the surface. This way a fluorine concentration gradient near the surface could be achieved. Others have since used this approach successfully, also with photo polymerisations and non-fluorine surfactants.

The system described by van de Grampel was prepared with an epoxy-diamine reaction following a two-step pathway as shown in Figure 1. First, the reaction of the primary amine with the epoxy group leaded to the formation of a secondary amine. In the second, rate-determining step, the secondary amine reacted with another epoxy group to form a tertiary amine. This way the system changed from a low-molecular weight liquid to a highly crosslinked network. Van Grampel found that the surface enrichment of the fluorinated species took places shortly after application. XPS was used to confirm that these modified coatings had a fluorine gradient in the surface region.

![Figure 1. The curing process of the Epikote 828/Jeffamine D230 coating system](image)

A possible solution to avoid the distortion of the depth profile during the pre-equilibrium phase can be to add a suitably thick sacrificial layer of approximately the identical density on top of the studied polymer layer. This way, a
steady state will have been obtained by the time the interface between the sacrificial and the studied polymer is reached.\textsuperscript{10}

A comparison between dynamic SIMS measurements of Au/coating and Au/PS/coating stacks showed that the added sacrificial PS layer is an efficient way of avoiding the loss of information due to the pre-equilibrium phase.

### 3.2 Experimental

A diglycidyl ether of bisphenol-A (DGEBA, Epikote 828, Shell, epoxy equivalent weight (EEW) \(\cong 187\)) was used as epoxy resin. A propyleneoxide diamine (Jeffamine D230, Huntsmann, amine-hydrogen equivalent weight (AHEW) = 60) was used as a curing agent. The fluorinated reagent (2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)oxirane (EP-F8, Aldrich) was used as received. For the AR-XPS measurements a slightly longer surfactant was used (EP-F10, Aldrich). Figure 2 shows the molecular structures.

To produce the fluorinated epoxy-amine coating a fluorinated prepolymer was first prepared by reacting Jeffamine D230 (a known excess) with a small amount of fluorinated epoxide at 100 °C. Subsequently, the fluorinated prepolymer, Epikote-828 and Jeffamine-230 (the NH to epoxy ratio was always 1:1) were mixed together with 10 wt% of toluene. This mixture was exposed to ultrasound for five minutes to remove air that might otherwise have resulted in bubbles during epoxy solidification. Finally, the mixture was cast on aluminum panels using a calibrated wire-wound applicator (100 \(\mu m\) wet thickness) and cured immediately for two hours at 100 °C. Under these conditions smooth transparent films with a layer thickness between 50-60 \(\mu m\) were obtained.

![Figure 2. The components used in the fluorinated coating.](image)

(a) diglycidyl ether of bisphenol-A (Epikote 828),
(b) propyleneoxide diamine (Jeffamine-D230),
(c) \((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9\text{-heptadecafluorononyl})\text{oxirane (EP-F8).}\)
The chemical incorporation of perfluorinated epoxides into the epoxy-amine network was verified by rinsing some of the epoxy films with acetone and 1,1,2-trifluoro-trichloroethane and measuring the wettability of these coatings before and after rinsing. It was found that the differences in contact angles before and after rinsing were negligible (within 1 degree), suggesting that the films were stable and the surface modification was permanent in nature.

All XPS and SIMS measurements were performed in the equipment described earlier in chapter 2. The angle-resolved XPS spectra were collected at angles of 0, 26, 37, 46, 53 and 60 degrees from normal, corresponding to a sampling depth of 3.0, 2.7, 2.4, 2.1, 1.8 and 1.5 times the inelastic mean free path of electrons trying to escape the polymer towards the surface.

The polystyrene sacrificial layers used for some dynamic SIMS measurements were prepared as follows. PS grains (\(M_n=47500\), \(M_w=49800\), polydispersity = 1.05) were dissolved in toluene (p.a., Merck) in a 2 volume weight % solution (2 grams per 100 ml toluene). A Si(100) slab of 3\(\times\)3 cm was cleaned by spraying toluene on it while spinning the slab at 3000 rpm to remove dust particles and adsorbed hydrocarbon contaminations. Immediately after stopping the spincoater the surface of the slab was completely covered with the PS solution, and the slab was again rotated at 3000 rpm for one minute. This procedure resulted in flat PS coatings with a reproducible thickness of 77 ± 1 nm. When such a freshly prepared coating was submerged in demineralised water under an angle of approximately 30 degrees, the coating rolled off the silicon surface and floated on top of the water. With some care this thin layer of PS could then be picked up with the fluorinated coatings. After drying the fluorinated coating was then covered with a smooth layer of PS.

The Mg K\(\alpha\) line was used for all XPS measurements, with the pass energy of the hemispherical energy set at 20 eV. All dynamic SIMS measurements were performed using 5-10 kV Ga ions, with a total current on the sample of approximately 5 nA.

### 3.3 Results and discussion

If the prepolymer segregates towards the surface, the fluorine concentration at the surface of the coating should rise faster than the expected bulk concentration when more prepolymer is added to the mixture. This was verified by XPS measurements. The measurement time was kept to a minimum to avoid degradation effects induced by X-rays. The left panel of Figure 3 shows a typical measurement. The C-C, C-O, CF\(_2\) and CF\(_3\) peaks could be reasonably well resolved, although the small C-N contribution was fitted together with the C-O contribution.
Results and discussion

The areas of the resolved peaks were used to calculate the measured surfactant concentration in the near-surface region that can be measured by XPS. By using only the C 1s areas, two problems were avoided. Firstly, when using two regions, e.g. the C 1s and F 1s regions, to determine the elemental ratio, such as the C to F ratio, some instrumental factors have to be taken into account as well as the difference in ionization cross section of both elements. Secondly, the difference in kinetic energy of the C 1s and the F 1s electrons implies that for each element a different surface volume is sampled.

Figure 3. The upper panel shows a typical XPS spectrum of the C 1s region of a EP-F8 modified coating. The lower panel shows the measured EP-F8 content vs. the expected bulk value in mol%. The drawn line has only been added to guide the eye.
The following effects are shown in the right panel of Figure 3. At low concentrations the surfactant molecules moved independently in the surface layer. Most of the added surfactant molecules adsorbed at the surface, which was visible as an increase in the CF:C_{rest} ratio. At some point the surface reached saturation, and the CF:C_{rest} ratio remained constant even though more surfactant was added. However, the decrease in surface area probably caused the formation of an insoluble two-dimensional monolayer of surfactant molecules. When more surfactant was added, the surfactant molecules in the monolayer became more closely packed together, coherently orienting towards the surface, which resulted in another rise of the CF:C_{rest} ratio.

These results correlate very well with the contact angle results of van de Grampel, which he obtained using the geometric mean method of Owens and Wendt, employing the advancing angles of the wetting liquids. These results indicated that the lowest surface tension obtained for the modified epoxy systems, 9.3 mN/m, was very close to the values of a closely packed perfluoralkyl surface, which exhibit surface tensions less than 8 mN/m.

Although these XPS measurements established that the surface becomes saturated with the surfactant after the addition of about 1 wt% of EP-F8, which is evidence that a gradient exists within the XPS sampling volume, angle resolved XPS, which was described in detail in Chapter 2, can give a clearer picture of the length scale of the gradient. The principle of ARXPS is that because the information depth of XPS is limited to approximately three times the inelastic mean free path (approximately 95% of the total signal originated from this surface volume), turning away the surface normal from the axis of the analyzer results in the measurement becoming more surface sensitive.

Figure 4 shows the results for an angular-resolved XPS experiment on an epoxy film containing 1 wt% of the fluorinated epoxide EP-F10. The TPP-2M formula, also described in Chapter 2, was used to calculate the inelastic mean free path \( \lambda \). The value for the free-electron plasmon energy was \( E_p = 20.52 \text{ eV} \), the bandgap \( E_g = 4.09 \text{ eV} \) (obtained from UV-VIS measurements), the number of valence electrons per molecule \( N_v = 432 \), and the density \( \rho = 1138 \text{ kg/m}^3 \) (obtained with volume-exclusion measurements). With \( \lambda = 30.33 \text{ Å} \) at 969 eV kinetic energy (which correlates to a binding energy of 285 eV, the C 1s region, when using Mg K\( \alpha \) radiation) the near-surface volumes that were sampled ranged from 4.5 to 9.1 nm. The measured CF:Crest ratio is a weighted average over the sampled depth of the polymer. Because the more surface sensitive measurements showed a higher fluorine concentration, a gradient must exist with a decay length within the depth scale of the XPS measurement, i.e. about 10 nm.
Results and discussion

To test the effect of a sacrificial PS layer, depth profiles of an as-prepared coating, and a coating with a layer of PS were measured. To make charge correction more easy, and to prevent ESIE of the fluorine from around the crater, both samples were first coated with 3 nm Au. The upper panel of Figure 5 shows the depth profile of the coating without a sacrificial layer. The pre-equilibrium phase is visible as the sharp rise of the C2 and C signal, and the dip in the O signal. The loss in F signal intensity is clear. A high initial value was expected, but instead a rise in signal was found until the ion/coating equilibrium was reached. Then the F signal dropped to the bulk value.

The lower panel of Figure 5 shows the depth profile of the coating with a sacrificial PS layer on top. The VG Ionex was first optimized on an area of the sample not coated with the PS, after which a position was found where the initial F signal was zero and the depth profile measurement was started directly. The maximum intensity of the fluorine signal relative to the bulk value was now much higher.

To study the influence of the acceleration voltage on the fluorine depth resolution, a coating with 0.73 wt% EP-F8 was prepared with a PS sacrificial top layer. The depth resolution was taken as the distance between the points where the signal reached 16 % and 84 % of the maximum intensity, as shown in the left panel of Figure 6. The depth scale was recalibrated by setting the interface at 77 nm to be able to express the depth resolution in nanometers. The right panel of Figure 6 shows the dependence of the depth resolution on the acceleration voltage. The depth resolution on the rising side of the interface is more or less independent of the acceleration voltage. The roughness of the PS sacrificial layer, and to a lesser extent the roughness of the fluorinated coating, probably causes the broadening of the interface.

Figure 4. Comparison between the theoretical and the measured molar percentage of EP-F10 in the sampled near-surface region of cured epoxy films with 1 wt% of EP-F10 as function of the information depth(\(\lambda\)).
Depthprofiling of surface regions

These parameters are independent of the acceleration voltage. On the other side of the interface the resolution is worse, and the added loss of resolution clearly dependent on the acceleration voltage. This is caused by atomic mixing, which will be described in detail in chapter 4.

Finally depth profiles were measured of coatings with different amounts of EP-F8 to study the remote possibility that some quantification of the surfactant concentration could be possible. Because the length scale of the gradient is so short, the assumption that the depletion of the bulk phase is negligible should be valid. Because the concentration of EP-F8 is known, it can serve as an internal reference. By calibrating the fluorine signal to the weight percentage of EP-F8 in the bulk, the enrichment of the outermost surface layers can then be calculated.

Figure 6 shows the calibrated depth profiles. Although the XPS measurements showed an enrichment of up to 80 times the bulk value, the highest value for the dynamic SIMS measurements is only about 15 times the bulk.

Figure 5. The upper panel shows a dynamic SIMS measurement of a Au/coating stack. Almost all information at the interface is lost due to the pre-equilibrium effect. The lower panel shows that adding a PS sacrificial layer largely solves this problem.

These parameters are independent of the acceleration voltage. On the other side of the interface the resolution is worse, and the added loss of resolution clearly dependent on the acceleration voltage. This is caused by atomic mixing, which will be described in detail in chapter 4.

Finally depth profiles were measured of coatings with different amounts of EP-F8 to study the remote possibility that some quantification of the surfactant concentration could be possible. Because the length scale of the gradient is so short, the assumption that the depletion of the bulk phase is negligible should be valid. Because the concentration of EP-F8 is known, it can serve as an internal reference. By calibrating the fluorine signal to the weight percentage of EP-F8 in the bulk, the enrichment of the outermost surface layers can then be calculated.

Figure 6 shows the calibrated depth profiles. Although the XPS measurements showed an enrichment of up to 80 times the bulk value, the highest value for the dynamic SIMS measurements is only about 15 times the bulk.
Results and discussion

Figure 6. The left panel shows a depth profile of a 0.73 wt% EP-F8 coating with a sacrificial PS layer on top, measured at 6.26 kV. The resolution was defined as the distance between the points where the signal was at 16% and 84% of the maximum intensity, after subtraction of the background. The right panel shows the depth resolution at different acceleration voltages. The influence of the acceleration voltage on the depth resolution is clear: the depth resolution scales linearly with the acceleration voltage.

Figure 7. After calibration of the depth profiles to the known EP-F8 weight percentage bulk values, the concentrations of EP-F8 at the surface of the coatings is found. The enrichment of the surface as found by XPS is lower than expected from the XPS measurements.
value. There are probably two reasons for this. At the surface the composition differs rather much from the bulk.

There is a large possibility that the ionization and sputter processes are different at the surface, so that both the number of sputtered particles and the ionization chance are lowered which should result in a lower signal than could have been expected if indeed the enrichment is as high as the XPS measurements suggest. The other reason is the difference in convolution of the dynamic SIMS depth profile and the ARXPS depth profile. The depth resolution of the SIMS profiles was at best 4.9 nm, but usually above that. If one assumes that the atomic mixing during the sputtering process homogenizes a surface region of that thickness, than the ion signal would represent an averaged concentration of EP-F8. The best depth resolution of the ARXPS measurements was 4.6 nm, which is not too different from the best SIMS resolution. However, the ARXPS signal represents a weighted average, in which the surface layers weigh more heavily than the deeper layers within the sampled surface volume. This means that in this case the ARXPS measurement was more surface sensitive than the dynamic SIMS measurement, resulting in a better quantitative determination of the EP-F8 concentration at the surface. By using a lower acceleration voltage the atomic mixing can be reduced. This may reverse the comparison between the two techniques, or at least give better quantitative similarity in the results.

3.4 Conclusions

The fluorine gradient in a modified epoxy-amine matrix was studied by (angle resolved) XPS and dynamic SIMS. Normal XPS measurements showed how the fluorine containing surfactant molecules adsorbed at the surface prior to curing. Angle resolved XPS measurements showed a high level of enrichment with the fluorinated surfactant of the near surface region.

Depth profiling by dynamic SIMS was shown to be problematic because of the pre-equilibrium phase, which distorted the depth profile in the region of interest. A PS sacrificial layer was used to circumvent this distortion. The addition of such a layer helps to remove the distortion of depth profiles measured close to the surface of a coating, because the period of equilibration between the ion beam and the polymer material is shifted from the coating into the sacrificial PS layer. However, direct spincasting of the PS sacrificial layer was problematic because of dewetting of the spincasted layer. A practical way of preparing a smooth PS sacrificial layer without the problem of dewetting was described. The best depth resolution obtainable in this way was 4.9 nm according to the 16-84 % definition, and was shown to be depending on the acceleration voltage, due to atomic mixing. The quantification of the amount of fluorine proved to be different from the ARXPS results, because of possible matrix effects and of the atomic mixing.
Conclusions

References

Depthprofiling of surface regions
4. The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using the mixing-roughness-information depth model

Abstract
The morphology and composition of the interfaces of multilayered metal/polymer stacks was investigated using dynamic SIMS and AFM. The obtained depth profiles were deconvoluted using the MRI model. The calibration of the depth profile depth scale was shown to be possible by assuming a linear relationship of the sputter rates with the local fraction of each layer at the interfaces, although carbonisation biased the depth calibration in the polymer layer where carbonisation occurred. AFM measurements showed that the crater bottom roughness, or the MRI parameter $\sigma$, was severely underestimated when calculated from AFM measurements of the original surface and interface roughness and dynamic Monte Carlo calculations of the ion straggle. An aluminium layer on top of the multi-layered system dramatically worsened the obtained depth resolution, which was avoided by sputtering the Al/MDMO-PPV interface from the other side. This revealed possible aluminium diffusion into the MDMO-PPV layer.

4.1 Introduction
In many multi-layered electronic devices, the interfaces between their layers govern their properties. Changes at these interfaces, such as oxidation or the formation of polar layers, affect their functioning.\textsuperscript{1-3} Hence, the study of these buried interfaces is important for the development of these devices. Dynamic SIMS can provide valuable information about diffusion processes and reactions that have occurred at these interfaces.

However, the SIMS measurements do not represent the true pre-measurement situation, because several causes for broadening of the depth profile exist, one of which is atomic mixing, which consists of three simultaneous and related processes: Cascade mixing, recoil implantation and defect enhanced diffusivity.\textsuperscript{4} Cascade mixing is caused when the primary ion hits a
target atom at a glancing angle, starting a collisional cascade. Because only a small fraction of the cascades results in sputter erosion, near-surface homogenization takes place in the order of the ion range. This process always broadens the depth profile with respect to the original depth distribution by the length of the mixing zone, i.e. the projected ion range. Equilibrium in this process is reached generally after twice the ion range has been sputtered away. Recoil implantation is the process in which the primary ion hits a target atom more or less head-on, transferring most of its energy in the process and implanting this single atom deeper, also broadening the depth profile because this atom will be encountered and detected once the sputter front has moved deeper into the surface. Finally, the generation of defects in cascade mixing generally results in enhanced diffusivity, another cause of broadening.

The choice of the primary ion species can affect this enhanced diffusivity in polymers. For example, in a study comparing sodium migration induced by $O_2^+$ and $Cs^+$ primary ion beams in a polyethylene terephthalate film, Mimori et al. found that at all measurement conditions the $O_2^+$ primary ions caused much deeper migration of Na than the $Cs^+$ ions. Electron flooding, primary beam spot size and current density had no substantial effect. XPS showed that the sputtered surface was entirely composed of amorphous carbon for $O_2^+$, but polar groups such as COO, C=O and C-O were observed for the surface sputtered with $Cs^+$. These groups could possibly suppress the migration of sodium through an electrostatic interaction.

Cascade mixing is the dominant part in atomic mixing because there is a larger chance to hit an atom at a glancing angle than head-on. It is possible to minimize the broadening of the depth profile by reducing the primary ion range as far as possible, by sputtering at low acceleration voltages, at near glancing angles and with poly-atomic primary ions that fragment on the surface, so that most energy is deposited at the surface and not in deeper layers.

Another cause of depth profile broadening is sputter-induced roughness, which will always develop in the order of a few monolayers, because the sputtering process is statistical in nature. However, on polymers there are more causes for sputter-induced roughness. Discharge of locally accumulated excess charge at the organic surface can cause the formation of numerous small holes or pits on polymer surfaces. Phenyl rings and similar structures in polymers help to delocalize this excess charge and hence to reduce this form of roughness formation. Cracking of the surface can take place, and when there is a balance between pattern producing ion-beam modifications and sputtering, structure formation at polymer surfaces can be observed at low primary energy and low current density. This structure formation can be explained by re-adsorption from the residual hydrocarbon atmosphere at radical sites that are formed during the sputtering process.
The density of the sputtered polymer film may be a factor in sputter-induced roughness, as well as preferential sputtering. Preferential sputtering can occur when one component in a layer has a higher sputter yield, the amount of secondary particles sputtered from the surface per primary ion, than the other components. If the components are not homogeneously mixed, then some areas will be sputtered away more quickly than the surrounding areas, resulting in roughening of the crater bottom. Poly-crystallinity can be another cause of preferential sputtering, because channeling of primary ions along the crystal lattice may occur at certain angles. This causes most of the energy to be deposited far from the sputtered surface, so that the sputter yield will drop and those surfaces will erode at a slower rate than the rest of the surface. The necessity of correcting these distortions was clear almost from the beginning of the development of dynamic SIMS as a technique. The shape of the function that describes the broadening of the profile of a thin (mono-atomic) layer, the depth resolution function (DRF), was demonstrated to have a sharply increasing leading edge and a less steeply decreasing trailing edge. This asymmetric behavior can be readily explained by the fact that the DRF is a superposition of the contribution of the atomic mixing, which is asymmetric (exponential decay), and the roughness of the sputtered surface, which is symmetric (Gaussian).

The first attempts made to remove the broadening of the depth profile concentrated on direct deconvolution using the van Cittert algorithm, an iterative procedure: 

\[
X_i(z') = X_{i-1}(z') + I(z) - \int_{-\infty}^{\infty} X_{i-1}(z') g(z-z')dz' \\
X_0(z') = I(z)
\]

With:
- \(z\) The depth where the detected atom/cluster was measured during the sputtering process
- \(z'\) The depth where the detected atom/cluster was located prior to the start of the sputtering process
- \(I(z)\) The measured depth profile
- \(X(z')\) The true depth profile
- \(g(z-z')\) The depth resolution function
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using

However, this algorithm introduces noise and faces some other problems such as insufficient data precision and a signal-to-noise ratio that is already too high.\textsuperscript{21}

Forward calculation of this problem circumvents this problem. The sputtering, \textit{i.e.} the convolution, process can be described by:

\[ I(z)/I_0 = \int_{-\infty}^{\infty} X(z')g(z-z')dz' \]  

(2)

with \( I_0 \) the maximum intensity. If the depth resolution function, \( g(z-z') \), is known and the true profile \( X(z') \) is estimated, a profile can be calculated and compared to the measured profile. The true profile can be reconstructed by adjusting the estimated \( X(z') \) till a match is found.

The most practical method based on this principle is the Mixing-Roughness-Information Length (MRI) model that was developed by Hofmann for the deconvolution of SIMS, XPS and Auger depth profiles.\textsuperscript{22} It assumes the DRF to consist of three functions: atomic mixing, the information length, and surface roughness. These functions are employed sequentially to the depth distribution of an element. The atomic mixing is assumed to occur instantaneously in a thin volume with width \( w \), homogenously redistributing the atoms present, and is described by the following exponential function:

\[ g_w = \frac{1}{w}\exp\left[-\frac{(z-z'+w)}{w}\right] \quad \text{for} \quad z'-w < z \]  

(3)

The atomic mixing length \( w \) can be predicted with the TRIM code for dynamic Monte Carlo calculations included in the SRIM-2000 software package, which can take special bond corrections into account for organic compounds.\textsuperscript{23} Wilson compared calculations with experiments, and found that the TRIM code on average underestimated the experimentally found values by 20 percent.\textsuperscript{24} The atomic mixing will make a larger impact on the shape of the DRF for polymers, because the ion range is generally higher in polymers than in semi-conductor material of metals, due to their lower density.

The information length \( \lambda \), the depth range from which ions (SIMS) or electrons (Auger, XPS) contribute to the measured signal, is described by another exponential function:

\[ g_\lambda = \frac{1}{\lambda}\exp\left[-\frac{(z-z')}{\lambda}\right] \quad \text{for} \quad z' > z \]  

(4)
Introduction

However, because the information length for SIMS measurements is no more than the width of a monolayer, i.e. approximately 0.4 nm, this contribution to the DRF is negligible.

The roughness contribution to the DRF is described by a gaussian term with standard deviation $s$: 

$$g_s = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[\frac{-(z-z_s)^2}{2\sigma^2}\right]$$  \hspace{1cm} (5) 

The parameter $\sigma$ is calculated from the original surface roughness $\sigma_s$, the roughness of the measured interface $\sigma_i$, and the mixing length straggle, $\sigma_w$: 

$$\sigma = (\sigma_s^2 + \sigma_i^2 + \sigma_w^2)^{1/2}$$  \hspace{1cm} (6) 

The latter can be calculated with the TRIM code, the former two can be measured during sample preparation with atomic force microscopy (AFM) as the obtained root-mean-square roughness of both surfaces.

How well the measured depth profile represents the true depth profile is determined by the depth resolution. The definition of the depth resolution as recommended by the IUPAC$^{25}$ and ASTM$^{26}$ still assumes a gaussian shape of the DRF, setting the resolution at $Dz = 2\sigma$, twice the standard deviation of the DRF. In practice this means measuring the distance $Dz$ between the points where the intensity is at 16% and 84% of the plateau, maximum value, respectively. However, Hofmann showed that a better definition of the depth resolution is: 

$$\Delta z = \left(\Delta z_w^2 + \Delta z_\lambda^2 + \Delta z_\sigma^2\right)^{1/2} = \left[(1, 668\lambda)^2 + (1, 668\lambda)^2 + (2\sigma)^2\right]^{1/2}$$  \hspace{1cm} (7) 

because two depth resolution functions with the same depth resolution according to the IUPAC definition can have completely different shapes, with different depth profiles as a result.

Still, there are some practical problems associated with the MRI model for dynamic SIMS depth profiles. First of all, there is no simple relationship between the measured intensity and the concentration in SIMS measurements because of the matrix effect and differences in sputter and ionization yield for every element. Without reference material, quantification to atomic fractions is not possible. Secondly, the conversion of the sputtering time to a depth scale can be problematic. If the sputter rate is known and constant, then the conversion is straightforward. However, in the case of multilayers this is somewhat more complicated because at the interface there will be a
mix of both layers because of the cascade mixing effects, so there the sputter rate will change gradually from one bulk sputter rate to the other.

For polymer containing multilayers the depth calibration can be even more complicated because of carbonization. This is a process in which the hydrogen atoms are preferentially sputtered from the polymer structure. This results in the formation of a carbonaceous structure that bears little resemblance towards the original one, and in which radical induced rearrangements occur. Because the sputter yield is mainly limited by the surface binding energy, this means that the sputter speed will slowly drop within a polymer layer because of the added surface binding energy from the newly formed bonds. The occurrence of carbonization should be clear from the hydrogen or related signals in the depth profile.

All these problems related to depth profiling polymer systems are probably the cause that almost all polymer system depth profiles are only reported as unprocessed data in the literature. Even the obtained depth resolution is usually not reported, or the IUPAC definition of the depth resolution is ignored when it is reported. Table 1 shows the depth resolution values reported by various authors. To facilitate any comparison, all quoted depth resolutions have been recalibrated, after reproduction, to the IUPAC $2\sigma$ definition. A conversion to the depth resolution after the definition of Hofmann, see equation 7, was not possible due to a lack of data.

Although at least some relation between the obtained depth resolutions and the used acceleration voltages of Table 1 is expected, because the detrimental effects of both the cascade mixing and the sputter-induced roughness can be decreased by sputtering at a lower acceleration voltage, no such relation can be found statistically with sufficient significance. Even though the sample size is rather small, this suggests that other factors such as sputter-induced roughness and carbonization must play a role. If sputter-induced roughness is the main factor in loss of depth resolution in polymers, then comparison between the literature values is impossible even though most studies were on the same polymer, polystyrene, due to the fact that these interfaces were not all measured at the same depth.

The purpose of this paper is to study the application of the MRI model to a polymer containing multilayered system in order to test the model's limitations. Dynamic SIMS measurements were performed on polymer light emitting diodes (pLED) using a ToF-SIMS instrument, because the parallel acquisition enabled the storage of the entire mass spectrum (m/z range = 0-900) at each cycle of the depth profile. This reduced the complexity of converting the sputter time into a depth scale as encountered on quadrupole systems, and the selection of fragments to follow could be made in hindsight. AFM scans of the crater surface were used to correlate the measured depth profile with sputter-induced changes of the surface.
Experimental section

4.2 Experimental section

The materials used were poly[2-methoxy-5-(3’,7´-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) synthesized via the Gilch-route, polyethylene dioxythiophene: polystyrene sulfonate (PEDOT:PSS) from Bayer AG, and Al from Engelhard-Clal. A glass plate covered with a thin layer of indium tin oxide (ITO) was used as the substrate. All samples were prepared by first spincoating a layer of PEDOT:PSS (~360 nm) on a cleaned ITO (~44 nm) covered substrate, followed by spincoating a layer of pure MDMO-PPV (~106 nm) from chlorobenzene on top. Figure 1 shows the molecular structures of these organic materials. A full device structure was obtained by the subsequent thermal evaporation under vacuum (5×10⁻⁶ mbar, <1 ppm O₂ and < 1 ppm H₂O) of an aluminum electrode (~110 nm). The devices were stored in a glove box until analysis, and during sample transfer from the glovebox to the ToF-SIMS machine they were transported in a vacuum exsicator.

Table 1. Depth resolutions as reported in the literature, after calibration to the IUPAC definition where necessary, and the measurement settings used to obtain these DR's as far as reported.  The DR quoted from this work is the DR obtained at the Al/MDMO-PPV interface, sputtering from the MDMO-PPV side after removal from its substrate.

<table>
<thead>
<tr>
<th>Primary ion</th>
<th>Energy [keV]</th>
<th>Current [nA]</th>
<th>Angle</th>
<th>Definition</th>
<th>Polymer</th>
<th>DR[nm]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁺</td>
<td>2</td>
<td>20</td>
<td>30</td>
<td>16%-84%</td>
<td>PVP-PS-D</td>
<td>16.7</td>
<td>29</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>2</td>
<td>20</td>
<td>30</td>
<td>14%-86%</td>
<td>PS/PS-D</td>
<td>11.0</td>
<td>30</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>8.11</td>
<td>212</td>
<td>NA</td>
<td>16%-84</td>
<td>MDMO-PPV</td>
<td>9.7</td>
<td>This</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>8.11</td>
<td>212</td>
<td>NA</td>
<td>16%-84</td>
<td>PS-D/PS</td>
<td>14.0</td>
<td>31</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>1.5</td>
<td>20</td>
<td>NA</td>
<td>Not mentioned</td>
<td>PEO-Li⁺ C F₃SO₃⁻</td>
<td>35.0</td>
<td>10</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>10</td>
<td>100</td>
<td>NA</td>
<td>10%-90%</td>
<td>PS-SO₂Cl</td>
<td>36.0</td>
<td>32</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>2</td>
<td>200</td>
<td>60</td>
<td>Not mentioned</td>
<td>PS-D</td>
<td>8.0</td>
<td>33</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>3</td>
<td>10</td>
<td>60</td>
<td>16%-84%</td>
<td>PS-PVP</td>
<td>15.0</td>
<td>33</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>3</td>
<td>200</td>
<td>NA</td>
<td>DRF fitting</td>
<td>PS-D/PS</td>
<td>20.1</td>
<td>34</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>5.5</td>
<td>100</td>
<td>60</td>
<td>20%-80%</td>
<td>Fe((CH₂Br)₂bpy)₃</td>
<td>12.2</td>
<td>35</td>
</tr>
</tbody>
</table>

4.2 Experimental section

The materials used were poly[2-methoxy-5-(3’,7´-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) synthesized via the Gilch-route, polyethylene dioxythiophene: polystyrene sulfonate (PEDOT:PSS) from Bayer AG, and Al from Engelhard-Clal. A glass plate covered with a thin layer of indium tin oxide (ITO) was used as the substrate.

All samples were prepared by first spincoating a layer of PEDOT:PSS (~360 nm) on a cleaned ITO (~44 nm) covered substrate, followed by spincoating a layer of pure MDMO-PPV (~106 nm) from chlorobenzene on top. Figure 1 shows the molecular structures of these organic materials. A full device structure was obtained by the subsequent thermal evaporation under vacuum (5×10⁻⁶ mbar, <1 ppm O₂ and < 1 ppm H₂O) of an aluminum electrode (~110 nm). The devices were stored in a glove box until analysis, and during sample transfer from the glovebox to the ToF-SIMS machine they were transported in a vacuum exsicator.
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using film densities for the TRIM dynamic Monte Carlo simulations\textsuperscript{23} were calculated by combining the carbon content of the material with the total mass of carbon present in the films as measured by a carbon and sulphur analyser by combustion and subsequent IR detection in He carrier gas.

The dynamic SIMS measurements were performed on an IONTOF IV ToF-SIMS apparatus (which saturates at $10^5$ counts/s) in dual-beam mode: a 35 nA, 3 keV Ar\textsuperscript{+} beam at 45\textdegree{} from the surface normal rastered over 150×150 µm\textsuperscript{2} for sputtering and a 1.5 pA, 11 keV Ar\textsuperscript{+} beam at 45\textdegree{} from the surface normal rastered over 50×50 µm\textsuperscript{2} for analysis. Wall effects were excluded by comparing some depth profiles to depth profiles measured at 300×300 µm\textsuperscript{2}. These were identical after calibration to crater size. The depth profiles were measured in the non-interlaced mode (longer sputter and data acquisition cycles) to avoid charging. Effective charge compensation was obtained by using an electron flood gun (20 eV). All depth profiles were mass calibrated on C\textsubscript{x}H\textsubscript{y} fragments.\textsuperscript{38} Only positive ions are shown in the depth profiles included in this chapter. A Tencor P10 surface profilometer was used to measure the thickness of the films and the depth of the sputtered craters.

4.3 Results and discussion

Because the MRI model uses measurable parameters, expressed in nanometers, it is important to accurately calibrate the depth when converting the sputter profile from a time scale, or number of sputter cycles, to a depth.

Figure 1. Molecular structures of MDMO-PPV (a), PEDOT (b), and PSS (c)
Results and discussion

The upper panel of Figure 2 shows an as-measured sputter profile of a stack of MDMO-PPV/PEDOT:PSS/ITO/Glass. In well-defined reference material, it is customary to set the interface between two layers at the point where the intensity of the signal is at 1/e (36%) of the maximum plateau value. The sputter rate can be measured by profiling through reference layers until the substrate has been reached, if the thickness of the sputtered layer is known from profilometer measurements. Alternately, the sputter rate can be estimated by selecting an ion unique to one layer, using the 1/e definition to set the interfaces of the layer it represents, again having measured the layer's thickness prior to the sputtering.

However, even if the thickness of each layer is known, and the sputter speed in each layer as well, it is impossible to convert the time scale into a depth scale from interface to interface by directly converting all points between both interfaces of a layer determined this way. First of all, inevitable there will be a discontinuity, or a kink, in the intensity as measured points are suddenly

![Figure 2](image_url)
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using placed nearer or further away from each other at the appointed interface. Furthermore, taking a look at the intensity of the S, $^{120}$Sn, and the $^{29}$Si signals it is clear that there can be no unambiguous assignment of the two ITO interfaces.

To solve both problems, ions were chosen to represent their layer. For the sample used in Figure 2, consisting of MDMO-PPV/PEDOT:PSS/ITO/Glass, these were the S ion for the PEDOT:PSS layer, the $^{120}$Sn ion for the ITO layer and the $^{29}$Si ion for the underlying glass substrate. The intensities of these ions were normalized to one at their maximum intensity. Then all intensities were summed up and normalized again so that the sum of these intensities would be one. Because there was no ion representative enough for the MDMO-PPV layer, and only the S ion could make the distinction between the MDMO-PPV and PEDOT:PSS layers at their interface, the MDMO-PPV layer was represented as one minus the intensity of S. For each sputter cycle, i.e. each measured point, the sputtered depth was calculated from this linear equation using the sputter rates $r_i$ shown in Table 2:

$$\Delta z = x_a \cdot r_a + x_b \cdot r_b + x_c \cdot r_c + \ldots with \sum x_i = 1$$  \hspace{1cm} (8)$$

After converting each sputter cycle to the calculated depth, the sputter profile shown in the lower panel of Figure 2 was obtained.

Of course, expressing these intensities as a fraction so that they represent the various layers present around the interface implicitly ignores matrix effects, which means that there could be a deviation from the real fractions, and hence a deviation from the real sputter speed. However, when comparing the obtained total depth, 574 nm, to the total crater depth measured with the profilometer, 591 nm, the error in the depth scale is less than three percent of the total depth scale, which is an acceptable deviation considering the simplicity of the conversion. The deviation caused by matrix effects may be responsible for the small error in the depth scale. It is impossible to correct for these effects however, because of the absence of reliable relative sensitivity factors.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sputter rate (nm/sputter cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDMO-PPV</td>
<td>5.1</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>8.8</td>
</tr>
<tr>
<td>ITO</td>
<td>3.7</td>
</tr>
<tr>
<td>Glass</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 2. Sputter rates of the various layers in the MDMO-PPV/PEDOT:PSS/ITO/glass stack, expressed in nanometers per measured cycle.
Another factor that may influence the depth calibration is carbonization. The intensities of the S, H and C signals in Figure 2 slowly decline from the MDMO-PPV/PEDOT:PSS interface. This is an indication that the sputter yield slowly diminishes because of bond rearrangements after the loss of hydrogen, implying that also the sputter speed slowly diminishes within the PEDOT:PSS layer. The H intensity drop starts later than that of C and S. This is possibly caused by initial adsorption of generated hydrogen to the diffused indium present at the MDMO-PPV/PEDOT:PSS interface, forming indiumhydride, because the hydrogen signal rises just after the indium signal decreases. This remains speculation, however. The change in sputter rate because of carbonization has only implications for the depth calibration within the PEDOT:PSS layer but not for the depth calibration over the whole multi-layered structure, because the sputter speed was measured over the total layer thickness of the PEDOT:PSS layer, i.e. the position of the PEDOT:PSS interfaces will not be affected. However, the occurrence of carbonization does affect the quality of the fit with the MRI model. By sputtering to different depths of the polymer the local sputter rate can be calibrated, and the depth scale corrected accordingly. This has not been done here.

In the MRI model the roughness parameter $\sigma$ consists of several contributions: the original surface roughness $\sigma_s$, the original interface roughness $\sigma_i$, and the mixing length straggle, $\sigma_w$, the former two shown in Figure 3. However, the model does not take the roughness that develops during the sputtering process into account. Figure 4 shows some AFM crater bottom measurements that show that the roughness increased with depth. There was no visible structure formation, such as crests and valleys in the scanning direction of primary ion beam. Figure 5 shows the RMS roughness values obtained with the AFM measurements shown in Figure 4 versus depth. The original surface roughness of the MDMO-PPV layer quickly increased linearly with depth, and at the MDMO-PPV/PEDOT:PSS interface the crater roughness became more than four times higher compared to the surface roughness. Because the sputter rate of the PEDOT:PSS layer was much higher than that of the MDMO-PPV layer, the roughness development suddenly increased. This happened because the forward front of the sputtered zone was suddenly sputtering faster than the trailing part of the sputtered zone, which still sputtered away at the old, slower rate. After the last of the MDMO-PPV layer was sputtered away, this trailing part of the sputtered zone assumed the same sputter rate as the forward front, so that the rate of roughness increase declined again to a slower, presumably linear rate. When the ITO layer was reached by the forward front of the sputtered zone, the reverse happened because the sputter speeds of the ITO and glass layers were much lower than that of the PEDOT:PSS layer. The trailing part of the sputtered zone was allowed to catch up with the forward front, resulting into a fast decline of the overall roughness.
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using

The roughness parameter \( \sigma \) as calculated according to the MRI model for the MDMO-PPV/PEDOT:PSS interface had a value of 3.4 nm. The crater roughness at this interface was approximately 7.4 nm, the value obtained after the interpolation of the linear relationship shown in Figure 5. Clearly, the MRI model seriously underestimates the roughness at this interface, because the model does not take into account the increasing sputter-induced roughness.

However, to see in how far it is possible to use the MRI model using the experimentally determined value for the roughness parameter \( \sigma \), the \( ^{113}\text{In} \) signal was chosen for deconvolution by the \textit{COMPRO 6} MRI module.\textsuperscript{41} Indium diffused out of the ITO layer all the way to the MDMO-PPV/PEDOT:PSS interface, and is therefore ideally suited to test the limitations of this adjustment to the MRI model because of its presence at three interfaces. Because the \textit{COMPRO 6} program can only deconvolute limited depth ranges, the total depth profile was cut into three pieces, and the results were put together again after deconvolution. The upper panel of Figure 6 shows the model used for the \( ^{113}\text{In} \) intensity, the lower panel the original \( ^{113}\text{In} \) signal

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.pdf}
\caption{The RMS roughness of the surface and interfaces of an Al/MDMO-PPV/ PEDOT:PSS/ITO/glass stack, each layer measured separately by AFM after deposition. This is a practical approximation of the roughness of each interface. The AFM inset shows the surface of the backside of a MDMO-PPV layer removed from the substrate.}
\end{figure}
and the fit of the model from the upper panel after convolution with the atomic mixing length \( w = 7.2 \) nm (calculated with the TRIM code for the PEDOT:PSS layer), the roughness \( \sigma = 7.4 \) nm, and the information length \( \lambda = 0.4 \) nm. The fit to the original intensity is rather good. Both the MDMO-PPV/PEDOT:PSS and the ITO/glass interfaces are well-defined and at the right position. However, the model shown in the upper panel of Figure 6 only has meaning at these interfaces, because there the used MRI parameters correlate reasonably well with the measured AFM data. In the bulk of the PEDOT:PSS layer a much higher value should have been used for the roughness parameter \( \sigma \). The depth resolution at the MDMO-PPV/PEDOT:PSS interface following the IUPAC definition was 22.0 nm for the S signal and 28.3 nm for the \(^{113}\)In signal. The depth resolution according to the definition of Hofmann (see equation 7) was 19.1 nm.

Although the MDMO-PPV/PEDOT:PSS/ITO/Glass stack studied thus far is already complex, solar cells and light emitting displays typically have an aluminum top layer serving the double function of electrode and protective coat-
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using

The crater bottom roughness measured by AFM increased linearly with depth, until the PEDOT:PSS interface was reached. Because the sputter rate of PEDOT:PSS was much faster than that of MDMO-PPV, the rate of roughness increase rose, until the last of the MDMO-PPV was sputtered away. When the ITO layer was reached, the reverse happened, and the aft sputter front caught up with the forward sputter front.

Because these authors used the same preparation procedures and starting conditions, a DRF could be constructed by interpolation from their AFM data. A split DRF was found for the aluminum layer at the depth (110 nm) of the Al/MDMO-PPV interface, as shown in Figure 7. The interpolated DRF suggests that the obtained depth resolution would be approximately 53 nm (defined as 2σ of the DRF, the IUPAC definition), or 50 nm following Hofmann's definition, with atomic mixing parameter w = 7.7 nm, RMS roughness parameter σ = 24 nm, and information length parameter λ = 0.4 nm, mainly because of the crater roughness of 24 nm at the Al/MDMO-PPV interface (value interpolated from Wöhner et al.). The upper panel of Figure 8 shows the Al/MDMO-PPV interface depth profile. The Al signal extends deeply into the MDMO-PPV layer. Clearly, deconvolution at this roughness is rather pointless.
However, the Al/MDMO-PPV interface can still be investigated when the interface is approached from the other side, by sputtering through the MDMO-PPV layer. The interface roughness should then be approximately the crater roughness of 7.4 nm obtained from Figure 5, the sputter induced roughness of the MDMO-PPV layer at a depth of 106 nm. The Al/MDMO-PPV layers were removed from the underlying layers by firmly pushing a sticky tape on top of the Al layer, and then gently pulling it off, removing the aluminum and MDMO-PPV layers with it. Although AFM measurements showed that the surface of the MDMO-PPV layer became less flat in the long range scale, because some creases were formed, no additional roughness was caused from pulling off these layers, such as from the formation of fibrils, as can be seen in the inset of Figure 3. Hence, the removal of the aluminum and MDMO-PPV layers did not affect the roughness. As a side note, appar-
The deconvolution of SIMS depth profiles of multilayered organic light emitting devices by using

ently there is a bad adhesion between the MDMO-PPV and PEDOT:PSS layers. This may explain why this interface acts as such a good barrier against the diffusion from indium across this interface.

The lower panel of Figure 8 shows the reverse depth profile. The improvement in depth resolution is remarkable, and a step in the Al profiles that was previously hidden was now detected. The upper panel of Figure 9 shows the deconvolution result, using the DRF from the MRI model, with atomic mixing $w = 4.3$ nm, RMS roughness $\sigma = 6$ nm, information depth $\lambda = 0.4$ nm. A somewhat lower value for the roughness had to be used, 6 nm instead of the expected 7.4 nm, to obtain a good fit. A possible explanation may be that the sputter speed of the aluminum layer was considerably slower than that of the MDMO-PPV layer. As seen earlier in Figure 5, this can rapidly lower the crater roughness. Because the interface is not very sharp, even at the interface this may affect the crater roughness.

The Al, Al$_2$ and Al$_3$ signals do not indicate the same position for the Al/MDMO-PPV interface. The AlO signal in the upper panel of Figure 8 shows that the Al layer had been oxidized over a substantial distance of approximately 40 nm (measured at the 1/e height) during the evaporation on top of the MDMO-PPV layer, probably due to water absorbed to the MDMO-PPV layer during sample transfer to the glove box, which confirms the findings of van Duren et al. Because the chance of sputtering an Al$_3$ cluster from an Al$_2$O$_3$ layer is significantly lower than from a polycrystalline Al layer, the Al$_3$ signal underestimates the thickness of the Al layer. The Al ion saturated the detector, so that the plateau cut-off is over-extended and the position of the Al/MDMO-PPV interface is overestimated. The Al$_2$ signal is the only reliable

---

**Figure 7.** The DRF reconstructed from Wöhner et al. show that at the depth of the Al/MDMO-PPV interface there were already two separated sputter regimes, which caused a large loss of depth resolution.
Results and discussion

The upper panel shows the region around the Al/MDMO-PPV interface from an Al/MDMO-PPV/PEDOT:PSS/ITO/Glass stack. The aluminum signals remained high throughout the MDMO-PPV layer. The Al layer at the Al/MDMO-PPV interface had at least been partially oxidized into AlₓOᵧ, possibly by water adsorbed onto the MDMO-PPV layer before the sample was transferred into the glove box. The middle panel shows that what seemed to be Al diffusion into the MDMO-PPV layer was caused by sputter induced roughness. However, there was a secondary plateau in the Al signal, which might indicate either that some Al diffused into the MDMO-PPV layer during the hot evaporation, or that some pinholes were formed in the MDMO-PPV layer that escaped detection by AFM, and were subsequently filled by the aluminum during evaporation.

Figure 8. The upper panel shows the region around the Al/MDMO-PPV interface, coinciding with the carbon plateau cut-off, at a depth resolution of 9.7 nm, following the IUPAC definition, or 14 nm following Hofmann’s definition.

The step observed in both the original and the deconvoluted Al signal shows that the aluminum extended approximately 26 nanometers into the MDMO -
Conclusions

PPV layer, which suggests that a small amount of aluminum diffused into the MDMO-PPV layer during the evaporation of the aluminum top layer. Another explanation could be the formation of pinholes in the MDMO-PPV layers during spin coating, which were subsequently filled with aluminum during the evaporation of the aluminum on top of the MDMO-PPV layer.

4.4 Conclusions

The conversion from a time to depth scale of dynamic SIMS depth profiles can be accomplished by choosing an ion unique to its layer, normalising the signals to unity, calculating the fraction of each layer present at each point,
Conclusions

and assuming a linear relationship of the local sputter rate at each measured point with the fraction of each layer and its sputter rate. Carbonisation may bias such calibration, but only within the layer in which this occurs, not affecting the total depth calibration. The obtained depth profiles were deconvoluted using the MRI model, although it was shown that the crater bottom roughness measured with AFM was more suitable for the estimation of the MRI parameter $\sigma$ than the interfacial and surface roughness measured with AFM prior to the sputtering. To avoid the worsening of the obtained depth resolution of a polycrystalline layer on top of a multi-layered system, the multi-layer may be sputtered from the other side.

Although the use of the MRI model can be extended to multiple layers if the crater roughness at the interfaces is known from AFM measurements, the use of a singular value for the RMS roughness $\sigma$ is an oversimplification for multilayers because of the changes in sputter rate. By measuring AFM crater bottom roughness at various depths, a roughness profile could be obtained by interpolation and a local DRF could be calculated at each depth. However, the sputter-induced roughness in polymers is such that the time and effort invested into this may not always be justifiable. Also, the COMPRO 6 code used is not capable of this and should be improved if this extension of the MRI model is needed.

Apart for SIMS, the MRI model may also be used for XPS and Auger depth-profiling. These methods have the advantage that the signal intensities are easier to quantify than the ion intensity obtained by dynamic SIMS. However, for these alternatives the information depth $\lambda$ starts to play a role in the DRF, so that a worse depth resolution than with dynamic SIMS will be obtained. Hence, the choice for dynamic SIMS or either Auger or XPS sputter profiling is defined by the question whether a qualitative or quantitative depth profile is required.

References

(9) A. Benninghoven, Zeitschrift für Physik 230, 403 (1971).
Conclusions

(20) P. H. van Cittert, Zeitschrift für Physik 69, 298 (1931).
(39) Gmelins Handbuch der anorganischen Chemie, Indium, Volume 37 (Verlag chemie, Berlin, 1936), 64.
5. Polymer-metal interfaces

Abstract
To study buried metal-polymer interfaces, the top layer generally has to be removed. To circumvent this problem the interface was simulated by evaporating a few angstroms of the metal on top of the polymer. This way, the interface could readily be studied without changing it prior to analysis.

To demonstrate this the interaction of oxygen with the PPV/calcium interface was studied with X-ray photoelectron spectroscopy and static secondary ion mass spectrometry. The interface was prepared by thermal evaporation of several angstroms of calcium on a spincoated OC₁C₁₀-PPV layer. The XPS spectra showed that the oxygen content in the polymer decreased dramatically, suggesting that the polymer was reduced, resulting in partial loss of the side chains.

*Important note*: This chapter has been published as a paper in *Chemical Physics*. However, an unfortunate choice of peak area normalisation and fitting constraints suggested results and conclusions that were not entirely correct or even justifiable. This chapter presents a more cautious approach and does not show any of the original figures as published in the *Chemical Physics* paper.

5.1 Introduction
Polymers that emit light (pLEDs) with a performance suitable for industrial applications have been developed in the last decade. Nevertheless, there is still a need for increased brightness, efficiency and long term stability, which requires a further investigation into the influence of the fabrication conditions on the performance and into the degradation processes of these devices.
Poly-(phenylene vinylene) (PPV) and its derivatives are commonly used for the fabrication of pLEDs. The degradation of the electroluminescent PPV, induced by e.g. photo-oxidation, has been investigated by several groups in detail.1-5 Xing et al. showed by studying XPS peak shifts that the degradation of PPV by photo-oxidation could be attributed to the oxidation of the phenylene and vinylene groups.1 The reaction mechanisms found were chain scission with the formation of carboxyl groups and the oxidation of the phenylene rings with a bridge of two oxygen atoms over the phenylene ring or between the phenylene ring and the vinylene group. Koch et al. found similar results with Fourier transform infrared spectroscopy (FTIR), investigating poly-(4,4'-diphenylene diphenylvinylene) (PDPV) and poly-(1,3-phenylene diphenylvinylene) (m-PPV-DP).5 Monkman et al. also showed that molecular oxygen present in a polyphenylenevinylene (PPV) film caused quenching of the luminescence.2

However, photo-oxidation is not the only possible degradation mechanism. Recently, Andersson et al. showed that devices fabricated with OC1C10-PPV as the electro-luminescent polymer failed when the polymer layer was exposed to oxygen in the dark after the deposition of five to ten nm of calcium.6 An increase of the oxygen concentration was found in these devices at the PPV/calcium interface with elastic recoil detection analysis (ERDA). The authors assumed that the device failure was caused by an enhanced oxidation of PPV due to its interaction with Ca. The best performance of LEDs using OC1C10-PPV was achieved if the calcium was deposited under UHV conditions with an oxygen pressure < 10^-9 mbar,7 which contradicts the findings from Bröms et al.,8 who showed that the device yield was very low and the electroluminescence lifetime extremely short when calcium was deposited on a clean CN-PPV surface under UHV conditions. The latter authors did not give any explanation for this unexpected result. They also found that the formation of oxides during magnesium deposition contributed negatively to device performance.

The interpretation of these results requires an understanding of the electronic and chemical state of the polymer–metal interface. Contradicting Bröms et al., Birgerson et al. suggested that an interface between PPV and calcium oxides might improve the electronic contact between electrode and polymer,9 since Lobach et al. showed that the most likely model for calcium oxide is Ca^{2+}O^{-}e^{-}, with e^{-} indicating a delocalized electron.10 They proposed that this model should be correct for both CaO and MgO.

Dannetun et al. suggested that calcium deposited as electrodes on poly(2,5-diheptyl-p-phenylenevinylene) is present on the surface as Ca^{2+} by looking at the binding energy shift of the Ca 2p spectrum in XPS.11 From the broadening and the small shift to lower binding energy of the C 1s spectrum they concluded that the calcium dopes the polymer at the vinyl bond. On the basis
of angle-dependent XPS spectra they proposed that the calcium diffuses somewhat into the polymer.

Unfortunately the authors did not show any Ca $2p$ spectra at all. There is not much doubt that the calcium is in a double charged state, but from the Ca $2p$ binding energy it is hardly possible to conclude that the calcium is present in a free state, since for calcium the following binding energies were found in different oxidized compounds such as CaO, Ca(OH)$_2$ and CaCO$_3$: 346.3 to 347.5 eV,$^{12-15}$ 346.7 eV,$^{16}$ and 346.9 to 347.2 eV,$^{17-19}$ respectively. Hence the conclusion of the authors that the interaction between calcium and PPV is ionic by nature is perhaps too strong on the basis of their XPS data alone. The observation by Dannetun et al. that the C 1$s$ spectrum widens and shifts to a slightly lower binding energy allows also another interpretation, namely that carbon and calcium form a carbide, which contradicts the authors conclusion that doping takes place.

The question is whether calcium could promote the degradation of PPV, which would lead to device failure, or not. Results obtained with XPS and SIMS will show that a PPV layer, on which some monolayers of calcium were deposited, will degrade upon exposure to oxygen.

5.2 Experimental

The samples were prepared in a setup described in detail elsewhere.$^7$ Layers of OC$_1$C$_{10}$-PPV, shown in Figure 1, with a thickness of ~130 nm were spin-cast on an indium tin oxide (ITO) covered glass substrate from a 0.71 wt% toluene solution in a glove box with a dry nitrogen atmosphere. The ITO was pretreated with UV-ozone for 20 minutes to remove adsorbed hydrocarbons. The samples were transferred without exposure to air into an UHV chamber, where calcium layers were deposited by thermal evaporation on top of the polymer film. Selected samples with and without a deposited calcium layer were exposed to oxygen for 20 minutes at an oxygen pressure of 1000 mbar as described in more detail elsewhere.$^8$ The samples were trans-

![Figure 1. The chemical structure of OC$_1$C$_{10}$-PPV](image)
ported in a dry nitrogen atmosphere to the modified VG Ionex system previously described in chapter 2. All C 1s peaks corresponding to hydrocarbon were calibrated at a binding energy of 285.0 eV to correct for the energy shift caused by charging. The static SIMS measurements were performed using Xe gas of purity 4.0 at 4 keV, staying well within the static limit.

Five different structures were investigated:

1. OC\textsubscript{1}C\textsubscript{10}-PPV / ITO;
2. OC\textsubscript{1}C\textsubscript{10}-PPV / ITO, exposed to oxygen;
3. 0.8 nm Ca / OC\textsubscript{1}C\textsubscript{10}-PPV/ITO;
4. 0.8 nm Ca / OC\textsubscript{1}C\textsubscript{10}-PPV / ITO, exposed to oxygen;
5. 1.2 nm Ca / OC\textsubscript{1}C\textsubscript{10}-PPV/ITO, exposed to oxygen.

### 5.3 Results

Figure 2 shows the XPS measurement results of the Ca 2p, C 1s and O 1s core levels. The integral intensities were calibrated on the C 1s C-C peak area.

The C 1s spectra in Figure 2a show up to four different features. The spectrum of the untreated PPV has only three. The main peak at 285.0 eV represents the hydrocarbon atoms in the OC\textsubscript{1}C\textsubscript{10}-PPV structure. The second peak at 286.5 eV is caused by the four oxygen bound carbon atoms (see Figure 1). A very small third peak at 288.2 eV represents some negligible oxidation of the polymer, a feature commonly seen. The spectrum of the oxygen-exposed PPV sample is essentially the same as that of the untreated PPV. In the spectra of the samples where calcium had been deposited on top of PPV, a fourth structure at 289.9 eV could be due to e.g. CaCO\textsubscript{3} (289.8 eV).\textsuperscript{17} Organic compounds containing carbon bound to several oxygen atoms also show strong chemical shifts.\textsuperscript{20} However, these chemical shifts deviate rather much from the shift found for the fourth carbon peak. Hence the peak should be attributed either to CaCO\textsubscript{3} or to a more unlikely complex formed by oxygen, calcium and PPV.

The O 1s spectrum of the untreated PPV shown in Fig 2b has a peak at 532.8 eV, which is the oxygen of the side group of OC\textsubscript{1}C\textsubscript{10}-PPV (see Figure 1). The oxygen correlating with the small contribution of oxidized PPV is covered by the much larger contribution of the side group oxygen. The O 1s spectrum of the oxygen-exposed PPV is identical to that of the untreated PPV. The spectra of PPV with deposited calcium show both the side group oxygen contribution at 532.8 eV and a pronounced peak at 530.9 eV. The
position of the second peak at 530.0 eV is in the range for oxygen of calcium oxide, calcium hydroxide and calcium carbonate. Reported values are 529.6 eV and 531.5 eV for CaO,15-21 531.2 eV for Ca(OH)$_2$,16 and 531.5 eV for CaCO$_3$.21 Hence the oxygen peak at 530.9 eV may be a mixture of oxides with a predominant portion of Ca(OH)$_2$. The intensity of the peak at 530.9 eV is high compared to the intensity of the oxygen peak of the untreated PPV.

Figure 2b shows that the position of the Ca 2p$_{3/2}$ peak varies between 346.8 and 347.2 eV. Again, these values are typical for CaO, Ca(OH)$_2$ and CaCO$_3$. The binding energies reported are in the range of 346.3 to 347.5 eV for CaO,12-15 346.7 eV for Ca(OH)$_2$,16 and 346.9 to 347.2 eV for CaCO$_3$.17-19

Since calcium hydroxide is most likely a product from a reaction between calcium and water, the origin of the water should be clarified. A possible source could be residual water in the PPV layer from the fabrication and processing of the polymer. Another possible source is the adsorption of water from the glove box atmosphere during the transport of the samples from the UHV evaporation chamber to the XPS/SIMS system, although the partial pressure of water was always below 1 ppm within the glovebox.

Figure 3 shows the as-measured positive SIMS spectra of the untreated PPV sample, the PPV sample with a thin layer of deposited Ca and a duplo of the
Polymer-metal interfaces

Figure 3. SIMS measurements of the investigated structures. The most striking feature in the spectra is the peak at m/z = 65, which is absent for the PPV without a Ca layer. The peak can only be attributed to CaC\textsubscript{2}H.

latter, but oxygen treated. There are some obvious differences between the samples. The most striking feature in the spectra is the peak at m/z = 65, which is absent for the PPV sample without a Ca layer. The peak can only be attributed to CaC\textsubscript{2}H, evidence of the formation of either a carbide bond between the calcium and the polymer, or at least a strong ionic interaction between the calcium and the polymer. Other peaks are caused by CaO, CaOH and CaCH\textsubscript{2}, although these peaks interfere with each other through isotope patterns. The presence of a strong CaOH peak supports the attribution of the oxygen peak at 530.9 eV in the XPS spectra to a mixture of oxides with a predominant portion of Ca(OH)\textsubscript{2}.

In general, SIMS is at best a qualitative technique, because the sputter and ionisation mechanisms are very complex. Quantification of absolute count rates can only rarely be attempted when well-defined reference samples are available. However, using ratios of count rates can be helpful to see whether correlations exist. Because \textsuperscript{39}K was present in all samples, and mass interference at this m/z value is not to be expected, this peak was used to normalise the other peaks in Figure 3. Because potassium was present as an impurity in OC\textsubscript{11}C\textsubscript{10-PPV},\textsuperscript{22} the assumption was that if the intensity of the \textsuperscript{39}K signal was made equal for all samples, the attenuating effect of the Ca top layer could be compensated for. The normalized intensities for selected m/z values are given in Table 1.

The fact that the calcium carbon interaction could not be recognized in the XPS spectra does not contradict the observation made with SIMS. Some
weak indication of the existence of a carbide in the XPS spectra can be derived from the fact that the C 1s peaks in the spectra of the PPV samples with deposited calcium show some broadening. The binding energy of the calcium carbide would be only some tenth of an electron volt lower than that of the C-C binding. However, an ionic interaction cannot be excluded.

Table 1. Relative intensities of selected ions in the SIMS spectra.

<table>
<thead>
<tr>
<th>m/z</th>
<th>species</th>
<th>PPV</th>
<th>PPV + O₂</th>
<th>PPV + 0.8 nm Ca</th>
<th>PPV + 0.8 nm Ca + O₂</th>
<th>PPV + 1.2 nm Ca+ O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>⁴⁰Ca</td>
<td>0.18</td>
<td>0.24</td>
<td>17.87</td>
<td>16.15</td>
<td>28.17</td>
</tr>
<tr>
<td>57</td>
<td>⁴⁰CaOH</td>
<td>0.42</td>
<td>0.50</td>
<td>2.29</td>
<td>3.64</td>
<td>2.96</td>
</tr>
<tr>
<td>65</td>
<td>⁴⁰CaC₂H</td>
<td>0.09</td>
<td>0.09</td>
<td>0.80</td>
<td>0.62</td>
<td>0.86</td>
</tr>
</tbody>
</table>

5.4 Discussion

By looking at the cross section corrected peak area ratios shown in Figure 4 some rather straightforward observations can be made. The ratio between the C-C and C-O (originating from the four oxygen bound carbon atoms of the polymer) peak areas shows that upon deposition of a thin layer of calcium the amount of oxygen-bound carbon atoms decreased, i.e. the polymer chain was reduced, which in turn implicates that somehow the sidechains, including the oxygen atoms, were removed from the system. The removal of the sidechain atoms could be facilitated by the ultra-high vacuum in the XPS setup after scission.

The C 1s structure at 289.9 eV could be caused by CaCO₃. Although the atmosphere within the glovebox consisted mainly of dry nitrogen, there were no filters for CO₂, so that Ca could have easily reacted with it. Oxidation of the Ca layer prior to transport from the evaporation chamber into the glovebox would prevent this reaction from happening. Figure 4 shows that the C 1s (CaCO₃) to Ca 2p ratio dropped after exposure of the Ca layer to oxygen, proof that the C 1s structure at 289.9 eV was indeed caused by CaCO₃.

Finally, the value of the Ca 2p to O 1s (Ca) ratio shown in Figure 4 is approximately 0.4, indicating that the Ca layer was in fact a mixture of CaO, Ca(OH)₂, and CaCO₃ with Ca(OH)₂ the main component, confirming the static SIMS findings. After the exposure of this layer to oxygen the CaO contribution rose somewhat. The presence of Ca(OH)₂ emphasizes the difficulty of transporting the samples without any contact with water.
The reaction mechanism must proceed in at least two steps. In the first step the polymer is reduced by the deposited Ca, which is then still in its metallic state (base pressure of the evaporation chamber is around $10^{-10}$ mbar). During the transport Ca(OH)$_2$ is formed. Because Ca(OH)$_2$ is a strong base, a reaction could take place between the polymer and Ca(OH)$_2$, resulting in the removal of the side chains. Exactly how is still unclear, however.

The observation of the CaC$_2$H ion raises the question whether Ca is covalently bound to polymer, or that it has an unusually strong ionic bond to it, e.g. by doping. Park et al. investigated the surface of oligo(phenylene vinylene) (OPV), which had been exposed to oxygen after calcium with a thickness of several angstrom had been deposited, with ultraviolet photo electron spectroscopy (UPS). They showed that the photoluminescence of a 300 Å layer of oligo(phenylene vinylene) with four units (4PV), which had been evaporated on top of gold or silicon, decreased strongly when calcium was deposited on the 4PV layer by thermal evaporation. The decrease of the photoluminescence was observed even at a calcium layer thickness of only 4 Å. UPS measurements showed that a gap state was formed in the band gap of the PPV after deposition of calcium. An exposure of the calcium/4PV layer to $10^3$ Langmuir of oxygen restored the photoluminescence partially, and the gap state vanished in the UPS spectra. This indicates that doping occured of the polymer. However, what can also be seen in the spectra, but was not pointed out by the authors, is that the highest $\pi$-state of the 4PV also van-
ished. The disappearance of this state was most probably caused by the degradation of the 4PV, which affected the conjugation of the oligomer and thus the π-states. The vanishing of the π-states in the UPS spectra was also reported by Xing et al. for the photo-oxidation of the PPV and was attributed to the oxidation of the phenyl ring and the vinyl unit and thus again to the destruction of the conjugation of the PPV.\(^1\)

Hence, the device failure caused by the exposure of a five to ten nm thick electrode of calcium to oxygen in the dark reported by Andersson et al. was probably caused by the formation of a carbide or ionic bond between Ca and the polymer, with reduction of the polymer, resulting in loss of conjugation.\(^6\) However, the precise mechanism could not be determined, so that further research is needed.

### 5.5 Conclusions

The influence of deposited Ca on top of PPV and the subsequent exposure to oxygen was studied. XPS measurements showed a reduction of PPV, indicating a loss of the PPV side chains. Not so much the presence of oxygen but the presence of water should be avoided as much as possible during the formation of the contact between the PPV and the calcium in the LED production process, because of the formation of the strong base Ca(OH)\(_2\), which is suspected to play a role in the degradation mechanism. The precise degradation mechanism is still not understood however.

### Reference

6. The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF studied by SIMS and XPS: formation of AlF₃ disproved

Abstract

Two mutually exclusive mechanisms have been proposed to explain the improved electron injection by the insertion of a LiF layer between the metal cathode and the active organic layer of organic photovoltaic devices: the dipole and the doping mechanisms. The possibility of the doping mechanism was studied by investigating the interface of poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) or 1-(3-(methoxycarbonyl)propyl)-1-phenyl[6,6]C₆₁ (PCBM) with Al, LiF or Al/LiF. In this mechanism, Li dopes the organic layer, after liberation via the reaction Al + 3 LiF → AlF₃ + 3 Li. If this reaction takes place, AlF₃ should be detectable at the surface. However, SIMS measurements showed that AlF₃ is not present at the Al/LiF/MDMO-PPV and Al/LiF/PCBM interfaces. This is evidence that the proposed reaction does not occur. Other evidence that the doping mechanism cannot be the general mechanism to explain the enhanced electron injection comes from the presence of LiF on both organic surfaces. XPS measurements indicate that there is a reaction of Al with the carboxylic oxygen of PCBM, and that a LiF layer between PCBM and Al prevents this reaction.

6.1 Introduction

Improving the electron injection into the active layer of polymer electronic devices, such as organic light-emitting diodes and polymer solar cells, is one of the critical issues in their development. One way to improve the electron injection is to insert a thin layer of LiF between for example tris-(8-hydroxyquinoline)aluminum (Alq₃) and the metal cathode.¹ Such a layer is already effective at the equivalent layer thickness of one angstrom;² layers of seven nanometers or more, however, become detrimental to the electron injection.³ The same beneficial effect of an inserted LiF layer was noted for several
The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF

other devices, containing organic compounds such as 4,4’-bis(2,2-diphenylvinyl)-1,1’-biphenyl (DPVBi), poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), and molecularly mixed layers of poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6,6]C61 (PCBM).

Several mechanisms to explain the beneficial effect of a thin layer of LiF on the electron injection at the cathode have been suggested: the formation of a Li+polymer- or Li+molecule- charge transfer complex after the reaction of LiF with Al to AlF3 and liberated Li, tunneling injection, formation of a dipolar layer, and the protection of the organic layer from reaction with aluminum.

The mechanism of electron injection enhancement by the formation of radical anions or charge transfer complexes, which could be responsible for the higher device efficiencies, was first suggested by Kido et al. They showed that an organic layer at the cathode interface shows electron injection improvement upon the co-evaporation of a low-workfunction metal and the organic layer, which suggests that doping takes place. However, when Le et al. used LiF instead of Li, they found that LiF alone does not decompose on Alq3, although a LiF layer also enhances the electron injection. Hence, they suggested that Li is liberated in the presence of Al and reacts with Alq3 to form the radical anion, although they proposed no reaction scheme. Piromreun et al. claimed that Al reacts with CsF on MEH-PPV to form AlF3 and free Cs, which subsequently dopes MEH-PPV. Others claimed the same mechanism for LiF on Alq3. Al/CsF on poly(9,9-dioctylfluorene) (PFO) follows the same reaction scheme according to Greczynski et al. However, these authors did not observe this for Al/LiF on PFO, which suggests that the proposed reaction scheme is not generally applicable. Also, Yang et al. noted that significant photoluminescence quenching should be expected if alkali metal ions diffuse into the active organic layer. However, when these authors measured the photoluminescence quantum efficiency of devices with and without an inserted LiF on MEH-PPV, they found essentially the same photoluminescence quantum efficiencies for both devices.

The tunneling injection mechanism explains the improved electron injection only in terms of the backflow current reduction, caused by the reduction of the electrode metal image force on the organic molecules by the insulating layer of LiF. This mechanism was investigated by Yang et al. when they studied devices with LiF, CsF, CaF2 and BaF2 layers stacked between different metal cathodes and an MEH-PPV layer. They found that tunneling through an insulating metal fluoride layer cannot be the correct mechanism because of the electron injection independence of the metal fluoride layer thickness and the strong performance dependence on the capping metals on top of the metal fluorides. Masenelli et al. numerically modeling experimental data from Stößel et al., confirmed that the reduction of the backflow
Introduction

current alone cannot explain the action of LiF, although it enhances the injection somewhat.

The aligned dipole mechanism explains the improved electron injection by the formation of a dipole in the LiF layer, which then lowers the workfunction of the metal cathode. Greczynski et al. showed that LiF deposited on a clean Al substrate shows weak dipole formation. Masenelli et al. demonstrated good agreement between simulations of a dipolar LiF layer and experimental data. Yang et al. found that devices with heavier metal fluorides exhibit less temperature dependence of the device lifetime. At an elevated temperature, thermal movement at the interface creates disorder, decreasing the orientation of the dipoles. Their interpretation was that since heavier metal fluorides show slower thermal movement, a better lifetime is expected. Baldo et al. remarked that an abrupt shift of approximately 1 eV in the vacuum level is observed at all metal cathode/Alq₃ interfaces studied to date with photoelectron spectroscopy. This is evidence for charge separation near the metal, which results in dipoles at its interface with the underlying organic semiconductor. They suggested that LiF/Al cathodes improve injection by raising the Fermi energy and shifting the effective injection interface deeper into the organic film where the distribution of organic states is narrower and the hopping barrier to injection is reduced.

Another mechanism is that LiF protects the active organic layer from the hot impinging metal atoms. Several authors reported on chemical damage to the Alq₃ layer upon deposition of the cathode material, not only with Al, but also with Mg, although according to Mason et al. no bond breaking is caused by Mg, Na, Li or K. Nevertheless, according to Baldo et al. chemical damage may explain the new gap states observed in UPS in several studies upon deposition of the metal cathode. However, all authors seem to agree that this is a secondary reason.

Obviously the two most likely mechanisms for electron injection enhancement, dubbed the doping and dipole mechanism, are mutually exclusive, but conclusive evidence for any of these two models is hard to find, because of the complexity of the interface and because spectroscopic methods such as XPS and UPS cannot always give unequivocal information on this problem.

Knowledge about the presence or absence of the elements and compounds around the interface enables us to discriminate between the dipole and the doping model. Just as for the mixture of MDMO-PPV and PCBM, the same beneficial effect of LiF/Al has been observed for the pure compounds. Therefore, SIMS spectra were measured at the interface of the organic and the LiF layers to determine the chemical state of the LiF layer on the surfaces of MDMO-PPV and PCBM substrates (Figure 1 shows the molecular formulas), taking into account the possible influence of aluminum. These spectra show
that LiF does not dissociate or react with aluminum to AlF₃ on both substrates, excluding the doping model for the explanation of enhanced electron injection in these substrates. Note that the validity of the dipole mechanism has not been proved, but that the validity of the doping model has been disproved.

Furthermore, to study possible interactions between deposited aluminum and the underlying organic layer, XPS measurements were performed using only relative shifts which indicated a reaction between aluminum and the carboxylic oxygen of PCBM. MDMO-PPV is resistant to reaction with aluminum.

**Figure 1.** Compounds used for semiconductive ((a) MDMO-PPV (b) PCBM) and conductive ((c) PEDOT (d) PSS) organic layers.

### 6.2 Experimental

The materials used were poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) synthesized via the Gilch-route,²⁴ 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6,6]C₆₁ (PCBM) generously provided by M.T. Rispens and J.C. Hummelen,²⁵ polyethyleneoxithiophene:polystyrenesulfonate (PEDOT:PSS) from Bayer AG, LiF from Aldrich, Al from Engelhard-Clal, and anhydrous AlF₃ from Aldrich. A glass plate covered with a 160 nm thick layer of indium tin oxide (ITO) was used as the substrate.

All samples were transported in a dry nitrogen atmosphere to a VG Ionex system equipped with a VG Clam II analyzer, Mg/Al Kα dual anode X-ray source, VG MIG-102 Ga⁺ and VG FAB61 ion source, LEG 31F electron flood gun and M12-2 s (<800 amu) quadrupole. The XPS measurements were carried out using the Al anode. All C1s peaks corresponding to hydrocarbon were calibrated at a binding energy of 285.0 eV to correct for the energy shift.
Results and discussion

caused by charging. The static SIMS measurements were performed with the electron impact gun (FAB 61) using Xe at 5 keV, while taking care to keep the total ion dose for each measurement within the static limit.

All samples were prepared as regular devices, except where mentioned otherwise. For this purpose the glass substrates were first cleaned by ultrasonic treatment in acetone, rubbing with soap, rinsing with de-mineralized water, refluxing with isopropanol, and finally UV ozone treatment. Subsequently, a layer of PEDOT:PSS was spin coated from an aqueous dispersion under ambient conditions on the cleaned substrates and the layer was dried by annealing the substrate. Then a layer of either MDMO-PPV or PCBM was spin coated from a chlorobenzene solution on top of the PEDOT:PSS layer and the sample was transferred to an N₂ atmosphere glove box. Finally, for some samples LiF and/or aluminum layers were deposited by thermal evaporation under vacuum (5×10⁻⁶ mbar, 1 ppm O₂ and < 1 ppm H₂O). The following samples were prepared:

1. Two reference samples of a 60 nm thick layer of Al or LiF deposited on a previously cleaned Si(100) wafer
2. One reference sample of AlF₃ powder pressed into indium foil
3. Two reference samples of pure MDMO-PPV or PCBM as the top layer of prepared-as-normal devices
4. Four samples with a 5 Å layer of Al or LiF deposited on top of either MDMO-PPV or PCBM as the top layer of prepared-as-normal devices
5. Two samples with a 5 Å layer of Al deposited on top of a 5 Å layer of LiF on top of either MDMO-PPV or PCBM as the top layer of prepared-as-normal devices

All samples were prepared in duplo, so that separate samples could be used for the SSIMS and XPS measurements.

6.3 Results and discussion

A popular explanation of the improved electron injection by LiF is the doping of the active polymer by Li liberated by a reaction between LiF and Al deposited on top of this. Although the Gibbs free energy required to liberate Li was estimated at 112.8 kJ/mol, making it an endothermic and hence unfavorable reaction, Mason et al. suggested that this is only the case for bulk LiF and that the reaction might be exothermic in the case of small isolated clusters of LiF₉.

Because the reaction would give rise to AlF₃ on the surface of the organic layer, we have investigated the presence of AlF₃. Figure 2 shows the com-
The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF

82

parison between the SIMS spectra of a pure AlF₃ reference sample and of the Al/LiF/MDMO-PPV and Al/LiF/PCBM interfaces. The peaks of interest of the AlF₃ reference samples are Al⁺, AlF⁺ and AlF₂⁺ at the m/z values of 27, 46 and 65 D. The AlF⁺ and AlF₂⁺ peaks should be present for the Al/LiF/MDMO-PPV and Al/LiF/PCBM samples, but they either have very low intensity or are completely missing. The low intensity of the AlF⁺ and AlF₂⁺ signals that are present are background signals caused by the underlying layers of MDMO-PPV and PCBM.

Hence, the absence of AlF₃ related signals in the SIMS spectra of the Al/LiF/MDMO-PPV and Al/LiF/PCBM samples is strong evidence that the proposed reaction between LiF and Al does not occur on MDMO-PPV or PCBM. Greczynski et al.¹³ claimed that CsF decomposes on PFO, based upon the ratio of CsF to the amount of Al needed to completely decompose CsF, and others have made the suggestion for LiF on Alq₃ based on rather indirect methods. However, Greczynski et al. showed with XPS that for the case of LiF on PFO no evidence can be found that LiF decomposes in the presence of Al.

Because all studied alkali and alkaline earth metal fluorides seem to improve the electron injection of the cathode,¹⁶ a general mechanism is likely to exist. Our results indicate, together with Greczynski et al.’s, that the proposed LiF/Al reaction to AlF₃ is not that general mechanism.

However, the reaction to AlF₃ was only proposed as a possible mechanism to obtain free Li atoms, which could subsequently dope the organic material. Kido et al. showed¹⁴ that a Li-doped Alq₃ layer exhibited a luminance an order of magnitude higher than an Alq₃ layer without Li, suggesting that Li-doping of the organic layer may also occur for alkali and alkaline earth metal fluoride containing devices.

If Li is liberated on the surface of the organic material, by reaction with Al or in any other conceivable way, then LiF should no longer be visible on the surface of the organic material. Figure 3 shows a comparison between SSIMS spectra from a LiF reference sample, and of LiF on MDMO-PPV, with and without Al on top. The LiF panel at the top of Figure 3 shows a clear ion cluster series of LiₙF⁺ₙ₋₁, although only a small part is shown here. The LiF/MDMO-PPV panel in the middle clearly shows the same ion pattern for LiF. Unfortunately, an Al layer on top of the LiF layer attenuates the LiF cluster ion signals, as shown in the Al/LiF/MDMO-PPV panel. Identical results have been obtained for the PCBM samples.

Because of the small amount of LiF deposited, the presence of LiF on top of the organic layers indicates that no liberation of Li takes place in any way, as the ion cluster series of LiₙF⁺ₙ₋₁ can only be formed if there are large clusters of LiF on the surface, which is a rather unlikely occurrence if most of the LiF
Results and discussion

Figure 2. AlF$_3$ reference comparison with Al/LiF/MDMO-PPV or Al/LiF/PCBM. Note the logarithmic scale of the ion intensity axis.

has reacted. Hence, a mechanism in which Li dopes the underlying organic layer is unlikely.

As mentioned before, one reaction that has been shown to occur is the reaction between Al and the underlying organic layer, for example with Alq$_3^{8,9}$ and PFO.$^{13}$ In the case of Alq$_3$, Le et al.$^8$ calculated, using density-functional theory, that the first four angstroms$^9$ of incoming aluminum will bond directly to oxygen atoms on two of the three quinolate rings in the Alq$_3$ molecule. Greczynski et al.$^{13}$ showed that only relatively small amounts of Al were needed in order to cause near complete degradation of the valence band, which sug-
The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF suggests that Al-C complexes are formed, although the authors did not claim any specific site of reaction on PFO.

To investigate the possibility of a reaction of Al with MDMO-PPV and PCBM, XPS was used to systematically measure the C1s, O1s and Al2p core-level regions of MDMO-PPV and PCBM layers with or without LiF, Al and Al/LiF layers on top. In the case of MDMO-PPV, shown in Figure 4, all binding energies were within 0.1 eV of the reference values. However, in the case of Al/PCBM a large shift of 1.5 eV was observed for the O1s peak originating from

Figure 3. Comparison of a LiF reference sample, a LiF/MDMO-PPV and an Al/LiF/MDMO-PPV sample shows that LiF stays intact on the surface of MDMO-PPV, regardless of the presence of Al.

To investigate the possibility of a reaction of Al with MDMO-PPV and PCBM, XPS was used to systematically measure the C1s, O1s and Al2p core-level regions of MDMO-PPV and PCBM layers with or without LiF, Al and Al/LiF layers on top. In the case of MDMO-PPV, shown in Figure 4, all binding energies were within 0.1 eV of the reference values. However, in the case of Al/PCBM a large shift of 1.5 eV was observed for the O1s peak originating from
the oxygen in PCBM compared to the same peak seen for the sample with no Al on top. Upon the insertion of a thin LiF layer, this peak shifted back 1.8 eV to a lower binding energy. The same binding energy shift was found for the Al2p peak. No difference in the C1s region could be observed at all, indicating that carbon atoms were unaffected.

The fact that the O1s and Al2p peaks both shifted to higher binding energies by the same amount is a strong indication that the carboxylic oxygen interacts with the aluminum. The aluminum is probably not metallic but in the form of AlₓO, because of the extreme broadening of the O1s peak upon adsorption of aluminum and the getter behavior of aluminum in vacuum. A possible reaction could be an acid-base reaction between the carboxylic group of PCBM and AlₓO, with methanol and an organo-metallic complex between the carboxylic group and the aluminum atom as reaction products. No comparison with literature values is possible, because a related complex could not be found in the literature.

Unfortunately, verification of the proposed organo-metallic complex formation by SIMS is doubtful, because the most obvious peaks to look for, such as AlO⁺, can also originate from AlₓO. Another consideration is that the nature of the carboxyl group bonds with the aluminum is not known, and these bonds may be too weak to survive the impact of the primary ions.

Figure 4. Comparison of the O1s and Al2p regions of MDMO-PPV and PCBM samples suggests that PCBM reacts with Al upon adsorption if the PCBM layer is not protected by a thin layer of LiF. MDMO-PPV is insensitive to this reaction.

85
The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF

Hence, DFT calculations should be performed to verify the probability of this reaction.

6.4 Conclusions

Some relevant sandwich-type interfaces related to solar cell devices and polymer LEDs have been studied using secondary ion mass spectrometry and X-ray photoelectron spectroscopy, including Al/MDMO-PPV, LiF/MDMO-PPV, Al/LiF/MDMO-PPV and similar interfaces containing PCBM instead of MDMO-PPV. SIMS measurements show that LiF does not react with aluminum to AlF₃, nor does it react in any other way to liberate Li as can be concluded from the detection of LiₙFₚ⁻ ions. The doping of the organic layer by Li suggested by various authors is unlikely as a mechanism for the improvement of electron injection into the polymer layer.

Although MDMO-PPV seems to be stable towards the deposition of aluminum by evaporation, XPS data give evidence of a reaction between aluminum and PCBM at the carboxylic group present in PCBM, as shown by the shift of the O1s carboxylic oxygen peak upon aluminum deposition. A thin layer of LiF is enough to undo this shift, evidence that the LiF layer protects the underlying PCBM from the aluminum atoms.

References

Conclusions


87
The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF
7. Quantification by multivariate statistical analysis of binary polymer blend depth profiles measured by dynamic secondary ion mass spectrometry

Abstract

The use of non-specific secondary ions to distinguish between polymers at primary ion doses far above the static SIMS limit was shown to be possible, using either canonical discriminant analysis or principal component analysis (PCA) on eleven different polymers. The possibility of quantifying a binary polymer blend was shown to be possible in a large range of compositions by checking the linearity of the relationship between the composition of the blend in solution and the composition of the blend in the depth profiled layer with canonical discriminant analysis. PCA was used to convert raw depth profiles (ion intensity vs. depth) into quantified depth profiles ($x_A$ vs. depth). These quantified depth profiles were compared to deuterium depth profiles within the same layers, which showed the sensitivity of the principal component analysis to local signal intensity changes during the pre-equilibrium sputtering phase.

7.1 Introduction

SIMS spectra, especially those obtained with Time-of-Flight SIMS, are often of a bewildering complexity. It is hence no surprise that most often only a few peaks are named and studied in the literature, whereas the rest of the information is discarded. However, there are two multivariate statistical analysis methods called principal components analysis (PCA) and discriminant analysis that provide a tool to take advantage of the wealth of information present in a series of mass spectra by reducing their complexity.¹

With principal components analysis combinations are found of $p$ variables $M_1, M_2, \ldots, M_p$, ion intensities of selected mass channels ($M_i$) in the case of SIMS, to produce uncorrelated indices $PC_1, PC_2, \ldots, PC_p$, called the principal components. These indices are ordered so that the variance (which is a measure of the scatter around the variable mean) captured by each consec-

---

⁠
Quantification by multivariate statistical analysis of binary polymer blend depth profiles measured...

...itive indice PC decreases: \( \text{var}(PC_1) \geq \text{var}(PC_2) \geq ... \geq \text{var}(PC_p) \). If the variables \( M_1, M_2, ..., M_p \) are highly correlated, which is very likely for the hydrocarbon fragments in the SIMS spectra, then most variation between polymers in the selected mass channels of the original spectra will be accurately described by the first few principal components \( PC_1, ..., PC_i \), so that the rest of the principal components \( PC_{i+1}, ..., PC_p \) can be ignored and data reduction of the original data set is achieved, so that the data becomes easier to interpret. However, if no correlation exists between the original variables \( M \), then principal component analysis will not lead to useful results.

If the data set contains \( p \) variables for \( n \) individuals, or measurements (for example \( p \) mass channels of the mass spectra of \( m \) measurements of \( n/m \) polymers), then the first principal component \( PC_1 \) is the linear combination of the original variables \( M_1, M_2, ..., M_p \) that maximizes the variance of \( PC_1 \):

\[
P C_1 = a_{11}M_1 + a_{12}M_2 + ... + a_{1p}M_p
\]

with the condition that:

\[
a_{11}^2 + a_{12}^2 + ... + a_{1p}^2 = 1
\]

to insure that the variation of \( Z_1 \) cannot be increased by simply increasing one of the \( a_{1j} \) values. This is repeated for each principal component \( Z_i \) with the additional condition that each principal component \( Z_i \) is uncorrelated with the other principal components.

Finding the principal components involves finding the eigenvectors of the sample covariance matrix:

\[
C = \begin{bmatrix}
c_{11} & c_{12} & \cdots & c_{1p} \\
c_{21} & c_{22} & \cdots & c_{2p} \\
\vdots & \vdots & \ddots & \vdots \\
c_{p1} & c_{p2} & \cdots & c_{pp}
\end{bmatrix}
\]

The sample covariance \( c_{jk} \) between variables \( j \) and \( k \), a measure of the extent to which the two variables are linearly related, is:

\[
c_{jk} = \sum_{i=1}^{n} \frac{(x_{ij} - \bar{x}_j)(x_{ik} - \bar{x}_k)}{(n-1)}
\]

This simplifies for the diagonal components \( c_{ii} \) to the sample variance:

---
Introduction

The eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_p$ of the sample covariance matrix $\mathbf{C}$ are equal to the variance of each principal component $\text{PC}_i$: $\text{var}(\text{PC}_i) = \lambda_i$, and the constants $a_{i1}, a_{i2}, \ldots, a_{ip}$ are the elements of the corresponding eigenvector, scaled to satisfy equation 2.

Often the correlation matrix is used, rather than the covariance matrix, to avoid one variable having a disproportionate influence on the principal components, in the case of SIMS to avoid having one mass channel with very high values (intensities) dominate the analysis. The correlation matrix is calculated by coding the variables $M_1, M_2, \ldots, M_p$ to have zero mean and a variance of one at the start of the analysis. First calculating the mean of each variable and subtracting this value from each sample value of that variable centers the variable at zero: $X_{i,\text{mean centered}} = X_i - \bar{X}$. Calculating the standard deviation for the variable and dividing each sample value by this standard deviation obtains a variance of one. If the covariance matrix is calculated with these coded variables, the correlation matrix is obtained instead:

$$
c_{ii} = s_j^2 = \frac{1}{n} \sum_{i=1}^{n} (x_{ij} - \bar{x}_j)^2 / (n - 1) 
$$

The eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_p$ of the sample covariance matrix $\mathbf{C}$ are equal to the variance of each principal component $\text{PC}_i$: $\text{var}(\text{PC}_i) = \lambda_i$, and the constants $a_{i1}, a_{i2}, \ldots, a_{ip}$ are the elements of the corresponding eigenvector, scaled to satisfy equation 2.

Often the correlation matrix is used, rather than the covariance matrix, to avoid one variable having a disproportionate influence on the principal components, in the case of SIMS to avoid having one mass channel with very high values (intensities) dominate the analysis. The correlation matrix is calculated by coding the variables $M_1, M_2, \ldots, M_p$ to have zero mean and a variance of one at the start of the analysis. First calculating the mean of each variable and subtracting this value from each sample value of that variable centers the variable at zero: $X_{i,\text{mean centered}} = X_i - \bar{X}$. Calculating the standard deviation for the variable and dividing each sample value by this standard deviation obtains a variance of one. If the covariance matrix is calculated with these coded variables, the correlation matrix is obtained instead:

$$
C = \begin{bmatrix}
1 & c_{12} & \cdots & c_{1p} \\
c_{21} & 1 & \cdots & c_{2p} \\
\vdots & \vdots & \ddots & \vdots \\
c_{p1} & c_{p2} & \cdots & 1
\end{bmatrix}
$$

with $c_{ij}$ the correlation between $X_i$ and $X_j$.

In principal components analysis, no prior knowledge is assumed about whether a sample originates from one group of samples, such as measurements on a specific polymer, or from another group (polymer). A method that tests how well two or more known groups of individuals or samples can be separated on the basis of a set of variables is called discriminant analysis. For $m$ random samples from different groups (polymers) of sizes $n_1, n_2, \ldots, n_m$ there will be $p$ variables $M_1, M_2, \ldots, M_p$ for each sample (Mass channels for SIMS). Because the outcome of discrimination analysis is not affected much by the scaling of individual variables, scaling of the data as with principal components analysis is not necessary (which in the case of PCA reduced the covariance matrix into the correlation matrix). However, the within-group covariance matrix should be the same for all groups $m$. Furthermore, in order to easily establish the statistical significance of the group differences it is preferable that the data has a normal distribution within groups.
Quantification by multivariate statistical analysis of binary polymer blend depth profiles measured

To separate the \( m \) groups as well as possible, canonical discriminant functions are calculated by taking linear combinations of the variables \( M_i \), not unlike the procedure used in principal components analysis, so that the first function is:

\[
Z_1 = a_{11}M_1 + a_{12}M_2 + \ldots + a_{1p}M_p
\]

(7)

This function is chosen in such a way that the linear combination has the maximum possible \( F \) ratio between the mean square of the between groups variation, \( M_B \), and the mean square of the within groups variation, \( M_W \), for a one-way analysis of variance. There may be several linear combinations possible, the number of functions being the smaller of \( p \) or \( m-1 \), which have no correlation between them.

However, the coefficients \( a_{ij} \) are not identical to the ones used in principal components analysis. To find the coefficients, the within-sample matrix of sums of squares and cross products, \( W \), and the total sample matrix of sums of squares and cross products, \( T \), first have to be calculated. The element in the \( r \)th row and \( c \)th column of matrix \( W \) is:

\[
w_{rc} = \sum_{j=1}^{m} \sum_{i=1}^{n_j} (x_{ijr} - \bar{x}_{jr})(x_{ijc} - \bar{x}_{jc})
\]

(8)

and the element in the \( r \)th row and \( c \)th column of matrix \( T \) is:

\[
t_{rc} = \sum_{j=1}^{m} \sum_{i=1}^{n_j} (x_{ijr} - \bar{x}_{r})(x_{ijc} - \bar{x}_{c})
\]

(9)

From \( W \) and \( T \) the between-groups matrix \( B = T - W \) can be calculated. From \( W^{-1}B \) the eigenvectors and eigenvalues have to be found. The eigenvalue \( \lambda_i \) is then the ratio of the between-groups sum of squares to the within-group sum of squares for the \( i \)th linear combination \( Z_i \), with the elements of the eigenvector \( a_i \) the coefficients of \( Z_i \).

The discriminant functions are chosen in such a way that each function shows as much group difference as possible not shown by the other discriminant functions. If the first few functions are sufficient to account for almost all group differences, preferably one or two, plotting the values of these few functions for each individual sample may then show the separation between the groups \( m \). It is important to note the difference between principal components analysis and discriminant analysis. The latter emphasizes only the dif-
Introduction

ferences between different groups of measurements, whereas the former emphasizes the differences between all measurements, ignoring any prior knowledge.

Principal components analysis of static SIMS spectra has already been applied to a multitude of problems. Adsorbed proteins and other natural organic molecules have been classified\textsuperscript{2-5} and their conformational changes upon adsorption have been studied.\textsuperscript{6,7} Other successful classification studies involved the comparison of solution assembled and stamped monolayers of dodecanethiol on gold,\textsuperscript{8} the differentiation between uncured and cured MF resins,\textsuperscript{9} or the differentiation between six calcium phosphates.\textsuperscript{10} More applied studies involved contamination investigations,\textsuperscript{11,12} whereas in more fundamental studies SIMS sputtering and fragmentation pathways were investigated.\textsuperscript{13,14} Principal components analysis of SIMS images has been performed in at least one case as well.\textsuperscript{15}

However, to our knowledge, multivariate statistical analysis has not been applied to dynamic SIMS depth profiles. Up to now, PCA has been performed only during relatively static conditions. The main reason for this is that for high ion fluences, such as encountered during dynamic SIMS, any characteristic fragments that are most often used for multivariate statistical analysis are unstable.\textsuperscript{16} However, it may be feasible to use non-characteristic hydro-carbon fragments to analyze polymer depth profiles, e.g. to quantify the fractions of polymers in binary polymer blends or polymer/organic compound blends.

Although non-characteristic hydro-carbon fragments such as C\textsubscript{2} and C\textsubscript{2}H are encountered in the mass spectra of most polymers, these fragments together contain information about the carbon-hydrogen ratio within each polymer, and the ratio between single and multiple carbon bonds, even if the precise fragmentation pathways are not known. Hence, it should be possible to separate the different polymers. Further differentiation may be possible by using fragments containing other elements commonly encountered in polymers, such as oxygen and nitrogen. The total separation process can be likened to plate chromatography, in which an unknown mixture (the data set of SIMS measurements) is deposited at the corner of a plate, after which a first separation (in our case on the basis of the hydro-carbon fragments) is reached by placing the plate upright in a shallow pool of solvent. After the first separation is complete, the plate is turned and a second separation takes place. The result is a plate full of dots, each dot representing a compound. To complete the analogy, the coordinates of each dot can be likened to the values of the first two indices, PC\textsubscript{1} and PC\textsubscript{2} for principal components analysis or Z\textsubscript{1} and Z\textsubscript{2} for discriminant function analysis.

To test this hypothesis, eleven common polymers were depth profiled until all secondary ion signals were stable, i.e. after possible carbonization had taken
place. The stable part of each depth profile was added to the dataset used for discriminant and principal component analysis. Discriminant analysis completely separated the polymers; principal component analysis was capable of separation in most cases, proving that even non-specific secondary hydrocarbon ions can be used to distinguish between common polymers.

Finally, depth profiles of binary polymer blends of different composition were analyzed with discriminant analysis that showed that a linear relationship could be obtained between the concentrations of the blend in the spin casting solution and in the obtained polymer layer. A quantified concentration profile could then be obtained with principal components analysis.

7.2 Experimental

Figure 1 shows the polymers used as reference in the first part of this chapter, with (a) Polyethylene terephthalate (PET), (b) Polypropylene (PP), (c) Polymethylmethacrylate (PMMA), (d) Polyetheretherketone (PEEK), (e) Polybenzimidazole (PBI), (f) Polyethersulphone (PES), (g) high density polyethylene (HDPE), (h) Polyamide – Nylon 6 (PA 6), (i) Polyvinylchloride (PVC), (j) Polyimide (PI), (k) Polyamide – Nylon 6,6 (PA 6,6). All filler-free polymers were obtained packaged in paper from Goodfellow. The polymer reference samples were packaged in kitchen aluminum foil and cut with a figure-saw previously rinsed with methylchloride, hexane, acetone and methanol, all of p.a. quality. The cut pieces were also cleaned with these solvents, if they were not soluble in these solvents, to remove possible contamination from prior handling and storage. A thin gold layer of approximately 30 Å was deposited on top of all cleaned polymer reference samples by sputter coating to facilitate charge neutralization during depth profiling, and stored in kitchen aluminum foil for storage. All polymer references (a-k) were measured in a VG Ionex system equipped with a MIG-102 Ga+ ion source, a LEG 31F electron flood gun and a M12-2 s (<800 amu) quadrupole, using 10 keV, 5.5 nA Ga+ and an electronic gate which only uses the center 10 % of the total sputtered area.

The materials used for the depth profiling quantification test, shown in Figure 2, were poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) synthesized via the Gilch-route,17 1-[3-(methoxycarbonyl)propyl]-1-d5-phenyl[6,6]C61 (d5-PCBM), and polyethylenedioxythioaphene:polystyrenesulfonate (PEDOT:PSS) from Bayer AG. A glass plate covered with a 44 nm thick layer of indium tin oxide (ITO) was used as the substrate.

All depth profile quantification samples were prepared as regular solar cell devices. For this purpose the ITO covered glass substrates were first cleaned by ultrasonic treatment in acetone, rubbing with soap, rinsing with.
Figure 1. The polymers used to establish the capability of canonical discriminant analysis and principal components analysis to distinguish between polymers using non-characteristic secondary hydrocarbon ions are (a) Polyethylene terephthalate (PET), (b) Polypropylene (PP), (c) Polymethylmethacrylate (PMMA), (d) Polyetheretherketone (PEEK), (e) Polybenzimidazole (PBI), (f) Polyethersulphone (PES), (g) high density polyethylene (HDPE), (h) Polyamide – Nylon 6 (PA 6), (i) Polyvinylchloride (PVC), (j) Polyimide (PI), (k) Polyamide – Nylon 6,6 (PA 6,6).
de-mineralized water, refluxing with isopropanol, and finally UV ozone treatment. Subsequently, a layer of PEDOT:PSS was spin coated from an aqueous dispersion under ambient conditions on the cleaned substrates and the layer was dried by annealing. Then a layer of either MDMO-PPV, d5-PCBM, or a mixture of both, was spin coated from a chlorobenzene solution on top of the PEDOT:PSS layer and the sample was transferred to an N2 atmosphere glove box for storage until it could be measured. For transport to the ToF-SIMS apparatus a vacuum exsicator was used.

The dynamic SIMS measurements for the depth profiling quantification test were performed on an IONTOF IV (which saturates at 10^5 counts) in dual-beam mode: 75 nA, 1 keV Cs+ at 45° rastered over 300×300 µm^2 for sputtering and a 1.5 pA, 15 keV Ga+ beam at 45° rastered over 50×50 µm^2 for analysis. The depth profiles were measured in the non-interlaced mode (longer sputter and data acquisition cycles) to avoid charging. Effective charge compensation was obtained by using an electron flood gun (20 eV). All depth profiles were mass calibrated on C_xH_y fragments.

7.3 Results and discussion

Although the ultimate goal was to quantitatively describe a dynamic SIMS depth profile of a binary polymer blend by using multivariate statistical analysis, the feasibility of distinguishing between polymers on the basis of non-characteristic secondary ions had to be proved first. These non-characteristic secondary ions, mostly short hydro-carbon fragments, are emitted from almost all sputtered polymers and exhibit a stable ion signal after a steady
state in the primary beam-polymer interaction has been reached. A stable ion signal is very important for the intended quantitative description.

To test whether the different polymers can be separated from each other, canonical discriminant analysis is a good technique, because this method separates groups on the basis of variation between the groups, as opposed to principal components analysis that separates every measurement as much as possible. Depth profiles were measured for all 11 polymer samples shown in Figure 1. Because these measurements were performed on a quadrupole system, the secondary ions to be used for the canonical discriminant analysis had to be chosen in advance. Only a limited number could be measured. If too many had been chosen, the secondary ions would not have originated from more or less the same depth within the polymer anymore, because of the sequential nature of the quadrupole measurement cycle.

The assumption behind the measurements was that the canonical discriminant analysis would separate the polymers by hydrogen-carbon ratio and type of carbon-carbon bonds present in the polymer. Furthermore, the intensity of the signal had to be high enough to ensure normality of the ion intensity distribution. Hence, the C, CH, O, OH, C\textsubscript{2}, C\textsubscript{2}H, C\textsubscript{2}H\textsubscript{2} or CN, C\textsubscript{4}, and the C\textsubscript{4}H ions were measured. The depth profiles were measured long enough that all secondary ion signals were stable, meaning no long-term changes in intensity, until at least ten cycles had been measured in this steady state. The ion intensities of these cycles were used in the canonical discriminant analysis. Figure 3 shows that all eleven polymers were well separated, with only the PVC, HDPE and PES groups close together. To classify each measurement to one of the eleven groups, the Leave-One-Out classification method was used. In this method each case is classified by the functions derived from all cases than that case. All cases were correctly classified to the group they originated from, which proves that non-specific secondary ions are together capable of distinguishing between various polymers.

Of course, the question is whether measurements can be classified when no prior knowledge is assumed about the group they originate from. Principal component analysis was performed on the same data set as used for the canonical discriminant analysis, using object principal normalization to normalize the data set. This method minimizes distances between objects, which is useful when the differences or similarities between the objects are of interest. Figure 4a shows that even when no prior knowledge is used, most polymers can still readily be identified. When PCA is performed on the dataset of only the six polymers that are closest to each other in Figure 4a, these polymers can also be separated completely except for PP and PES, as shown in Figure 4b. This proves that using non-specific secondary hydrocarbon ions can be used to differentiate between different polymers.
Quantification by multivariate statistical analysis of binary polymer blend depth profiles measured

However, when the loading of the first two principal components of the principal components analysis from Fig. 4a is studied, shown in Fig. 5, the hypothesis that the separation would take place on the basis of the carbon-hydrogen ratio, the single to multiple bond ratio, and the presence of oxygen or nitrogen in the polymers, seems to be false. No direct relationship can be found between these parameters and the loading of these ions in principal component 1 and 2. Nevertheless, the separation of these polymers on the basis of non-characteristic secondary ions is still a fact.

The next step is to determine the fraction of both polymers in a binary polymer blend. If reference measurements are available of pure polymer A, pure polymer B and mix A<sub>x</sub>B<sub>y</sub>, then a dataset that contains these three measurements can be analyzed with multivariate statistical analysis to determine the fraction of polymer A in the mix. The fraction of either polymer in the blend can be calculated from the distance of a measurement point of the blend to both centroids of the pure reference measurements:\(^18\)

\[
X_A = 1 - \frac{D_{AM}}{D_{AM} + D_{BM}}
\]  

(10)

---

Figure 3. Canonical discriminant analysis of the stable part of dynamic SIMS measurements of polymers (a)-(k). The first two functions shown captured 78.2 % of the between-groups variance.
Results and discussion

With:

- $x_A$: The fraction of polymer A in the polymer blend
- $D_{AM}$: The distance between the centroid of all polymer A measurement points and the polymer blend measurement point
- $D_{BM}$: The distance between the centroid of all polymer B measurement points and the polymer blend measurement point

This approach implicitly assumes a linear relationship between the fraction $x_A$ and the distance between the measurement point of the blend and both reference centroids. To test this assumption, datasets were constructed containing stable dynamic SIMS measurements of d5-PCBM, MDMO-PPV, and one blend of d5-PCBM and MDMO-PPV each, with varying composition. Because the secondary ions are measured simultaneously with a time-of-flight mass analyser, and because such an analyser has a much higher mass resolution than a quadrupole, more secondary ions can be used in the multivariate analysis. Hence, about 60 hydrocarbon fragments were used that had been checked for overlap with other secondary ions.

These data sets were analyzed with canonical discriminant analysis to determine the average composition in the layer, because this analysis maximizes the distance between groups, but not between cases belonging to the group, so that variation in composition within one layer will not overly influence the general calculated fraction. Figure 6a shows the result of a canonical discriminant analysis on a dataset containing the measurement of a 40.6 wt% d5-PCBM sample. Figure 6b shows the calculated fraction of d5-PCBM for every data point. Because the distance of each d5-PCBM measurement point is calculated using Pythagoras' theorem ($A^2 + B^2 = C^2$), the average of the calculated d5-PCBM fraction in the pure d5-PCBM reference sample will always be less than one. This means that the fraction calculated with equation 10 should be normalized with the fraction found for pure d5-PCBM:

$$X_{PCBM,\, blend} = \left(1 - \frac{D_{PCBM \leftrightarrow blend}}{D_{PCBM \leftrightarrow blend} + D_{MDMO - PPV \leftrightarrow blend}} \right) / X_{PCBM,\, pure}$$

Of course, when this normalization is performed on the pure d5-PCBM fraction, the mean of the d5-PCBM fraction will be centered at one. The error made in the calculation of the fraction of d5-PCBM, caused mainly by the noise in the SIMS data, is equal to the fraction of d5-PCBM calculated to be in the MDMO-PPV reference data (which should contain no d5-PCBM at all).

---

<table>
<thead>
<tr>
<th>DAM</th>
<th>The distance between the centroid of all polymer A measurement points and the polymer blend measurement point</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBM</td>
<td>The distance between the centroid of all polymer B measurement points and the polymer blend measurement point</td>
</tr>
</tbody>
</table>

Of course, when this normalization is performed on the pure d5-PCBM fraction, the mean of the d5-PCBM fraction will be centered at one. The error made in the calculation of the fraction of d5-PCBM, caused mainly by the noise in the SIMS data, is equal to the fraction of d5-PCBM calculated to be in the MDMO-PPV reference data (which should contain no d5-PCBM at all!).

---

99
Quantification by multivariate statistical analysis of binary polymer blend depth profiles measured

Figure 4. a) Principal components analysis of the stable part of dynamic SIMS measurements of polymers (a)-(k). The first two principal components captured 74.6% of the total variance. b) Principal components analysis of the stable part of dynamic SIMS measurements of polymers (b), (c), (f), (g), (j), (k). The first two principal components captured 73.4% of the total variance.
Results and discussion

Analyzing blends of different composition, Figure 7 can be constructed. The assumption of linearity is cannot be rejected in the $x_{PCBM} = 0.2 - 0.8$ interval on the basis of the available data. However, the linear fit does not go through zero. In all cases, the calculated fraction of d5-PCBM is higher than in the solution used to prepare the layer. The consequence is that close to $x_{PCBM} = 0$, non-linear behavior has to be expected. A possible explanation could be a mismatch between the solvability of MDMO-PPV and PCBM, so that more PCBM is deposited during spin coating than could be expected from the solution concentration. This effect should be less for blends in which both polymers have more or less the same solubility in the solvent used. Another cause might be that the reference and blend measurements have not been performed on the same day. Small variations in the settings might have influenced the quantification. So far, there have been no tests to study the influence of variations in the measurement conditions on the quantification. Further tests are needed to determine the precise cause.

The same data sets of d5-PCBM:MDMO-PPV blends were analyzed with principal components analysis and quantified. Because PCA maximizes the distance between all data points, variation in composition within each layer should be visible. The analysis was only carried out until the depth in which the sulphur signal started to rise, indicating that the PEDOT:PSS layer had been reached. Figure 8a shows the resulting quantified depth profiles. The
Figure 6. a) Canonical discriminant analysis of a dataset of dynamic SIMS measurements on a d5-PCBM reference, an MDMO-PPV reference, and a d5-PCBM:MDMO-PPV layer. The first two functions captured 100% of the between-group variance. b) The calculated fraction of d5-PCBM per case. The average calculated d5-PCBM fraction in the PCBM reference was used to normalize the d5-PCBM fraction in the MDMO-PPV reference and the blend layers. The d5-PCBM fraction in the MDMO-PPV reference, which should of course be zero, was used to calculate the error in the calculated d5-PCBM fraction in the blend. The expected fraction of d5-PCBM in the layer was 0.406, because the solution contained 40.6 wt% d5-PCBM and 60 wt% MDMO-PPV, ignoring the solvent. The calculated fraction was 0.50 after normalization.
fraction of d5-PCBM at the outer layer was much higher than could be expected from the d5-PCBM to MDMO-PPV ratio in the spin casting solution. However, some of this deviation from the expected d5-PCBM fraction has to be attributed to the pre-equilibrium phase, in which no steady-state had been reached yet. In this phase, the intensities of the secondary ions are not stable yet, so that these measurement points were most probably attributed different coordinates in the PCA analysis than the points measured during the steady state sputtering condition. Still, a higher d5-PCBM concentration at the surface of the layers was also found with cross section TEM in samples spin cast from solutions above approximately 70 wt% d5-PCBM, which even showed small conglomerates of d5-PCBM close to the surface due to de-mixing (to be published elsewhere). Again, a possible explanation could be a solubility mismatch between d5-PCBM and MDMO-PPV.

Figure 8b shows the original deuterium profiles. The pre-equilibrium phase is clearly recognized in the rising signal close to the surface, up to a depth of approximately 10 nanometers. Ignoring this first region in the comparison between both sets of depth profiles, the deuterium profiles show a trend towards a slightly higher d5-PCBM fraction close to the PEDOT:PSS interface rather than at the surface, except for the 80.1 wt% d5-PCBM sample.

**Figure 7.** Test of linearity of the d5-PCBM fraction $x_{PCBM}$ calculated with Equation 11 with the PCBM fraction $x_{PCBM}$ in solution.
Results and discussion

Distribution that seems to follow the same trend as for the quantified depth profiles, probably because of pronounced phase segregation as indicated also by the TEM measurements. An explanation may be that the single D signal may be influenced by sputter and matrix effects, which possibly do not

Figure 8. (a) Depth profiles of d5-PCBM:MDMO-PPV layers prepared from solutions containing 21.1 wt%, 40.6 wt%, 59.8 wt%, and 80.1 wt% of d5-PCBM, ignoring the solvent. The depth profiles were calculated by principal components analysis, using the same data sets as for the canonical discriminant analysis. (b) The original deuterium depth profiles.
play such a large role in the quantified depth profiles. However, further
research is needed to elucidate this problem.

7.4 Conclusions

A test on eleven common polymers showed that it is possible to distinguish
between polymers by analyzing the intensities of non-specific secondary
hydrocarbon ions with canonical discriminant analysis or principal compo-
nents analysis, if the intensities of these secondary ions used in the multivari-
ate statistical analysis are stable in depth, i.e. if they are measured after a
steady-state between the primary ions and the polymer has been reached.

At least in the case of d5-PCBM:MDMO-PPV blends, both multivariate statis-
tical analysis techniques captured 100 percent of all variation in the data in
the first two functions or indices. Even more promising is that a linear rela-
tionship between the composition of the blend in solution and the composi-
tion of the blend in the depth profiled layer in a large range of compositions,
calculated with canonical discriminant analysis could not be rejected.

In the first 10 nanometers of the blend layer the intensities of the secondary
ions were not stable yet, so that these measurement points were most prob-
ably attributed different coordinates in the PCA analysis. Hence, these points
should be ignored until further studies clarify the reliability of the PCA analy-
sis in this pre-equilibrium phase. The rest of the quantified depth profiles
showed the reverse trend of the raw deuterium depth profiles, except the
profile from the layer containing 80.1 wt% d5-PCBM. A possible explanation
can be that the single D signal may be influenced by sputter and matrix
effects, which possibly do not play such a large role in the quantified depth
profiles. Again, further research is needed to elucidate this.

Taken all this into consideration, the overall conclusion has to be that the use
of multivariate statistical analysis for the quantification of depth profiles of
binary polymer blends shows much promise. However, all measurements
should ideally be made under the same, and more importantly, stable mea-
surement conditions. Furthermore, although the choice for MDMO-PPV and
d5-PCBM for the first test was made from the point of view that these mole-
cules have a very different hydrogen to carbon ratio, which was expected to
be important for the quality of the separation by the multivariate statistical
analysis, this may be less important than choosing two polymers or organic
compounds that have more or less identical solubility, to check for a linear
relationship between the composition of the blend in solution and the compo-
sition of the blend in the depth profiled layer.
Conclusions

Reference

Summary

In many cases, knowledge of the in-depth distribution of compounds or elements in layers is crucial in order to understand the material and physical properties of that layer. Often, the deviations in the depth distribution are found at the interfaces. The material at these interfaces may be oxidized or contaminated. Material may have diffused across the interfaces, which can have both positive and negative results, depending on the application.

A technique that is capable of measuring the elemental or compound distribution in materials up to a depth of several micrometers is secondary ion mass spectrometry (SIMS). With this technique, interface reactions, diffusion, and segregation processes can be studied at a depth resolution of only a few nanometers in favourable cases. However, the sputtering process involved can alter the original distribution, so that a distorted depth distribution is measured instead. During the pre-equilibrium phase the secondary ion intensities can change rapidly, resulting in an unreliable measurement. Atomic mixing causes the redistribution of species into neighboring layers. The sputtering process can alter the surface roughness, causing a loss of depth resolution.

In applications where the near-surface region is the region of interest, the pre-equilibrium phase is a real problem because it is exactly in this region where the distortion takes place. To illustrate this a system was chosen in which a gradient should exist in the surface region. First, the fluorine gradient in a modified epoxy-amine layer was studied by (angle resolved) XPS and dynamic SIMS. Normal XPS measurements showed that the fluorine containing surfactant molecules adsorbed at the surface prior to curing, until the surface was saturated. Angle resolved XPS measurements showed a high level of enrichment with the fluorinated surfactant of the near surface region.

Depth profiling by dynamic SIMS was shown to be problematic because of the pre-equilibrium phase, which distorted the depth profile in the region of interest. A PS sacrificial layer was used to circumvent this distortion. The
addition of such a layer helps to remove the distortion of depth profiles measured close to the surface of a coating, because the period of equilibration between the ion beam and the polymer material is shifted from the coating into the sacrificial PS layer. However, direct spincasting of the PS sacrificial layer was problematic because of dewetting of the spincast layer. A practical way of preparing a smooth PS sacrificial layer without the problem of dewetting was described. The best depth resolution obtainable in this way was 4.9 nm according to the IUPAC definition, and was shown to be depending on the acceleration voltage, due to atomic mixing. The quantification of the amount of fluorine proved to be different from the ARXPS results, possibly because of matrix effects and of the atomic mixing. However, using a sacrificial layer seems to be a simple way of circumventing the pre-equilibrium phase.

In some applications, such as organic light emitting displays, which consist of a stack of various metal, inorganic and polymer layers, the interaction and the diffusion of material between the layers is of interest in terms of long-term stability of the device. The analysis of such stacks comes with some unique problems. For example, the differences between the sputter rates in the various layers complicate the depth calibration. However, this conversion from a time to depth scale of dynamic SIMS depth profiles was shown to be possible by choosing an ion unique to its layer, normalising the signals to unity, calculating the fraction of each layer present at each point, and assuming a linear relationship of the local sputter rate at each measured point with the fraction of each layer and its sputter rate. Carbonisation may bias such calibration, but only within the layer in which this occurs, not affecting the total depth calibration.

Another problem was the sputter-induced roughness, which seriously distorted the obtained depth profiles. The profiles were deconvoluted using the MRI (mixing-roughness-information depth) model, although it was shown that the crater bottom roughness measured with AFM at different depths was more suitable as the MRI parameter than the interfacial and surface roughness measured with AFM prior to the sputtering. To avoid the worsening of the obtained depth resolution by preferential sputtering behavior in a polycrystalline layer on top of a multi-layered system, the multi-layer was also sputtered from the other side with much improved results.

Although use of the MRI model can be extended to multiple layers if the crater roughness at the interfaces is known from AFM measurements, the use of a singular value for the RMS roughness was shown to be an oversimplification for multilayers because of the changes in sputter rate. By measuring AFM crater bottom roughness at various depths, a roughness profile could be obtained by interpolation and a local DRF could be calculated at each depth. However, the sputter-induced roughness in polymers is such that the time and effort invested into this may not always be justifiable. Also, the
COMPRO 6 code used does not have this feature and should be improved. To avoid extreme crater roughness development in polymer depth profiles altogether, sample rotation should be applied.

When interface reactions without further diffusion are the topic of interest, it is important to measure this interface without perturbing the interface with the probing technique. However, because the interface is usually buried under a thick layer that has to be removed prior to analysis, this is quite difficult. An alternative approach could be to simulate the interface by only depositing a very thin layer of the normally thick top layer. This way the interface can be probed with static SIMS and XPS.

The influence of deposited Ca on top of PPV and the subsequent exposure to oxygen was studied using this approach. XPS measurements showed a reduction of PPV, indicating a loss of the PPV side chains. Not so much the presence of oxygen but the presence of water should be avoided as much as possible during the formation of the contact between the PPV and the calcium in the LED production process, because of the formation of the strong base Ca(OH)$_2$, which is suspected to play a role in the degradation mechanism. The precise degradation mechanism is still not understood however. Static SIMS showed close contact between calcium and the polymer, indicating a high dispersion of Ca. The question whether Ca reacted with the polymer to form a carbide, or that the interaction was ionic, could not be resolved.

Another case in which an interface was simulated is the study of a possible dissociation reaction of LiF on MDMO-PPV and PCBM, induced by an Al toplayer. This reaction was disproved by using secondary ion mass spectrometry and X-ray photoelectron spectroscopy to study the Al/MDMO-PPV, LiF/MDMO-PPV, Al/LiF/MDMO-PPV and similar interfaces containing PCBM instead of MDMO-PPV. SIMS measurements showed that LiF did not react with aluminum to AlF$_3$, nor did it react in any other way to liberate Li, as can be concluded from the detection of Li$_n$F$_{n-1}^+$ ions. Hence, the doping of the organic layer by Li suggested by various authors was shown to be unlikely as a mechanism for the improvement of electron injection into the polymer layer because no Li is liberated.

Evidence of another reaction at the interface was found, however. Although MDMO-PPV seemed to be stable towards the deposition of aluminum by evaporation, XPS data gave evidence of a reaction between aluminum and PCBM at the carboxylic group present in PCBM, as shown by the shift of the O1s carboxylic oxygen peak upon aluminum deposition. A thin layer of LiF was enough to undo this shift, evidence that the LiF layer protects the underlying PCBM from the aluminum atoms.

Simulating an interface seems to be a valid and fruitful way of investigating interface reactions, especially when the combination of static SIMS and XPS
is used. However, these interfaces are especially sensitive so that care must be taken to exclude any external influences.

A problem arises when a blend of two polymers has to be profiled, because most polymers show similar mass spectra, and possible characteristic secondary ions are usually not stable during sputtering. A test on eleven common polymers showed that it is possible to distinguish between polymers by analyzing the intensities of non-specific secondary hydrocarbon ions with canonical discriminant analysis or principal components analysis, if the intensities of these secondary ions used in the multivariate statistical analysis are stable in depth, i.e. if they are measured after a steady-state between the primary ions and the polymer has been reached.

At least in the case of d5-PCBM:MDMO-PPV blends, both multivariate statistical analysis techniques captured 100 percent of all variation in the data in the first two functions or indices. Even more promising is that a linear relationship between the composition of the blend in solution and the composition of the blend in the depth profiled layer, calculated with canonical discriminant analysis, could not be rejected in a large range of compositions.

In the first 10 nanometers of the blend layer the intensities of the secondary ions were not stable yet, so that these measurement points were most probably attributed different coordinates in the PCA analysis. Hence, these points should be ignored until further studies clarify the reliability of the PCA analysis in this pre-equilibrium phase. ARXPS should be helpful in this case, because of the compatibility of the information depth with the depth range of the pre-equilibrium phase. The rest of the quantified depth profiles showed the reverse trend of the raw deuterium depth profiles, except the profile from the layer containing 80.1 wt% d5-PCBM. A possible explanation can be that the single D signal may be influenced by sputter and matrix effects, which possibly do not play such a large role in the quantified depth profiles. Again, further research is needed to elucidate this.

The use of multivariate statistical analysis for the quantification of depth profiles of binary polymer blends shows much promise. However, all measurements should ideally be made under the same, and more importantly, stable measurement conditions. Furthermore, although the choice for MDMO-PPV and d5-PCBM for the first test was made from the point of view that these molecules have a very different hydrogen to carbon ratio, which was expected to be important for the quality of the separation by the multivariate statistical analysis, this may be less important than choosing two polymers or organic compounds that have more or less identical solubility, to check for a linear relationship between the composition of the blend in solution and the composition of the blend in the depth profiled layer.
Het is belangrijk om te weten hoe elementen verdeeld zijn over de diepte van lagen materiaal om de materiële en fysische eigenschappen van die lagen te begrijpen. Afwijkingen van de bulk samenstelling zijn vaak aan de grenslagen te vinden. Het materiaal aan deze grenslagen kan geoxideerd of vervuild zijn. Er kan materiaal over de grenslagen heen zijn gediffundeerd, wat een positief of negatief effect kan betekenen, afhankelijk van de toepassing.

Een techniek die in staat is de element verdeling in materialen te meten tot een diepte in de ordegrootte van micrometers is secundair ion massa spectrometrie (SIMS). Met SIMS is het mogelijk om grenslaag reacties, diffusie en segregatie processen te bestuderen met een diepteresolutie die in gunstige gevallen slechts enkele nanometers bedraagt. Het sputter proces dat plaats vindt tijdens de metingen kan echter de originele distributie veranderen, zodat een vertekend diepteprofiel gemeten wordt. Zo kunnen tijdens de periode waarin nog evenwicht bereikt moet worden in het sputter proces de secundaire ion intensiteiten snel veranderen, wat resulteert in een onbetrouwbare meting. Atommenging veroorzaakt verder een redistributie van elementen vanuit de originele laag naar nabijgelegen lagen. Het sputter proces kan ook de oppervlakteruwheid veranderen zodat de diepte resolutie verslechtert.

Bij toepassingen waar de verdeling in de oppervlakte regio het belangrijkste is, vormt de eerste sputterfase een serieus probleem omdat precies in de tijd waarin evenwicht bereikt wordt de meeste informatie gemeten zou moeten worden. Als voorbeeld hiervoor werd een systeem gekozen waarin een gradiënt vlakbij het oppervlak zou moeten bestaan. Om dit te controleren werd de fluor gradiënt in een gemodificeerde epoxy-amine laag eerst gemeten door middel van röntgen photo-electronen microscopie (XPS). Deze metingen toonden aan dat een fluor bevattend oppervlak actieve stof het oppervlak van de polymeer laag verzadigde voordat de laag gehard werd.
Hoekafhankelijke XPS metingen toonden een hoge verrijking van het oppervlak met deze oppervlakte actieve stof.

Diepteprofiëring door middel van dynamische SIMS bleek inderdaad problematisch vanwege de eerste sputter fase, omdat het diepteprofiel ernstig verstoord bleek. Een polystyreen opofferingslaag werd daarna gebruikt om dit probleem te omzeilen. De eerste sputter fase werd hierdoor verschoven van het te onderzoeken oppervlak naar de opofferingslaag. Het bleek echter problematisch deze laag direct op de te onderzoeken laag aan te brengen vanwege de oppervlakte actieve eigenschap van deze laag. Een procedure om de opofferingslaag indirect aan te brengen werd daarom gebruikt en besproken.

De beste diepteresolutie volgens de IUPAC definitie die met deze methode bereikt werd was ongeveer 4,9 nanometer. Aangetoond werd dat deze afhankelijk was van de versnelspanning van de toegepaste ionenbron, vanwege atoommenging. De met SIMS gemeten hoeveelheid fluor in de toplaag bleek te verschillen van de hoek afhankelijke XPS resultaten, waarschijnlijk vanwege de invloed van de matrix effecten op de secundaire ionen intensiteit en atoommenging. Het voordeel van het gebruik van een opofferingslaag werd in ieder geval overtuigend aangetoond.

In toepassingen die uit verschillende lagen van metalen, organische en anorganische materialen bestaan, zoals organische licht voortbrengende schermen, is de interactie en de diffusie tussen de verschillende lagen van belang vanwege eventuele stabiliteitsproblemen op de langere termijn. De analyse van deze systemen brengt enkele unieke problemen met zich mee. Het verschil in de sputtersnelheid tussen de lagen compliceert de conversie van tijdschaal naar diepteschaal bijvoorbeeld behoorlijk. Deze conversie was echter wel mogelijk door voor iedere laag een uniek secundair ion te kiezen, de “fractie” van iedere laag in elk meetpunt uit te rekenen en een lineair verbandoen te nemen van de bijdrage aan de totale sputtersnelheid met deze fractie. Verkorting kan deze kalibratie vertekenen, maar echter alleen in de laag waarin dit gebeurt, en niet daarbuiten.

Een ander probleem was de ruwheid veroorzaakt door het sputter proces, welke de verkregen diepteprofielen serieus vertekende. Deze vertekening werd gedeeltelijk opgeheven door deconvolutie van het gemeten signaal door middel van het MRI model (mixen-ruwheid-informatiediepte), hoewel aangetoond werd dat de ruwheid van de sputter krater beter was te gebruiken voor de MRI parameter s dan de vóór de SIMS meting verkregen atoom kracht microscopie (AFM) waarden voor de grenslaag en oppervlakte ruwhenen. Om verlies van diepteresolutie door preferent sputteren in een poly-kristallijne aluminium laag te voorkomen werd dezelfde multilaag ook gemeten van de andere kant, wat resulteerde in een veel betere diepte resolutie.
Hoewel het MRI model ook kan worden toegepast op multilaag systemen indien de grenslaag ruwheiten bekend zijn door middel van AFM metingen, bleek dat het gebruik van een enkele waarde voor de ruwheid een oversimplificatie voor deze lagen vanwege de voortdurende veranderingen in sputter snelheden tijdens het sputteren. Door het meten van krater bodem ruwheiten met AFM kan een ruwheids profiel verkregen worden, en door middel van interpolatie kan dan voor iedere diepte een diepte resolutie functie berekend worden. De ruwheid veroorzaakt door het sputterproces is echter zodanig dat het te verwachten resultaat de tijd en moeite die hierin gestoken zouden moeten worden waarschijnlijk niet waard zijn. Verder heeft het gebruikte computer programma COMPRO 6 deze functionaliteit niet en deze optie zou eerst daaraan moeten worden toegevoegd. Een veel simpelere methode is trouwens het gebruik van monster rotatie.

Wanneer grenslaag reacties zonder verdere diffusie bestudeerd moeten worden, dan is het belangrijk om de metingen aan de grenslaag te verrichten zonder perturbatie door de meettechniek. Omdat grenslagen meestal met een dikke laag bedekt zijn, die voor de meting moeten worden verwijderd, is dit echter niet altijd even eenvoudig. Door de grenslaag te simuleren door slechts een zeer dun laagje te deponeren bij het maken van de grenslaag kan de grenslaag wel bestudeerd worden met statische SIMS en XPS.

De invloed van op PPV gedeponederd calcium en toegevoegd zuurstof werd bestudeerd met deze methode. XPS metingen toonden een reductie van PPV aan, met het verlies van de PPV zijketens. De aanwezigheid van zuurstof had hier niet veel invloed op, maar de aanwezigheid van water des te meer. Dit moet dus vermeden worden tijdens de productie van het contact tussen PPV en calcium in LED productie, ook vanwege de formatie van Ca(OH)₂. Dit is een sterke base die wellicht een rol speelt in het degradatie mechanisme, welke nog niet helemaal begrepen is. Statische SIMS metingen toonden aan dat calcium en het polymer een grote interactie vertonen, hoewel niet duidelijk was of het een covalente binding betrof, dan wel een ionische interactie (wat op doping zou wijzen).

Een ander geval waarin een grenslaag werd gesimuleerd was de studie van een mogelijke dissociatie reactie van LiF op PPV, geïnduceerd door een aluminium toplaag, waarin AlF₃ gevormd zou worden. Met statische SIMS en XPS werd aangetoond dat deze reactie niet plaatsvindt. Ook werd er geen bewijs gevonden voor een andere dissociatie reactie, zoals geconcludeerd kan worden uit de detectie van LiₙFₙ₋₁⁺ ionen. Dit betekent dat doping van de organische laag door Li zoals voorgesteld door verschillende auteurs niet aannemelijk is als mechanisme voor de verbetering van de elektroneninjec-tie in de polymeerlaag.

Er was echter wel bewijs gevonden voor een andere reactie aan de grens-laag. Hoewel MDMO-PPV onverschillig leek te zijn ten opzichte van de
depositie van aluminium door middel van opdamping, gaven XPS metingen aan dat er een reactie plaats vond tussen aluminium en PCBM bij de carboxyl groep in het PCBM, vanwege een verschuiving van de O 1s carboxylische zuurstof piek na opdamping van aluminium. Het aanbrengen van een zeer dunne laag LiF voor het opdampen van aluminium was voldoende om deze verschuiving te voorkomen. Dit bewijst dat LiF het onderliggende PCBM beschermd tegen een reactie met de aluminium atomen.

Het simuleren van een grenslaag blijkt een valide en waardevolle manier te zijn om grenslaag reacties te bestuderen, vooral indien statische SIMS en XPS gecombineerd toegepast worden. Deze grenslagen zijn echter uiterst gevoelig en getracht moet dan ook worden alle externe invloeden te vermijden.

Het meten van een SIMS diepteprofiel van een binair mengsel van twee polymeren is problematisch, omdat de meeste polymeren gelijksoortige massa spectra opleveren, en mogelijke karakteristieke secundaire ionen bijna altijd niet stabiel zijn gedurende het sputteren. Een test met elf veelgebruikte polymeren toonde echter aan dat het mogelijk is om onderscheid te maken tussen polymeren door de intensiteiten van niet-specifieke secundaire ionen te analyseren met multivariabele statistische methoden zoals canonical discriminant analysis en principal components analysis (PCA), nadat een evenwicht bereikt is in de interactie tussen de primaire ionen en het bestudeerde polymer.

Bij het toepassen van beide methoden op diepteprofielen van een binair organisch mengsel, namelijk d5-PCBM:MDMO-PPV mengsels, konden beide methoden succesvol alle variatie in de signalen samenvatten in slechts de eerste twee functies. Een lineair verband werd aangetoond met canonical discriminant analysis tussen de compositie van het mengsel in oplossing en de compositie van de laag, zodat quantificatie over de laag mogelijk was. De intensiteiten van de secundaire ionen waren echter nog niet stabiel in de eerste sputter fase, i.e. de eerste 10 nanometer van de meting, zodat deze meetpunten verkeerde coördinaten werden toegewezen tijdens de PCA analyses. Deze punten werden dus genegeerd in de discussie. Eerst zal de betrouwbaarheid van de met PCA berekende quantificatie voor deze punten moeten worden aangetoond. Hoekafhankelijke XPS zou hierbij behulpzaam moeten zijn, vanwege de compatibiliteit van de informatie diepte van XPS met het diepe interval van de eerste sputter fase.

De rest van het gequantificeerde diepteprofiel vertoonde een omgekeerd verband met het diepteprofiel verkregen door het volgen van het deuterium signaal. Een mogelijke verklaring kan zijn dat het enkele D signaal beïnvloed kan zijn door sputter en matrix effecten, die mogelijkerwijs een kleinere rol spelen in de gequantificeerde diepteprofielen. Meer onderzoek is ook hiervoor gewenst.
Het gebruik van multivariabele statistische analyse voor de quantificatie van diepteprofielen van binaire polymer mengsels lijkt een waardevolle toevoeging te zijn aan de huidige meetmethoden. De invloed van andere meetcondities zijn echter niet uitgeprobeerd. Het zal waarschijnlijk het beste zijn de meetcondities stabiel te houden voor alle metingen gebruikt in dezelfde multivariabele statistische analyse. Hoewel de keuze voor MDMO-PPV en PCBM voor de eerste test gemaakt werd vanuit het oogpunt dat deze moleculen een zeer verschillende waterstof-koolstof verhouding hebben, waarvan verwacht werd dat dit belangrijk zou zijn voor de kwaliteit van de scheiding door de multivariabele statistische analyse, kan dit wellicht minder belangrijk zijn dan de keuze voor twee polymeren of organische stoffen die dezelfde oplosbaarheid hebben, omdat er dan waarschijnlijk een beter lineair verband bestaat tussen de compositie van het mengsel in oplossing en de compositie van de daarna geproduceerde laag.
List of publications

Characterization of polymer solar cells by TOF-SIMS depth profiling

Photoinduced electron transfer and photovoltaic response of a MDMO-PPV:TiO2 bulk-heterojunction

Surface studies of partially fluorinated polymethacrylates: a combined XPS and LEIS analysis

The interfaces of poly(p-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF studied by secondary ion mass spectroscopy and x-ray photoelectron spectroscopy: Formation of AlF3 disproved
Calcium induced oxidation of PPV studied with X-ray photoelectron spectroscopy and secondary ion mass spectrometry


Alumina-Supported Cu-Ag Catalysts for Ammonia Oxidation to Nitrogen at Low Temperature


Applications in catalysis of ToF-SIMS surface analysis by mass spectrometry


Surface studies of partially fluorinated polymethacrylates by XPS and LEIS: the outermost atomic layer of polymer films


Low surface energy polymeric films from partially fluorinated photocurable solventless liquid oligoesters


Bonding of Supported Chromium during Thermal Activation of the CrOx/SiO2 (Phillips) Ethylene Polymerization Catalyst

Surface modification of epoxy films by crosslinkable fluorinated surfactants


Reactions between NO and CO on rhodium (111): an elementary step approach


Ordening & Orientatie van 4T: een studie naar de ordening en orientatie van organische moleculen op verschillende substraten, Si(100) en SiOx/Si(100)

Dankwoord

Ultra hoog vacuüm apparatuur gaat vaak kapot, en meestal als je wilt gaan meten. Mijn geliefde VG Ionex machine vertoonde die eigenschap helaas ook, en zonder goed functionerende apparatuur is een promotie onmogelijk. Het lijkt mij dan ook passend om onorthodox te beginnen met de vele mensen die geholpen hebben bij het draaiend krijgen en de pogingen tot het draaiend houden van de VG Ionex opstelling. Tiny, bedankt voor de spilfunc-tie binnen onze vakgroep. Zonder jou zaten de meeste AIO's hier met hun duimen te draaien. Jan en Paul van de GTD, bedankt dat jullie zo vaak meteen zijn komen opdraven om weer eens een aansturingkast door te meten. Zo hebben jullie er fouten uit gehaald die wij nog niet eens hadden opgemerkt. Ook Theo van de CTD bedankt voor het in elkaar zetten van de MIG 102, hij heeft het nog nooit zo lang gedaan als na jouw operatie. Ook Jurgen bedankt, ik hoop dat dat ook voor jouw operatie zal blijken. Bruce McIntyre, thanks for the crunching operation on the MIG 102 ion source. I never knew you could compress ceramic in such a way (and I still don’t want to try). Terry Wilson, bedankt voor de moeite die je voor ons gedaan hebt om informatie en onderdelen te bemachtigen. Na jouw vertrek hebben we je nog behoorlijk gemist. To the guys at VG: Thanks for the help with the ion gun as well, and the fixing of the software conversion problem. However, it might be practical to put your clients name on the outgoing packages from now on, instead of just the address of the university. Considering the number of people working here the change of any package arriving to the right person is close to nil.

Hans, je hebt ooit gezegd dat de promotor niet in het dankwoord hoort, aangezien het begeleiden van de AIO tot zijn werkzaamheden behoort. Met die redenering was ik zo klaar met dit dankwoord. Dus wil ik je toch bij deze bedanken voor de losse en prettige manier van overleg. Ook qua presentatietechnieken heb ik veel van je geleerd. Peter, bedankt voor het bij tijd en wijle kritisch doornemen van mijn resultaten.
Tijdens mijn periode als promovendus heb ik samengewerkt met een aantal personen. Het begon al even geleden met de fluorcoatings van Robert van de Grampel. Robert, het heeft lang geduurd voordat we ons project konden afronden, maar de uiteindelijke resultaten mogen er volgens mij wel zijn. Bedankt voor de soepele samenwerking. Ook dank aan beide afstudeerders van Robert, Ben Wassing en Frans van der Velde, voor de vele uren coatings bakken. Rob van der Linde en Jos Laven, bedankt voor de waardevolle discussies die we in de loop der tijd gehad hebben. Weihua Ming, or Marshal for short, thanks for the infectious enthusiasm and patience from your side.

Een project dat een nieuwe insteek gaf aan mijn promotie was het onderzoek aan Ca-PPV interfaces met Gunther Andersson. Gunther, immer hast du Niederländisch mit mir geredet, jetzt bin ich daran einmal etwas zu schreiben in Deutsch. Gunther, danke für die gemütliche Zusammenarbeit, und ich hoffe dich hier noch einmal zu sehen.


122
eens te werken (je voorganger weet er meer van). Armando, good luck in the States. Stay off the burgers, though.

Twee studenten hebben mij onder andere meegeholpen de karakteristieken van de VG Ionex opstelling door te meten. Carlos was hiervan de eerste. Helaas kan ik hem door zijn tragische overlijden kort na het volbrengen van zijn research stage niet meer bedanken. Eén minuut stilte kan ik hier niet houden, dus bij deze maar een regel wit:

Jules, bedankt voor je hulp bij het meten, het heeft mijn kennis van het Limburgs ook weer danig opgefrist.

Enkele mensen wil ik graag bedanken voor hun belangeloze inzet bij het meten van (onder andere) mijn samples met AFM en SEM, en wel Joachim, Daan, Eero en Pascal. De leden van de AIO commissie worden bedankt voor hun inzet en ideeën. Hopelijk wordt ons opzetje een succes.

Matti, kiitos revontulikuvasta kanttani varten. Toivottavasti lopputulos kelpaa.


Mijn ouders en zus, John, Marijke en Esther, bedankt voor jullie ondersteuning en interesse op afstand (Frankrijk, Peru) en de geboden mogelijkheid zo nu en dan naar Frankrijk te ontsnappen. Als voorlaatste bedank ik Angelica, mijn vriendin, niet in het minst vanwege het feit dat ze daadwerkelijk heeft meegeholpen aan dit proefschrift door de opmaak te verzorgen. Angelica, estas como un tren.

Als laatste mijn excuses aan diegenen die ik in dit dankwoord vergeten ben en die vinden dat ze er eigenlijk bij hadden moeten staan. Het zij zo, bij deze zijn jullie ook bedankt.
Curriculum Vitae