Introduction
Organic thin films are increasingly employed in advanced and innovative products, such as medical devices, organic electronics, optical devices and packaging materials. In these areas it can be of critical importance to understand the distribution of molecular components as a function of depth into the material. Since the materials often consist of layers with thicknesses of the order of nanometres, the determination of depth distributions is a significant analytical challenge. Additionally, there is an ongoing need to find better ways to understand and visualise the three-dimensional distribution of components in biological systems. All these molecular materials present severe constraints on the methods that may be used. The fact that the components are composed of the same elements means that elemental detection methods lack the requisite selectivity to distinguish different components. Organic compounds are also prone to change upon exposure to ionising radiation and therefore lose their structural identity. Over the last ten years outstanding advances have been made in applying SIMS to these problems and molecular depth profiling is now on the cusp of becoming a recognised analytical method. In this chapter, these exciting developments will be described, including a perspective of recent innovations and the future direction of this evolving application of SIMS. Firstly, it is instructive to briefly describe the use of SIMS in depth profiling and provide an historical perspective on the application of this technique to organic materials.

Secondary ion mass spectrometry relies upon the sputtering of fragments from a sample following the impact of energetic primary ions. For the purpose of surface analysis the dose of primary ions is minimised to ensure that the fragments generated arise from areas of the surface that have experienced no alteration due to previous impacts. The fact that the surface
layer is removed from the sample implies that, in an extended SIMS experiment, information may be obtained from the exposed subsurface of the material being analysed. By monitoring changes in secondary ion intensities as a function of the ion dose it is therefore possible to obtain information on sample chemistry as a function of depth. This represents one of the major applications of the SIMS technique and is termed dynamic SIMS. The approach has been extensively used to analyse thin films of inorganic materials, where the elemental composition and thickness of layers are of critical importance. The utility of SIMS for this purpose over many other methods is the ability to identify chemical species with high sensitivity and specificity. In the major application area of semiconductors, reference materials and standard methods have enabled the technique to be employed in a quantitative manner and it is now in routine use as an analytical method. The maturity of traditional dynamic SIMS has proven helpful for the rapid development of molecular depth profiling because many of the issues encountered are common.

Prior to the start of this century, the application of dynamic SIMS to organic materials was primarily limited to systems in which a unique element or isotope could be detected from the components of interest. In some cases these requirements can be met and there have been a number of studies which employ isotopically labelled polymers to examine the structures of blends. Deuterium labelling is often used due to the applicability of other techniques, such as neutron reflectometry, forward recoil elastic scattering and nuclear reaction analysis, which provide complementary information. These studies have provided useful information in the development of blends that exhibit desirable structural features, in particular interfacial segregation and self-stratification which could, for example, simplify the manufacture of polymer electronic devices. Despite these successes, the applicability of this approach to most organic materials is limited since there is no ability to detect unlabelled species or identify unknown organic components. To do this, one requires a means of detecting intact molecular species from a sample which has received a dose of ions well in excess of the static limit, this constitutes ‘molecular’ or ‘organic’ depth profiling.

The first serious attempts to investigate the limitations of SIMS for molecular depth profiling was described by Gillen et al in 1990. Using conventional ion sources, they noted that secondary ion signals from organic materials typically demonstrated a rapid decay with increasing primary ion dose as expected. However, after extended sputtering, the rate of decay dramatically slowed and molecular signals could be detected well beyond the static limit. Changing the mass and kinetic energy of the sputtering ion moderated these effects and
their investigations led them to conclude that molecular depth profiling could be possible if the damage depth was small in comparison to the sputtering rate. Independently, Cornett et al investigated the use of massive clusters of glycerol as a primary source for SIMS of biomolecules\(^5\). Although both the cluster source and a monatomic xenon source were capable of generating quasi-molecular secondary ions with comparable intensities at low doses, these intensities rapidly decayed when xenon was employed, but declined more slowly when the glycerol clusters were used, tending towards a constant signal. This was followed closely by the report that massive glycerol clusters were able to remove the damage previously imparted by a caesium ion beam\(^6\). In 1998, Gillen and Roberson\(^7\) reported the use of an SF\(_5^+\) cluster ion source for molecular depth profiling. They used a variety of organic materials cast as thin films onto flat substrates and showed that the sputtering source was able to completely remove a section of the film, whilst retaining significant intensity for structurally characteristic secondary ions throughout the profile. The end of the profile was observed in the analysis by the drop in intensity of these characteristic secondary ions and the rise in intensity of secondary ions characteristic of the substrate material. These remarkable results clearly indicated that cluster ion sources provided the necessary sputtering characteristics to enable the depth profiling of organic materials. The explanation for this phenomenon was linked to the higher sputtering yield and lower penetration depth of cluster ions in comparison to atomic ions with comparable kinetic energies. It was argued that the damage created from the impact is largely removed in the course of the same impact event and therefore a steady state is reached whereby damage creation and removal are balanced. This argument has stood the test of time and received support from numerous subsequent investigations.

In the decade following this work there have been major improvements and innovations in instrumentation, notably the development and commercial availability of buckminsterfullerene\(^8\) and massive gas cluster ion sources\(^9\). Understanding of the mechanisms and limitations of molecular depth profiling developed in the same period as data from detailed fundamental investigations became available. In 2009, molecular depth profiling had reached a state of sufficient maturity that an international VAMAS (Versailles project on Advanced Materials and Standards) study\(^10\) was carried out with over twenty participating laboratories, which assessed the repeatability and reproducibility of this new analytical technique. The results not only confirmed that comparable data could be obtained by the majority of participants, but resulted in a reference material against which new methods and approaches could be benchmarked.
1 Experimental considerations

In performing any depth profiling experiment, it is important to ensure that the sputtering beam current is evenly spread across the analysis area. In most modern instruments a focussed sputtering beam is rastered over an area larger than the beam diameter to ensure that a sufficiently large central area receives a constant average current of sputtering particles. If the sputtering beam current is measured and the rastered area known, then the average number of ion impacts per unit area, or ‘dose’ (see footnote A), can be straightforwardly calculated. Local variations in dose need to be minimised in a depth profiling experiment to obtain optimal depth resolution.

For a stationary sample there are two main considerations in this respect. Firstly, the width of the sputtering beam should be sufficiently large that identical doses are received both on the raster lines and at a point equidistant between two raster lines. For a Gaussian beam profile and a stationary sample, this condition is met if the full width at half maximum of the ion beam spot on the sample is twice as large as the spacing between the raster lines. Secondly, the edges of the sputtered area receive a smaller dose than the central area, therefore the analysis area should be smaller than the sputtered area. One may consider a border region at the edge of the sputtered area that should not be included in the analysis area\textsuperscript{11}. To achieve better than 1% consistency in dose for a Gaussian beam profile, this border should be larger than the full width at half maximum of the ion beam by a factor of at least 1.3.\textsuperscript{12} Note that this only relates to the sputtering dose; the width of the analysis beam, which may be the sputtering beam itself, needs to be taken into account to avoid sampling the border region.

Many instruments employ separate ion sources for sputtering and analysis. The advantage of this approach is that the two sources can be optimised for their specific roles. It is important to consider the effect of the analysis beam on the depth profile, which can influence the observed sputtering rate, depth resolution and the amount of damage imparted to the sample. A recent study has highlighted these effects\textsuperscript{13}, with a careful investigation of the depth profiling of a plasma polymer film\textsuperscript{14} indicating that the analysis beam dose should be restricted to less than 5% of the sputtering beam dose and monatomic analysis sources should be avoided in combination with cluster ion beam sputtering due to the extensive subsurface damage they impart.

As described later, there are certain advantages that accrue from performing depth profiling experiments with non-standard experimental parameters. In particular, it may be necessary to
perform experiments with samples at cryogenic temperatures, with grazing incidence angles for the sputtering beam or with sample rotation. The latter two methods present some additional considerations for obtaining a constant sputtering dose across the analysis area. At grazing angles, the beam profile on the sample is unlikely to be radially symmetrical and therefore careful consideration is required in setting the size of the analysis and sputtered areas. The simultaneous rotation of a sample under a rastered ion beam has been considered in detail\textsuperscript{15} {Fig?}, and can result in rather severe inhomogeneities in ion dose across the sputtered area especially when the rotational frequency is higher than the raster frame frequency. Ideally rotation should be performed in a stepwise fashion alternating with sputtering and analysis.

An interesting and reproducible observation is that cluster ion beam sputtering does not lead to the significant accumulation of charge on electrically insulating samples in the absence of an extraction field, especially when the material under study is known to have a large and constant sputtering yield\textsuperscript{16}. This means that the use of charge compensation using an electron flood gun is often not required. It should be noted however, that this observation depends upon the electric field applied to the sample during ion bombardment. If, for example, an extraction field is applied the surface potential reaches a self-biasing steady state provided the yield of positively charged secondary particles exceeds the charge on the primary ion. Interestingly, this observation demonstrates that the total yield of positive secondary ions obtainable under cluster ion bombardment has to be of the order of 1 (e.g. a secondary yield of at least three positive secondary ions for each C\textsubscript{60}\textsuperscript{3+} impact), a condition which is almost impossible to reach under atomic ion bombardment. The fact that a limited number of available measurements\textsuperscript{17} of total secondary ion yield have provided values significantly smaller than 1 may be due to the limited collection efficiency of time of flight analysers, especially for secondary ions with high kinetic energy and velocity components tangential to the analyser\textsuperscript{18}.

2 Sputtering yields

In depth profiling experiments data is acquired as a function of sputtering time, or equivalently, sputtering beam dose and the conversion of this into a depth is the usual aim. The conversion factor involves the sputtering yield, which provides the number of target atoms removed per incident sputtering atom or ion. This is useful for elemental solids, but a more pragmatic approach in molecular depth profiling expresses the sputtering yield, \( Y \), as a volume,

\[
Y = \frac{dD}{dF}
\]  

\( (1) \)
where $D$ is the eroded depth and $F$ is the sputtering ion dose. The depth scale is therefore straightforwardly obtained if the yield volume and its dependence on the dose, $F$, is known. Although it may be expected that sputtering yields will vary for different organic materials, it appears that under C$_{60}$\textsuperscript{\pi\textsuperscript{+}} bombardment the initial sputtering yield volumes of many organic materials are rather similar\textsuperscript{19-21} as shown in Figure 1. Furthermore, the initial sputtering yield appears to increase with impact energy in a close to linear manner. A useful estimate for the initial value ($F = 0$) of $Y$ may be found from the results of the VAMAS study carried out in 2009,\textsuperscript{11}

$$Y_{F=0} \approx 8.4E - 12.6 \quad (2)$$

where $Y$ is given in nm\textsuperscript{3} per incident ion and the sputtering particle kinetic energy, $E$, is in keV and in the range 10 to 40 keV. It is notable that SF$_5$\textsuperscript{+} also produces similar sputtering yields, for example poly(lactide)\textsuperscript{22} with SF$_5$\textsuperscript{+} [Mahoney et al Anal Chem 2004] at 5 keV has a similar yield to C$_{60}$\textsuperscript{\pi\textsuperscript{+}} at the same energy\textsuperscript{19} with $Y \approx 45$ nm\textsuperscript{3} per incident ion, which is slightly underestimated by Equation (2), and for poly(methyl methacrylate), SF$_5$\textsuperscript{+} at 8.75 keV gives $Y \approx 65$ nm\textsuperscript{3} per incident ion\textsuperscript{23}, which is only slightly larger than the estimate of Equation (2). Initial studies of argon cluster sources\textsuperscript{24, 25} indicate that, these sources also demonstrate a linear relationship between $Y$ and $E$ and the sputtering yields are similar to those provided by Equation (2).

One may expect the sputtering yield to depend upon the choice of experimental conditions such as different sample temperatures and beam incidence angle. However, it appears that these parameters do not have a strong influence. The initial sputtering yields of Irganox 1010 with 10keV C$_{60}$\textsuperscript{+} is unaffected by sample rotation ($Y \approx 80$ nm\textsuperscript{3}), as may be expected, but decreases somewhat upon cooling to temperatures below $-40$ °C ($Y \approx 60$ nm\textsuperscript{3})\textsuperscript{26}. The insensitivity of sputtering yield with incidence angle may be rather surprising because monatomic beams give a strong dependence, which approximately scales as $(\cos \theta)^f$, where $\theta$ is the angle between the surface normal and the beam direction and $f$ is usually\textsuperscript{27} between 1 and 2. Energetic monatomic ions deposit their energy at some depth into the sample and as $\theta$ increases this energy profile gets closer to the surface increasing the sputtering yield. However, cluster ions deposit their energy very close to the surface and a much weaker dependence of sputtering yield upon impact angle should be observed, with $f$ tending toward 0. Predictions from molecular dynamics models\textsuperscript{28} indicate that the maximum sputtering yield should occur at an intermediate angle of $\sim 40^\circ$ and fall off at more grazing angles due to reflection from the surface. There has only been
one comprehensive study on the effect of C$_{60}^+$ impact angle on sputtering yield$^{29}$ which indeed demonstrated a maximum yield at $\theta \approx 40^\circ$, as shown in Figure 2.

One of the most challenging aspects of the depth profiling of organic materials is finding conditions that provide a constant sputtering yield throughout the profile. Maintenance of the sputtering yield is essential if the data from a molecular depth profile is to provide useful information. It is well known that, for monatomic ions, sputtering yields can change in the early stages of a depth profile$^{30}$, this is termed the ‘transient’ region of the profile. Indeed, it is routine to use sacrificial layers to avoid these effects$^2$. The same effects have been demonstrated for organic materials under cluster ion beam bombardment by using films of a variety of thicknesses and measuring the ion dose required to remove them$^{19}$, examples are shown in Figure 3. A simple model of the dose dependent transient decrease in sputtering yield uses an exponential decay with a cross-section $a$, from an initial yield, $Y_0$, to a final yield, $Y_\infty$,

$$Y_F = Y_\infty + (Y_0 - Y_\infty) \exp(-aF)$$  \hspace{1cm} (3)

This may be integrated, by insertion into Equation (1), to provide the dose-depth relationship.

$$D_F = Y_\infty F + \frac{(Y_0 - Y_\infty)}{a} (1 - \exp(-aF))$$  \hspace{1cm} (4)

This model appears to effectively describe the transient behaviour of sputtering yield for organic materials under ion bombardment, with characteristic transient depths ($Y_0/a$) for C$_{60}^+$ sputtering ranging from ~50 nm for aluminium trishydroxyquinolate (Alq$_3$)$^{19}$ to >400 nm for Irganox 1010$^{31}$. The difference between $Y_0$ and $Y_\infty$ can be orders of magnitude and even involve a change of sign. For example, during 10 keV C$_{60}^+$ sputtering of Alq$_3$ there is a positive initial sputtering yield and a negative final sputtering yield, i.e. net deposition of carbon from the “sputtering” source occurs. For SIMS depth profiles of homogenous materials it is rather straightforward to identify changes in sputtering yield. As will be described later, the sputtering yield strongly influences the intensity of molecular secondary ions, therefore a sensitive probe of a declining sputtering yield in a pure material is provided by a decay in molecular secondary ion intensities. Guidance for assessing the quality of a depth profile using secondary ion intensities has been given by Mahoney$^{16}$, which are summarised in Figure 4.

We have not provided a mechanistic explanation of the change in sputtering yields with dose. The most obvious explanation is that accumulated chemical damage causes this effect, in particular cross-linking reactions which tend to change the organic material to an amorphous state with a sputtering yield more typical of an inorganic material. However, this explanation does not seem entirely adequate for materials that have a slow decline in sputtering yield over
depths far in excess of the penetration length of the sputtering ion. Whatever the explanation, it seems clear that the decline in sputtering yield is also associated with an increase in surface roughness\textsuperscript{31, 32} and methods which lead to a maintenance of the initial sputtering yield also result in lower roughness.

### 3 Depth resolution

Depth resolution represents the certainty to which a depth can be assigned to a detected species. The three main limitations to achieving good depth resolution are the information depth of the analytical technique, mixing induced by the sputtering process and topography\textsuperscript{33}. The microscopic insight gained from molecular dynamic simulations has been developed into a statistical model\textsuperscript{34} which elegantly combines these effects and predicts a limiting depth resolution of $\sim10$ nm for molecular depth profiles with C\textsubscript{60}\textsuperscript{9+} sputtering. The initial topography of the sample certainly contributes to the achievable depth resolution when this implies that the layers of interest are of uneven thickness. However, the development of topography by the sputtering process itself is of significant concern. The measurement of depth resolution is best achieved by using a sharp interface between two organic materials, since the interface between organic and inorganic materials presents interesting interpretational problems, which arise from the large changes in sputtering yield\textsuperscript{35}. Attempts have been made to create sharp organic interfaces using the sequential spin-coating of polymers\textsuperscript{36}, multilayered Langmuir-Blodgett films\textsuperscript{37} and vacuum sublimation\textsuperscript{19, 31}. The latter approach is a useful analogue for the production of some organic electronic devices, however the range of molecular materials that may be sublimed are somewhat restricted. Spin-coating is used to create a wide range of polymeric devices and Langmuir-Blodgett films are representative of some biological systems therefore useful and relevant reference materials can be produced by a variety of methods.

The best way to obtain a direct visualisation of the depth resolution is to create an extremely thin marker layer within a matrix material, and then the response signal from the marker layer provides a direct visualisation of the depth-resolution function at that depth, providing that the function is not rapidly changing with depth. These ‘delta-layer’ reference materials have been employed for inorganic depth profiling extensively\textsuperscript{38} and a series of sequential layers may be employed to establish the dose dependence of sputtering yield and depth resolution. Organic delta-layers have been used to show that the typical resolution obtained in C\textsubscript{60}\textsuperscript{9+} molecular depth profile is 10 nm or greater, as shown in Figure 5. This is far larger than most estimates of the information depth of SIMS and it is unlikely that mixing effects will be evident on such a
scale length, therefore it appears that topography may be a limiting factor for depth resolution in cluster ion beam sputtering. In one example, the link to roughness was made very clear by a direct comparison of the resolution function of a depth profiling experiment and topography measured by atomic force microscopy (AFM)\textsuperscript{31}. These studies clearly demonstrated that sputter-induced roughening could be a severe problem, with a rapid onset and growth such that useful (<30 nm) depth resolution is lost within the first few hundred nanometres of the surface. The development of topography has also been clearly shown during the cluster ion beam sputtering of polymers\textsuperscript{32}. It should be noted that other experiments have failed to find a correlation between observed depth resolution and surface roughness\textsuperscript{37, 39}. These observations suggest that other factors, such as mixing or the statistical nature of the sputtering process can also significantly contribute to the measured depth resolution.

It is interesting that the depth response function in organic delta layer experiments appears to be adequately modelled\textsuperscript{19, 40} by a convolution of an exponential rise and fall in intensity convoluted with a Gaussian as proposed by Dowsett\textsuperscript{41} for inorganic depth profiling, although it is not clear how the values extracted from such fitting should be interpreted. A practical expression of the depth resolution from a thin layer is the full width at half maximum (FWHM) of the response function. An extensive comparison of the initial depth resolution for C\textsubscript{60}\textsuperscript{+} sputtering at \(\sim45^\circ\) incidence angle using 3 nm Irganox 3114 layers at 50 nm depth in Irganox 1010 showed\textsuperscript{11} that the depth resolution was approximately three times the cube root of the sputtering yield, which is a useful estimate of the initial depth resolution for these experiments.

It is also possible to estimate the FWHM of the response function from the signal intensities at the boundary between two different materials. Assuming that the sputtering yield volumes of the two materials are the same, the response of the underlayer should have the shape of the integral of the normalised depth-resolution function. The response of the overlayer should have the shape of the integrated function subtracted from one. If the depth-resolution function is approximately Gaussian the FWHM can be expressed as the depth required for the substrate intensity to rise from 16% to 84% of the value of the pure material, or conversely for the overlayer signal to drop from 84% to 16%. However, if the sputtering yield is not constant, especially if it changes abruptly at the interface, this method needs to be used with extreme caution for the reasons given earlier\textsuperscript{35}.

4 Materials
From the earliest days of molecular depth profiling, it was realised that some organic materials were not amenable to sputter depth profiling. The use of cluster ion beams for this purpose relies upon sputtering yields being high enough that damage induced by previous impacts is removed. Yet it is this induced damage that is likely to cause a reduction in the sputtering yield and therefore prevent the continuation of the process. This Red Queen’s race is often lost because any decline in sputtering rate leads to a self-amplifying build up of damage. The classification of materials into those that perform well (constant sputtering yield) and those that do not has been attempted and is useful to guide the selection of experiments. However, as techniques improve, the classification of particular materials has changed and it is likely that this will continue in the next few years.

The chemistry of the organic sample is clearly one of the most important factors in determining whether it is amenable to depth profiling. Materials that undergo cross-linking reactions under irradiation will have a higher cohesive energy after ion bombardment than those which predominantly react through chain scission. Archetypal materials are, or were, poly(lactide), poly(methyl methacrylate) and poly(styrene).

Poly(lactide) is a polyester with a main chain consisting of only one carbon-carbon bond per repeat unit, the carbonyl moiety in the main chain will promote chain scission under irradiation. This material displays excellent depth profiling qualities both in pure form and in mixtures and may be profiled over depths of micrometres before failure occurs for reasons that are not yet clear. Poly(methyl methacrylate) consists of a main chain with only carbon-carbon bonds, but a side chain with a carbonyl group and is known to undergo a combination of depolymerisation and cross linking reactions. This material proves somewhat more intractable, often displaying a dose dependent decline in sputtering yield. Poly(styrene) contains no oxygen, has a carbon backbone and pendant phenyl groups, it is known to readily cross link under irradiation. It is difficult to profile with $C_{60}$ $^+$ sputtering, however low incidence angles and argon cluster sources have been shown to improve the quality of poly(styrene) depth profiles. Mahoney has provided a useful list of polymeric materials that are claimed to have been successfully depth profiled in her excellent review. It should be noted that the criteria for a successful profile are rather variable within the literature. Molecular materials that can be easily profiled include sugars, lipids, cholesterol with others such as irganox displaying characteristics similar to poly(methyl methacrylate) and some, such as Alq3 being rather awkward, like poly(styrene).
5 Parameters

The selection of experimental conditions for molecular depth profiling is no simple task, there is a large parameter space and, although it can be argued that optimal conditions may vary for particular materials, it is now becoming evident that some experimental arrangements are clearly better than others. The parameters that have been shown to have a critical influence are: choice of ion for sputtering beam; beam energy; incidence angle; sample temperature; sample rotation; background gas. In the following section these are described, where possible with data from the NPL Irganox multilayers used in the VAMAS study on organic depth profiling, as shown in Figures 5b and 6. These are currently employed as reference materials to establish the best conditions for molecular depth profiling and, although they are not representative of all materials, it is helpful to compare data from a single type of material to enable a comparison of the effects of the various parameters. The most important criteria on which to compare parameters are: the ability to detect molecular species, the constancy of sputtering yield with dose, the depth resolution and the range of materials that may be profiled. The parameters described below that improve molecular depth profiles are not mutually incompatible and there may be benefit in combining them.

5.1 Choice of ion beam

Molecular depth profiling has been attempted with many different ion sources. Atomic and diatomic sources, such as Ar⁺, Xe⁺, Cs⁺, O₂⁺ may, for some materials, provide profiles with some molecular ion intensity. For the Irganox multilayer materials non-molecular depth profiles were obtained in many instances, through the observation of fragments such as CN⁻ and CNO⁻. Interestingly, SF₅⁺ sputtering also resulted in the loss of molecular information from these materials and there was a dramatic loss of depth resolution early in the profile so that none of the marker layers could clearly be observed, except for the first (50 nm) layer and then only if the sample was cooled to −100 °C. These results add to the note of caution given above that results from one material may not be representative of other materials because SF₅⁺ usually performs better than atomic sources for molecular depth profiles. However, they also serve to highlight that Irganox is a somewhat challenging material for molecular depth profiling and is therefore useful in demonstrating improved methods.

Under normal conditions C₆₀⁷⁺ beams allow a true molecular depth profile of Irganox, although the sputtering yield slowly declines and there is significant loss of depth resolution with sputtered depth, see Figure 6. Other carbon and hydrocarbon cluster ions such as C₈⁻ and coronene, C₂₀H₁₂⁺, have not been extensively investigated but the latter, at least, does not
behave significantly differently based on XPS investigations\textsuperscript{53}. With the exception of Irganox 1010, there is little indication in the literature that C\textsubscript{60}\textsuperscript{q+} offers significant advantages over SF\textsubscript{5+} for molecular depth profiling in terms of the materials that may be profiled, although side-by-side comparisons are rare.

Large argon clusters, Ar\textsubscript{x}\textsuperscript{+}, with \(x\) typically larger than 500, appear to have considerable advantages over the smaller clusters described above. Results on Irganox reference samples\textsuperscript{24} demonstrate clearly that the sputtering yield is constant over the full depth of the material and the depth resolution is better than can be achieved with C\textsubscript{60}\textsuperscript{q+} and is maintained with depth into the material. In 2011, an extension to the initial VAMAS study was carried out using argon cluster sources and the outcome confirmed the initial expectations that depth resolutions significantly better than 10 nm could be achieved, as shown in Figure 6. Furthermore, materials that cannot easily be profiled by C\textsubscript{60}\textsuperscript{q+}, such as Alq\textsubscript{3}, provide true molecular depth profiles under large argon cluster bombardment\textsuperscript{54,55}.

It is somewhat surprising that the massive liquid clusters\textsuperscript{5}, which provided some of the initial impetus for molecular depth profiling, have not been further developed. However electrosprayed water clusters have successfully been used for the molecular depth profiling of poly(styrene)\textsuperscript{56} and further developments may be forthcoming.

\textbf{5.2 Incidence Energy}

The effect of incidence energy has been described earlier in terms of its effect on sputtering yield and depth resolution. For difficult materials, in which the useful profiling depth is limited, higher beam energies may be preferred since a greater depth is achieved before the loss of useful information. There is a consequent loss of depth resolution and, for this reason, it is preferable to use a lower kinetic energy for the sputtering species and find alternate methods to increase the useful depth of analysis. One may expect that, because the sputtering yield is higher with greater kinetic energies, there would be an increased ability to sputter difficult materials since the removal of damaged material would be faster. However, for Irganox at least\textsuperscript{31} the damage volume also increases linearly with energy. From these observations, the useful depth of profiling will be limited by the ion dose and should be proportional to the sputtering yield and consequently the beam energy, as demonstrated for poly(methyl methacrylate)\textsuperscript{57}.

\textbf{5.3 Incidence Angle}

For cluster ions, the effect of incidence angle on sputtering yield is weak. However there are substantial advantages to increasing the angle of incidence in depth profiling experiments. In
atomic ion depth profiling of inorganic materials, the improvement in depth resolution at higher incidence angles is well known\(^5\). This is certainly replicated for the cluster ion sputtering of organic materials\(^4\) and clearly shown in studies of the Irganox multilayer, see Figure 6. Molecular depth profiling of poly(styrene) and poly(carbonate) has been demonstrated using 20 keV \(\text{C}_{60}^+\) at a 76° incidence angle to a depth of several hundred nanometres\(^5\). This is in stark contrast to the performance at 48° or even at 66° in the same study. The ability to profile difficult materials simply by changing the angle of incidence can be explained by the change in the depth of energy deposition\(^2\). At low incidence angles this damage remains close to the surface and therefore is more readily removed by subsequent sputtering events. As long as there is a reasonable sputtering yield, it would appear that the higher the incidence angle, the better the profile. There are some practical issues with very high angles of incidence that relate to the ability to achieve both a significant and even dose in the analysis area and application to samples that have initial topography.

### 5.4 Sample Temperature

Several studies by Mahoney using different sample temperatures\(^3\) demonstrated that cooling polymeric samples with liquid nitrogen dramatically improved the quality of molecular depth profiles using \(\text{SF}_5^+\). Cryogenic temperatures had been used previously with a different motivation\(^6\), which was to study molecular materials in water ice and provide fundamental understanding for studies of frozen biological samples. It is abundantly clear from Mahoney’s work and from later studies\(^4\) that sample cooling extends the useful depth of profiling and maintains both the constancy of sputtering yield and depth resolution, this is shown in Figure 5b. In particular, it has been demonstrated that both Irganox1010 [Dan Mao, Caiyan Lu, Nicholas Winogran and Andreas Wucher, Anal. Chem. 2011, in press] and Langmuir-Blodgett multilayer \([37,40]\) films can be depth profiled to hundreds of nanometers depth without any loss in sputter yield and depth resolution. A possible explanation for this phenomenon, given by Mahoney\(^1\), is that the rate of cross-linking is substantially reduced at lower temperatures. However, it is not entirely clear which species are generated during the sputtering process that can penetrate into the bulk of the material and cause this accumulation of cross-links.

### 5.5 Sample Rotation

Sputter induced roughening is a problem in traditional depth profiling experiments. A simple method to reduce this effect is to rotate the sample\(^6\) so that the surface is irradiated from different azimuthal angles. This has been shown to provide substantial benefits in the \(\text{C}_{60}^+\) sputtering of Irganox\(^2\), with a nearly constant depth resolution and sputtering yield, as shown...
in Figure 6. This observation is somewhat surprising if chemical effects, such as cross-linking reactions, are responsible for the decline in sputtering yield. Sample rotation is not without practical issues. As well as the problem of establishing a constant dose across the analysed area, current implementations of the method do not allow for imaging to be combined with depth profiling. Since three-dimensional reconstruction of sample chemistry is a major goal of molecular depth profiling this issue needs to be addressed.

6 Data interpretation

Studies of model materials have enabled a general description of SIMS molecular depth profiling to be established. The phenomenological features of a molecular depth profile are given in Figure 4: (i) the transient region in which chemical damage is imparted to the initially undamaged surface and a rapid decline in molecular secondary ion intensities is usually observed; (ii) a steady state, or 'quasi steady state' region in which a balance has been set up between damage accumulation and removal and the only changes are those associated with a decline in sputtering yield; and (iii) a change in intensity associated with reaching an interface, as outlined previously.

6.1 The transient region

Wucher\textsuperscript{47} provided an erosion model by which molecular secondary ion intensities in the transient region of a pure material can be described. This model is based upon the assumptions that the sputtering yield is constant and that there exists a surface ‘altered’ layer of well-defined thickness with a well-defined concentration of molecules that is different to the bulk of the material. The concentration of molecules in the altered layer is determined by a balance between the resupply of molecules from the bulk due to the receding surface, the damage induced to molecules in the altered layer by the sputtering beam and the removal of both intact and damaged species by sputtering. The important parameters are: the sputtering yield, $Y$; the concentration of molecules in the pure material, $c_b$; the damage cross-section for molecules within the altered layer, $\sigma_d$; and the depth of the altered layer, $d$. The evolution of the concentration of intact molecules in the altered layer, $c_s$, is described as a function of sputtering ion dose, $F$, by Equation (5).

$$\frac{dc_s}{dF} = \frac{Y c_b}{d} - \frac{Y c_s}{d} - \sigma_d c_s$$

One may then define an effective ‘disappearance cross-section’, $\sigma_{\text{eff}}$. 
and a steady state concentration of intact molecules in the altered layer, \( c_{SS} \), obtained by setting Equation (5) to be equal to zero.

\[
c_{SS} = \frac{Y c_b}{d \sigma_D + Y} \tag{7}
\]

To model secondary ion intensities a further assumption must be made that the partial secondary ion yield of molecular ions is proportional to the concentration of intact molecules in the altered layer and there is no contribution to this secondary ion signal from damaged species. The descriptive equation of the transient behaviour of molecular secondary ion intensity, \( I \), is then provided by Equation (8).

\[
I_F = I_{SS} + (I_0 - I_{SS}) \exp(-\sigma_{eff} F) \tag{8}
\]

where \( I_0 \) represents the initial and \( I_{SS} \) the steady state molecular secondary ion intensity. Their relationship to the parameters from the erosion model may be found by the direct replacement of \( I \) for \( c \) in Equation (7).

\[
\frac{I_{SS}}{I_0} = \frac{Y}{d \sigma_D + Y} \tag{9}
\]

Equation (8) provides an excellent description of the decline in molecular secondary ion intensities in the transient region for a wide range of molecular materials\(^{31, 47, 64}\), examples are given in Figure 7.

In some cases it has been noted that there is a rapid initial rise in molecular secondary ion intensity \( \{Fig\} \) that has been attributed to either perturbations associated with the incident ion beam or to the removal of surface contaminants\(^{47}\). The presence of thin overlayers with a different composition to the bulk have been shown to exhibit this effect\(^{44}\), however charge redistribution or bombardment induced chemical reactions at the irradiated surface may be responsible for the phenomenon in some cases. As an example, it has been suggested that \( C_{60}^{+} \) irradiation may lead to a liberation and accumulation of free protons which may then enhance the probability of generating protonated molecular secondary ions\(^{65-67}\). A comparison of SIMS and SNMS molecular depth profiling of guanine provides strong evidence that of such a bombardment induced transient in ionisation probability\(^{64}\). Since these effects on the secondary ion signal are usually more rapid than the changes characterised by \( \sigma_{eff} \), the erosion model may still be applied with suitable corrections.
The application of the Equation (8) to fragmented secondary ions should by treated with caution since it is likely that damaged material may also contribute to their intensity. Therefore, it is unlikely that this scheme will be valid for polymeric materials without some modification. It is has been shown that certain secondary ions from polymers increase in intensity during the transient, an example is C\textsubscript{3}H\textsubscript{5}O\textsuperscript{+} from pure poly(lactide) during C\textsubscript{60}\textsuperscript{+} sputtering. A detailed model to account for fragmentation has recently been developed [A. Wucher in "Cluster Secondary Ion Mass Spectrometry: Advances and Applications", ed. Ch. M. Mahoney, to be published by Wiley, 2011].

The assumption of a constant sputtering yield within the erosion model is entirely justified in many cases. Experience shows that the damage accumulation described in this model is at least one order of magnitude faster than changes in sputtering yield and in the case of Irganox 1010, there are two orders of magnitude difference in the rapidity of these processes.

6.2 The steady state region

For pure materials with a constant sputtering yield this region of the depth profile is rather uneventful. The steady state secondary ion intensities do not change unless there is a change in sputtering yield. For polymeric materials where series of fragment secondary ions which contain multiple repeat units can be observed it is possible to establish the degree of damage induced by the sputtering process. This has been demonstrated for the (nM-O)\textsuperscript{+} series from poly(lactide) with \(n = 1\) to 4 under C\textsubscript{60}\textsuperscript{+} bombardment, see Figure 8. These secondary ions demonstrate transient effects similar to molecular species and therefore it is reasonable to assume that the ratio of their steady state to initial intensities is representative of the fraction of intact precursor units at the sputtered surface. If the probability of finding an intact repeat unit at the surface is \(P\), and all repeat units are identical, the intensity ratios should follow Equation (10).

\[
\frac{I_{\text{SS},n}}{I_{0,n}} = P^n
\]  

(10)

The data for poly(lactide) were best fit with the \(P = 0.7\), indicating that 30% of the monomer units are damaged in the steady state. This is not inconsistent with Equation (9), since \(\sigma_0\) and, possibly, \(d\) will be a function of molecular (or precursor) size. During the development of molecular depth profiling, the main interpretational problem in the steady state region has been the effect of the decline in sputtering yield. In this case, a true steady state is not reached and the region beyond the transient is best termed a “quasi
steady state’. A detailed consideration of these effects for pure molecular materials has been provided\(^69\). The approach used to model the behaviour is to insert a functional form for the dose-dependent yield, \(Y_F\), into Equation (5) and solve it. In the case of the validated behaviour of \(Y_F\) shown in Equation (3) this must be done numerically. An alternative approach is to recognise that, for depth profiles which contain useful information, transient behaviour is far more rapid than changes in sputtering yield, i.e. \(\sigma_{\text{eff}} \gg a\). In this case it is possible to use the steady state approximation where the fluence-dependent concentration of intact molecules at the surface is provided by Equation (7) by direct insertion of \(Y_F\), as suggested earlier\(^31\).

Molecular secondary ion intensities are affected not only by the concentration of intact molecules, but also by the partial secondary ion yield. This, in turn, is expected to be strongly dependent upon the sputtering yield. Seah\(^70\) demonstrated that, within the SIMS regime, the partial secondary ion yield of the (M-H)\(^-\) molecular secondary ion of Irganox 1010 is proportional to the square of the total negative secondary ion yield and therefore, one may assume to the square of the sputtering yield volume, \(Y\). This may not be true for all materials and it is safest to proceed by assuming that, within a particular experiment, the partial sputtering yield of a molecular ion is proportional to \(Y^\alpha\), where \(\alpha\) may be 1, 2 or some other number\(^31, 69\). Neglecting the possibility of matrix effects from the altered surface, the quasi steady state molecular secondary ion intensity, \(I_{\text{QSS}}\), can then be expressed as the product of the partial secondary ion yield and the surface concentration of intact molecules, leading to Equation (11).

\[
\frac{I_{\text{QSS}}}{I_0} = \frac{1}{Y_0^\alpha} \frac{Y_F^{(\alpha+1)}}{d\sigma_B + Y_F}
\]

Equations of this form have been shown to adequately describe molecular depth profiles of pure materials that display an inconstant sputtering yield. Inversion of the relationship to enable a characterisation of the change in sputtering yield using secondary ion intensities has not been performed, presumably due to the uncertainty surrounding the value of \(\alpha\). This may be useful in practical applications, to provide a linear depth scale in situations were no independent determination of sputtering yield behaviour is possible.

**6.3 Mixed materials**

Fundamental understanding the behaviour of mixed materials is critical to the application of molecular depth profiling to real systems. The goal of a molecular depth profile experiment is to establish the in-depth composition and thickness of the material. Studies of idealised
binary mixtures are the first step in providing this understanding. There are several concerns regarding the behaviour of mixed materials in molecular depth profiling, the most critical being changes in the sputtering yield and the possibility of preferential sputtering of the components. Another concern, which is less tractable, is the matrix effect which affects the ability of SIMS to provide quantitative concentration information in a straightforward manner. This can be rather extreme for molecular secondary ions\textsuperscript{71} to the extent that one of the components may be effectively invisible to SIMS.

There are only a few studies of the effect of composition on sputtering yield. Mahoney \textit{et al} examined binary blends of PLA with Pluronic P104 (a triblock copolymer of polyethyleneoxide – polypropyleneoxide – polyethyleneoxide) with SF\textsubscript{5}\textsuperscript{+} sputtering\textsuperscript{43}. P104 was the minority component, with up to 25% by mass, see Figure 9. They demonstrated that the blends had the same sputtering yield as pure PLA, even though pure P104 had a six times lower average sputtering yield. Similarly, a study of codeine as a minority component of up to 28.6\% by mass in PLA with C\textsubscript{60}\textsuperscript{+} sputtering demonstrated no significant change in sputtering yield with composition\textsuperscript{44}. Inclusion of 4-acetamidophenol in PLA resulted in a decline in sputtering yield as the composition of the minority component increased to 20\% or more\textsuperscript{22}, and the inclusion of peptide into trehalose to a mole fraction of as little as 1\% reduces the sputtering yield by more than 10\%\textsuperscript{47}. Therefore, while there is a reasonable indication that if the majority component behaves well in molecular depth profiling then the mixture will have a sputtering yield similar to that component, this is not true in all cases. If the two components are not mixed, then the minority component can dramatically affect the sputtering yield in regions where it is in high concentration, as exemplified by thin layers of Alq\textsubscript{3} in Irganox 1010\textsuperscript{19}.

Analysis of the transient region in blends is complicated by the near certainty of surface segregation of one of the components. This can result in rather complicated features\textsuperscript{43}, demonstrated in Figure 9, where the effects of damage described by the erosion model are convoluted with a rapidly changing composition. The intensities of characteristic secondary ions from each component, calibrated to the known bulk concentrations and steady state intensity ratios, were used to extract compositions throughout the transient. There is some danger in using this method that the ions chosen have different transient behaviours in terms of damage accumulation (see e.g. Equation 10). Conversely, analysis of the transient behaviour of mixtures under the assumption of no surface segregation may lead to erroneous conclusions regarding damage cross-sections or preferential sputtering. Where the near-
surface compositional changes can be determined by other methods, such as XPS, these effects can be accounted for. A knowledge, or description, of erosion model parameters for components could enable a more confident analysis of compositional changes in the near surface by SIMS, but the general method for this has not yet been developed.

Within the steady state region, it seems clear that secondary ion intensities can be related directly to the composition of a binary blend. As with static SIMS, secondary ion intensities in depth profiles are strongly affected by matrix effects for which a complete and validated description is still absent. Addition of a third component may complicate the situation dramatically. For example, the admixture of sodium chloride at 1% by mass to a mixture of peptide in trehalose results in an order of magnitude reduction in the steady state intensities of both the trehalose and peptide molecular ions. The diminution in secondary ion intensity for these molecular secondary ions was counterbalanced by the appearance of sodium adducts of the molecules in the secondary ion spectra. In the case of trehalose, these were more intense than the original molecular secondary ions, but for the peptide they were rather weak. The strength of such effects on secondary ion intensities means that quantification of the amount of material can only be carried out in cases were adequate reference materials of known composition are available.

**Conclusions and outlook**

The development of molecular depth profiling over the first decade of the twenty first century has been rapid. In the last edition of this book, the possibility of performing molecular depth profiles was a brief note in a larger chapter on polyatomic ion beams. Since then, there have been major developments both in the instrumentation and in the understanding of this new modality of SIMS. This chapter does not pretend to be a comprehensive list of all the molecular depth profiling experiments in the literature. Rather it is a summary of works that deal with the fundamental aspects of the technique and encapsulates the main findings of these. We have not covered the large body of work on the applications of molecular depth profiling to drug delivery devices, biological specimens and organic electronic devices. Neither have we described the steps required to combine depth profiling with 2D SIMS imaging to produce 3D reconstructions, although such methods are reliant upon the understanding described here. We have shown that a judicious choice of experimental conditions is often sufficient to enable a successful molecular depth profile and the critical considerations are the choice of sputtering source, angle of incidence, sample temperature and sample rotation. With our current state of
knowledge, the best conditions appear to be given by one or more of the following: argon cluster ion beams, grazing angles of incidence, as low a temperature as is feasible and rotation of the sample. The benefits of combining these have not yet been explored thoroughly and may not lead to significant improvements. The problems of poor depth resolution and inconstant sputtering yields that beset the early days of molecular depth profiling are starting to become the exception rather than the rule. Although there are still materials that remain a challenge and issues with transitions between organic and inorganic materials in a depth profile, there is no reason to suppose that these cannot be overcome.

The erosion model\textsuperscript{47} and description of sputtering yield behaviour\textsuperscript{19} have provided substantial insight into the mechanism of molecular depth profiling of pure materials. There are strong indications that these models can be developed to accommodate polymeric materials, fragment secondary ions and mixed materials. These developments are necessary for a proper understanding of molecular depth profiles of real systems. For relatively simple systems which comprise only a few components, such as organic electronic devices, optical coatings and drug delivery systems, there is adequate evidence that molecular depth profiling can already provide useful data on layer thickness, interface quality, intermixing and phase separation. These are issues of critical importance to high value, innovative industries and it is clear that the technique should already be able to make a substantial impact in product development and failure analysis for these industries.

Application of molecular depth profiling to massively multicomponent systems with high spatial variability in concentration is a remaining challenge. 3D imaging of biological systems falls into this category. The substantive issue that requires attention in the future is to understand the factors that affect the production of molecular ions in mixed materials and therefore to find mitigations for the matrix effect in SIMS. Without these developments, molecular depth profiling with SIMS can only be used for the identification of components in a depth profile or 3D reconstruction, with no certainty that all of the components are detected or that the intensities can be considered indicative of the concentrations. It is also of paramount importance to increase the ability of SIMS to distinguish different, but structurally similar, materials such as proteins through, for example, extending the mass range or increasing the mass resolution of the technique. With these developments, molecular depth profiling can be envisaged as an extremely useful tool for the nanoscale analysis of biological material, especially for problems where the traditional optical methods are inapplicable.
Footnotes

A. In the SIMS literature, there are two common conventions employed to describe the current density of particles impacting upon a surface. In one convention, the areic dose, often abbreviated to ‘dose’, represents the number of particles that have impacted a unit area of a flat surface. The sputtering beam current per unit area of the sample is the dose per unit time and may be described as the ‘dose rate’. A second convention employs the terms ‘fluence’ and ‘flux’ (i.e. fluence rate) apparently as substitute terms for ‘dose’ and ‘dose rate’. This may lead to confusion because, according to IUPAC, irradiative fluence and flux are formally defined in relation to surfaces perpendicular to the flow, or the cross sectional area of a sphere, which is equivalent in this context. Thus, fluence and areic dose are only formally equivalent when the irradiated surface is perpendicular to the sputtering beam. In the text, we use the first convention to avoid confusion.

References


Figure 1: Summary of sputtering yield volumes calculated from literature and NPL data for organic materials under $C_{60}^q^+$ bombardment, adapted from a paper presented at the 44\textsuperscript{th} IUVSTA Workshop: Sputtering and Ion Emission by Cluster Ion Beams, April 2007 by A. G. Shard and I. S. Gilmore. The solid line shows Equation (2), obtained from the VAMAS inter-laboratory study on Irganox 1010. © Crown copyright 2011. Reproduced with the permission of Her Majesty’s Stationery Office.
Figure 2: Variation of average sputtering yield with incidence angle for 277 nm thick cholesterol films under 40 keV $C_{60}^+$ bombardment. Reproduced with the permission of the American Chemical Society.
Figure 3: Plots showing eroded depth as a function of C$_{60}^{q+}$ sputtering dose for Alq$_3$ and Irganox 1010 at various energies. Solid lines are fits using Equation (4) with the exception of Alq$_3$ at 10 keV where the curve is based upon extrapolated parameters from the 20 keV and 30 keV fits. With 10 keV C$_{60}^{q+}$, Alq$_3$ films of 37 nm or greater thickness could not be eroded. © Crown copyright 2006 and 2007. Reproduced with the permission of Her Majesty’s Stationery Office.
Figure 4: Different scenarios (a–d) in polymeric depth profiling: In thin films, there are typically 3 regions: (1) Initial drop, or transient, in signal intensity often defined by disappearance cross section of the material. (2) A steady state region (or quasi steady state region in the case of b) and (3) interfacial region. In bulk materials (d) there is almost always an eventual loss of signal intensity (4) after a certain critical fluence. This critical fluence varies with source and energy. Reproduced with the permission of Wiley © 2010.
Figure 5: Delta layer reference materials. (a) Films of barium arachidate with two 4.4 nm barium dimyristoyl phosphatidate marker layers at depths of 103 nm and 209 nm profiled with 40 keV $C_{60}^+$ ions at 40° incidence, a sample temperature of 100 K and average FWHM depth resolution of 21.5 nm. Reproduced with the permission of the American Chemical Society. (b) Films of Irganox 1010 with four 2.7 nm Irganox 3114 marker layers at depths of 50 nm, 101 nm, 199 nm and 299 nm profiled with 10 keV $C_{60}^+$ ions at 45° incidence, a sample temperature of 195 K and average FWHM depth resolution of 12 nm.
Figure 6: Depth profiles of Irganox delta layer reference materials using the parameters provided in each graph, see also Figure 5b. The FWHM of the first layer is also provided. © Crown copyright 2011. Reproduced with the permission of Her Majesty’s Stationery Office.
Figure 7: Molecular ion intensity versus dose graphs for the transient region of C$_{60}^{q+}$ depth profiles of (a) cholesterol, reproduced with the permission of Wiley © 2008 and (b) Irganox 1010, © Crown copyright 2007, reproduced with the permission of Her Majesty’s Stationery Office. Fits are based upon Equation (8) and demonstrate an excellent description of the data. Note that, in both these cases, there is a slow decline in sputtering yield which has been accounted for.
Figure 8: The ratio of steady state to initial secondary ion intensities for the PLA ion series \((\text{nM-O})^+\) at a number of \(C_{60}\) impact energies. The solid lines indicate the relationship provided by Equation (10). © Crown copyright 2006. Reproduced with the permission of Her Majesty’s Stationery Office.
Figure 9: Secondary ion intensities as a function of $\text{SF}_5^+$ primary ion dose for PLA films containing (a) 25% (w/w) (b) 10% (w/w) and (c) 5% (w/w) Pluronic P104. ($\blacktriangle$: 128 u, PLA), ($\bullet$: 59 u, P104), and ($\blacksquare$: 28 u, Si). Note the complexity of the transient region and the relative simplicity of the steady state region. Reproduced with the permission of the American Chemical Society.