MOLECULAR DEPTH PROFILING AND CHEMICAL IMAGING WITH CLUSTER TOF-SIMS

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by
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The work presented in this dissertation is concentrated on improving the fundamental understanding of molecular depth profiling and chemical imaging associated with time-of-flight secondary ion mass spectrometry (ToF-SIMS) equipped with cluster ion sources, mainly C\textsubscript{60} and argon gas cluster ion beams (Ar-GCIBs). A gold-cholesterol hybrid system is used to elucidate the reasons for the difficulties of depth profiling of heterogeneous thin film structures. The model study provides mechanistic insight into depth profiling of hybrid materials and offers an appropriate strategy for improving the quality of the depth profiles. Depth profiling of trehalose thin films is investigated under different Ar-GCIBs bombardment conditions to elucidate the influence of cluster size and kinetic energy on the formation of molecular ions. The study provides insight into selecting optimal Ar-GCIBs characteristics for molecular depth profiling of organic materials. Finally, room temperature ionic liquids (ILs) are employed in mass spectrometry imaging experiments. The surface and the internal structure of microspheres synthesized in ILs are investigated by the high spatial resolution imaging and depth profiling capabilities of cluster ToF-SIMS. The study introduces a new type of matrix for imaging mass spectrometry and provides insight into the key drivers and restraints behind ToF-SIMS three-dimensional (3D) molecular analysis. Overall, the thesis work is of great value for the fundamental understanding cluster ion-solid interactions in ToF-SIMS analysis and is beneficial for the advancement of the technique.
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Chapter 1

Introduction

1.1 Overview of SIMS

Secondary ion mass spectrometry (SIMS) is one of the most widely used techniques for surface and materials analysis. In brief, an energetic primary ion beam is used to bombard a surface under ultra-high vacuum conditions, generating secondary ions related to atoms and molecules located at the surface which are then separated and detected according to their mass-to-charge ratio \( (m/z) \). The resulting mass spectrum provides information regarding the nature of sample surface constituents.\(^1\)\(^-\)\(^3\) In addition to spectral information, SIMS is able to map the distribution of the elemental and molecular species present in a sample surface via a microprobe approach.\(^4\)\(^,\)\(^5\) Basically, a chemical image is acquired by scanning a focused primary ion beam across a predefined sample area in a pixel by pixel fashion along the x and y directions. Mass spectra are stored for each pixel in the image and are summed up and presented as one mass spectrum for the entire scanned area at the end of the analysis process. From this summed spectrum, \( m/z \) values of interest can be selected, and their intensities and distributions can be mapped across the imaging area.

Historically, SIMS instruments employ atomic ion sources, such as Cs\(^+\) and O\(_2^+\), as the primary ion sources, and there are two distinct operational modes for generating secondary ions: dynamic SIMS\(^6\) and static SIMS.\(^7\) For dynamic SIMS, a high ion dose, typically \(~10^{16}\) to \(10^{17}\) ions/cm\(^2\), is utilized to cause substantial erosion of the sample surface, yielding mostly elemental and small fragment ions. This approach has found wide applications in semiconductor industry.\(^8\)
where it has been established as an effective bulk analysis tool to monitor the concentration of specific species as a function of depth, a process known as depth profiling. In contrast, analysis with static SIMS usually requires a low ion dose of $<10^{13}$ ions/cm$^2$, which is called the static limit to ensure that no same area or even the near vicinity would receive more than one primary ion strike. Under these conditions, only less than 1% of the sample surface is impacted during an experiment and all ions are generated from previously undamaged areas of the surface. In general, the information gathered from this mode is representative of the chemistry of the uppermost layer of a sample, and, since this is nearly a non-destructive surface analysis approach, larger fragments and intact molecular ions can be detected.$^{13-16}$

The two modes of SIMS are usually equipped with different mass analyzers. To produce high ion dose, a DC primary ion beam is used in dynamic SIMS, and correspondingly, secondary ions are constantly being generated. It is therefore necessary for dynamic SIMS instruments to be equipped with a scanning mass analyzer, such as a magnetic sector or a quadrupole, to allow the sequential transmission of selected ions. In general, a magnetic sector and a quadrupole are suited for high voltage extraction field and low voltage extraction field over the sample surface, respectively.$^{17}$ For static SIMS, a pulsed primary beam is normally employed. In this way, the ion flight time can be established without the need for ion scanning, which allows the use of time-of-flight (ToF) mass analyzer. A ToF analyzer offers the merits of parallel ion detection and high transmission of ions, which can help compensate the low yield of secondary ions inherent in static SIMS.$^1$ Depending on the type of information being sought, the instrumentation would need to be chosen based on the type of analysis desired. However, with the development of cluster ion sources, the restriction is changing. In the next section, the development of primary ion sources will be highlighted.
1.2 Development of Cluster Ion Sources

As mentioned earlier, before the development and application of cluster ion sources for SIMS surface analysis, single atomic particles were the most commonly used primary ion beams. The atomic ion beam bombardment causes a collision cascade of particles in the sample being analyzed, which is termed as a billiard-ball collision process.\textsuperscript{3} As the Figure 1-1 shows, when high-energy primary ions collide with the sample surface, the ions transfer their kinetic energy to the sample which leads to a cascade of collisions between the atoms and molecules within the sample. Part of the energy can return to the surface region and allow the emission of secondary particles. This type of ion source is able to provide a fine beam, but removes only a very limited amount of material from the sample surface and induces severe material disruption and damage at the subsurface.\textsuperscript{18} Therefore, it is difficult to preserve the molecular specificity of organic and biological materials for molecular depth profiling and chemical imaging with atomic ion sources.
The emergence of Au$_3^+$ and Bi$_3^+$ primary ion sources in the early 2000s revolutionized SIMS analysis. Liquid metal ion sources (LMIGs) quickly replaced traditional atomic ion source since the LMIGs not only retain the high spatial resolution and brightness of the single atomic ion beams, but also provide an increased secondary ion yields in the high mass range, which is essential for the analysis of organic and biological samples. However, the limitation of LMIGs is that they behave similar to the monoatomic ion sources in terms of ion beam bombardment induced chemical damage, and, thus sample analysis is still restricted by the static limit. Therefore, it is still not possible to probe the molecular information at sub-surface level.
This limitation of acquiring molecular information has been greatly changed by the development of C\textsubscript{60}\textsuperscript{+} cluster ion source. This source greatly reduces ion bombardment induced damage and exhibits an extended mass range for desorbed molecules, which, for the first time, makes molecular depth profiling and three-dimensional (3D) imaging analysis possible.\textsuperscript{22,23} In order to understand the unique properties associated with C\textsubscript{60}\textsuperscript{+} bombardment, molecular dynamics computer simulations have been utilized to compare the differences in the behaviors of 15 keV Ga\textsuperscript{+} and C\textsubscript{60}\textsuperscript{+} bombarding a Ag\{111\} surface.\textsuperscript{24} As shown in Figure 1-2, when Ga\textsuperscript{+} hits the sample surface, the projectile dissipates its kinetic energy along the way it travels and penetrates deep into the sample. As a result, very little material is ejected from the surface and, in addition, there is intermixing of sample layers and chemical damage in the sub-surface. However, for C\textsubscript{60}\textsuperscript{+}, the cluster dissociates into individual C atoms with 15keV/60, or 250 eV, of kinetic energy once it impinges on the solid surface. The total kinetic energy of the C\textsubscript{60}\textsuperscript{+} cluster ion is deposited closer to the surface and over a larger surface area by formation of a crater. Therefore, it delivers enhanced yields and causes less topography and interlayer mixing. In addition, there is no disappearance of useful molecular information beyond the static limit, since now the damage created during a single ion impact is largely removed by its own impact, leading to erosion of material without loss of chemical information. These advantages of C\textsubscript{60}\textsuperscript{+} cluster ion source enable the scope of SIMS analysis to expand into the investigation of organic samples and make molecular depth profiling of organic material become possible.
Figure 1-2: Molecular dynamics computer simulation of 15 keV Ga\(^+\) and C\(_{60}\)^+ bombardment of a silver surface at normal incidence.\(^{24}\)
Recently, argon gas cluster ion beams (Ar-GCIBs) (Ar\textsubscript{n}\textsuperscript{+}, where n = 500-5000) have been introduced as a new type of the cluster ion sources\textsuperscript{25}. This ion source generates simplified SIMS spectra, namely there are less fragments but more intact molecular information. Also, it seems to yield better depth resolution and produce reduced surface roughness in comparison to C\textsubscript{60}\textsuperscript{26-28}. A reasonable explanation for these observations is that upon colliding with the sample surface, the gas cluster dissociates into its individual components with even lesser energy when compared to C\textsubscript{60}\textsuperscript{29}. Take 15 keV Ar\textsubscript{500}\textsuperscript{+} as an example, energy per Ar atom is 15 keV/500, or 30 eV, about 10 times lower than that of C\textsubscript{60}. In order to further increase the ionization efficiency of the target molecules, there also have been attempts to replace Ar gas with other chemical compositions, such as water, N\textsubscript{2} and C\textsubscript{2}H\textsubscript{5}OH.\textsuperscript{30-33} Overall, the implementation of GCIBs has broadened the scope of molecular SIMS even further.

1.3 Molecular Depth Profiling and Three-dimensional Imaging

Over the past decade, successful molecular depth profiling on many types of organic molecules has been reported\textsuperscript{34-42}. The first successful attempt at molecular depth profiling in our lab was obtained on a peptide-doped trehalose thin film with a 20 keV C\textsubscript{60}\textsuperscript{+} projectile, as shown in Figure 1\textsuperscript{39}. As seen from the depth profiles, all the molecular ions exhibit an initial drop in intensity, an intermediate steady-state erosion, and a loss of intensity at the film/Si substrate interface. According to Gillen et al\textsuperscript{43}, this signal dynamic can be explained as a balance between the rate of chemical damage accumulation and the rate of chemical damage removal. Based on this idea, an erosion model has been developed by Cheng et al\textsuperscript{44,45} to help quantify the important parameters that control the shape of the molecular depth profiles, including sputtering yield volume, the altered layer thickness and damage cross section. The information gathered from this erosion model has been successfully applied as a guidance in developing protocols for optimizing
the useful content of these types of measurement, such as the experiment temperature,\textsuperscript{46,47} the incident angle of the projectile,\textsuperscript{48} the impact energy of the beam\textsuperscript{49} and sample rotation.\textsuperscript{50} An example is shown in Figure 1-4, where the results suggest that the key to a successful molecular depth profile is to deposit the impact energy of the beam as close as possible to the sample surface region, therefore, glancing incident angles are most appropriate for molecular depth profiling.\textsuperscript{48}

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Figure 1-3: Molecular depth profiles of peptide-doped trehalose thin films.\textsuperscript{39}
The successes in molecular depth profiling of organic model systems are quite encouraging and have inspired a tremendous amount of effort to be put into the exploration of 3D characterization of a sample. The motivation behind the attempts is that the maximum signal in imaging mode will increase by a factor of $10^5$ theoretically if the static limit no longer applies and chemical images are taken in a voxel (a pixel that has volume) by voxel fashion, which clearly is going to offer many new application possibilities. The most common strategy is to acquire a stack of chemical images as a function of depth and then to create a 3D rendering of the sputtered volume on a nanometer scale. A few notable examples of 3D imaging using ToF-SIMS have
been reported in recent years. For example, Fletcher et al. successfully used a 40 keV $^{12}$C$^{60+}$ ion beam to map the biomolecule distributions within a freeze-dried Xenopus laevis oocytes, as shown in Figure 1-5.$^{52}$ Breitenstein et al. used a dual beam approach to reconstruct the chemical composition of normal rat kidney cells, as shown in Figure 1-6.$^{53}$ Robinson et al. used a z-correction method on NIH/3T3 fibroblasts to solve depth scale issues related to the conversion of the acquired data into 3D volumetric information, as shown in Figure 1-7.$^{54}$

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Figure 1-5: The distributions of four different types of lipids within the freeze-dried oocyte. (a) phosphocholine, (b) signal summed over the m/z range 540-650, (c) signal summed over the m/z range 815-960, and (d) cholesterol.$^{52}$
Figure 1-6: ToF-SIMS 3D microarea analysis of normal rat kidney cells. Amino acid, phospholipids and substrate signals are represented in red, green, and blue, respectively.\textsuperscript{53}
Figure 1-7: Visualization of a single NIH/3T3 fibroblast by ZCorrectorGUI. The data set consists of 56 images of a lipid peak at m/z 58. Each image contained 256 × 256 pixels and was 86 × 86 μm² in size.⁵⁴

1.4 Thesis Overview

The work presented in this thesis is mainly focused on understanding the fundamental aspects of ion-solid interactions associated with cluster ToF-SIMS analysis, and applying the knowledge towards applications such as molecular depth profiling and chemical imaging.

In Chapter 2, the design and performance characteristics of two ToF-SIMS instruments used in the thesis study, the Bio-ToF SIMS and the J105 3D Chemical Imager, and the operational principles for two cluster ion sources, C₆₀⁺ and Ar-GCIBs, are described in detail.
Sublimation and solution based organic thin film preparation methods and AFM based thin film characterization method are also discussed.

In Chapter 3, a model system composed of a thin gold layer of 1.4 to 3.5 nm deposited, either on top of or sandwiched within a cholesterol thin film matrix, which is several hundred nanometers thick, was developed in order to unravel the factors that lead to the difficulty of depth profiling of heterogeneous thin film structures. This model provides mechanistic insight into the depth profiling of hybrid materials consisting of both organic and inorganic layers. In addition, this study offers a possible path for improving the quality of the depth profiles by employing low energy atomic ion sputtering in the metal layer region.

In Chapter 4, the effect of cluster size and kinetic energy of Ar-GCIBs on the quality of molecular depth profiling is investigated on a simple model system composed of trehalose thin films to acquire more fundamental information about the ion/solid interaction. The results show that optimal conditions for molecular depth profiling will be obtained using the highest kinetic energy with the largest clusters, while maintaining a value of E/n near a threshold of 5 eV/atom. In general, this study provides insight into selecting optimal Ar-GCIBs characteristics for molecular depth profiling of organic materials.

In Chapter 5, TiO₂ microspheres with diameters of 5-30 µm, formed by interfacial sol-gel reactions, embedded in an ionic liquid are employed as a 3D object model. The results demonstrate that, with high spatial resolution imaging and depth profiling capabilities, SIMS analysis can be used to characterize the surface and the internal structure of such inorganic microspheres.

Future directions of cluster ToF-SIMS in the applications of molecular depth profiling and chemical imaging are discussed in Chapter 6. Other methods such as laser post-ionization and image fusion are briefly introduced with the aim to show how they can be incorporated and help expand the scope of this technique even further.
1.5 Reference


(54) Robinson, M. A.; Graham, D. J.; Castner, D. G. ToF-SIMS Depth Profiling of Cells: z-Correction, 3D Imaging, and Sputter Rate of Individual NIH/3T3 Fibroblasts. *Analytical Chemistry* 2012, 84, 4880-4885.
Chapter 2

Instrumentation

2.1 Introduction

The main focus of this thesis is to understand fundamental ion-solid interactions, specifically the interaction of energetic cluster ion beams with organic solids. In this chapter, two SIMS instruments (Bio-ToF SIMS and J105 3D Chemical Imager) as well as two representative cluster ion beams used for the study ($C_{60}$ ion source and argon gas cluster ion beams), have been described in detail. In addition, two purely physical methodologies of preparing organic thin films and an AFM device used for thin film characterization have also been briefly introduced.

2.2 Bio-ToF SIMS

2.2.1 Operation Mechanism of Bio-ToF SIMS

The Bio-ToF SIMS used in this thesis was initially designed and built by Kore Technology Ltd. (Cambridge, UK) and our lab and the characteristics of the instrument have been described in detail elsewhere.\(^1\) As shown in Figure 2-1, the instrument is equipped with a 25 kV Au\(_n\) (n=1-3) liquid metal ion source and a 40 kV $C_{60}$ ion source, both of which are mounted at an angle of 40º with respect to the surface normal. The liquid metal ion source is able to deliver high current density into a small spot since the ions are emitted from a point source via field emission,\(^2,3\) while the $C_{60}$ ion source is known for its high secondary ion yield and low chemical damage.\(^4,7\) The work presented in this thesis was performed using the 40 kV $C_{60}$ ion source.
Figure 2-1: Front view of the Bio-ToF SIMS: (A) fast entry port, (B) transfer arm, (C) preparation chamber, (D) surface analysis chamber, (E) cold stage, (F) optical microscope, (G) secondary electron detector, (H) liquid metal ion source, (I) C$_{60}$ ion source and (J) ToF mass analyzer.
The basic operation mechanism of Bio-ToF SIMS in the positive ion mode is illustrated in Figure 2-2. In brief, in order to obtain compositional information from a sample surface, a pulsed primary ion beam is used to bombard the sample resulting in the emission of neutrals, electrons and ions from the surface. The ejected secondary ions are then extracted and accelerated into a time-of-flight mass analyzer by applying +2500 V to the sample stage. Note that the instrument employs delayed extraction for the secondary ions produced, meaning that there is no voltage applied to the sample stage during primary ion impact and that there is a delay of a few nanoseconds between the completion of the primary ion packet interaction with the sample surface and the rise of the extraction potential. With this extraction method, all secondary
ions are first generated and then accelerated at the same time, therefore, narrowing the peak width, indicating an improved mass resolution in comparison to non-delayed extraction method. In the ToF mass analyzer, secondary ions are separated by their flight time to reach the detector via

\[ zV = \frac{mv^2}{2} \quad (2-1) \]

\[ v = \frac{L}{t} \quad (2-2) \]

\[ t = L \sqrt{\frac{m}{z} \times \frac{1}{2V}} \quad (2-3) \]

where \( z \) is the charge of an ion, \( V \) is the accelerating voltage, \( m \) is the mass of an ion, \( v \) is the velocity, \( L \) is the length of the flight path, \( t \) is the flight time and \( m/z \) is the mass to charge ratio. It is obvious that for ions having the same charge, heavy ions with a high mass to charge ratio will arrive at the detector later than the lighter ones. One problem which needs to be addressed is that ions with the same charge oftentimes do not have exactly the same initial kinetic energy. In order to compensate for the initial energy dispersion, a dual-stage reflecton is used in the instrument, which allows ions of higher kinetic energy to penetrate deeper into the reflection and spend longer time there before being reflected back to the detector. As a result, secondary ions of the same \( m/z \) but different kinetic energies will arrive at the detector at the same time, once again improving the mass resolution. This instrument is able to routinely deliver a mass resolution \((m/\Delta m)\) of 3000. The mass-separated secondary ions are detected by a Chevron microchannel plate (Burle Electro-Optics Inc., Sturbridge, MA), where post acceleration is incorporated to facilitate the detection of high mass ions. The detected ions are registered in single ion counting mode using a time-to-digital converter (Fast ComTec, Munich, Germany) with a time resolution of 1 ns. Note that if the detection of negative ions is desired, one only needs to reverse the polarity of voltage applied.

In addition to detailed surface composition analysis, the instrument can also be used for depth profiling, where the mass spectrometer is set to operate alternatively between erosion
cycles and data acquisition cycles. In a typical depth profiling experiment setting, ~150 pA 40 keV C\textsubscript{60}\textsuperscript{+} ion beam in DC mode is used to etch through the sample at an area of 400 µm × 400 µm in 6 s intervals. The ion fluence applied for etching can be calculated via

$$\text{Ion fluence for etching} = \frac{I \times t}{1.6 \times 10^{-19} \times A} \quad (2-4)$$

where \(I\) is the ion beam current, \(t\) is the sputter time and \(A\) is the size of the etched crater. In this case, the ion dose used for etching is approximately \(3.5 \times 10^{12}\) ions/cm\(^2\) per cycle. Between erosion cycles, SIMS images of 256 × 256 pixels and corresponding mass spectra are collected from a zoomed area of 200 µm × 200 µm within the etched crater using a pulsed C\textsubscript{60}\textsuperscript{+} ion beam with a pulse width of 60 ns. The ion fluence applied during each acquisition cycle can be calculated via

$$\text{Ion fluence for imaging} = \frac{I \times S \times W \times P}{1.6 \times 10^{-19} \times A} \quad (2-5)$$

where \(I\) is the ion beam current, \(S\) is the number of pulses per pixel, \(W\) is the ion pulse width, \(P\) is the number of pixels and \(A\) is the size of the sample analysis area. The ion fluence applied during each acquisition cycle is \(~0.9 \times 10^{10}\) ions/cm\(^2\), which is much lower than the ion fluence used for etching, ensuring negligible erosion accumulated even after collecting several hundred data points in the depth profile. The collected data reflects the variation of composition within the sample as a function of ion fluence. By coupling with AFM measurements, the ion fluence can be converted to establish a depth scale, from where properties associated with the primary ion beam, such as sputter yield and depth resolution, can be determined.

A special depth profiling scheme, the so called wedge-crater beveling, has also been developed and written into the Bio-ToF SIMS software. A detailed description of the method can be found elsewhere\(^{9,10}\). Briefly, the sample is subjected to only a few erosion cycles with the 40 keV C\textsubscript{60}\textsuperscript{+} ion beam, which is operated in DC mode and set to scan across a 500 µm × 500 µm area using a 256 × 256 pixel raster. The wedge crater is created by repeating the raster as many times
as there are pixels in one line or lines in one raster frame. In each of these raster frames, one more line is skipped in the y direction. In our case, the raster is set to repeat 256 times, scanning 256 lines in the first frame, 255 lines in the second frame, etc., until the last scan is only over one single line. One set of these wedge frames therefore consists of 256 rasters and each line along the y direction receives linearly increasing ion fluence. The dwell time on each pixel is set to about 20 μs, which is the minimum dwell time that ensures stable beam position on a pixel. The number of wedge frame sets during a sputter erosion step is calculated such that the set total sputtering time in an erosion cycle is reached. The shape of the eroded crater is investigated using an AFM after the completion of the erosion, which provides valuable information regarding how sputter yield and/or sample surface topography change as a function of ion fluence.
2.2.2 40 kV C\textsubscript{60} ion source

![Figure 2-3: (a) A 40 kV C\textsubscript{60} ion column.\textsuperscript{11} (b) Schematic of C\textsubscript{60} ion optics.\textsuperscript{5}]

A 40 kV C\textsubscript{60} ion source, as shown in Figure 2-3, is installed on the Bio-ToF SIMS. The design and characteristics associated with the C\textsubscript{60} ion source can be found in the literature.\textsuperscript{2,5-7,12} It is a type of electron bombardment source, the main components of which are shown in Figure 2-4. During routine operation, C\textsubscript{60} powder is first heated to 410 °C. C\textsubscript{60} vapor generated by sublimation of C\textsubscript{60} powder diffuses into an ionization cell through a nozzle, and then collide with electrons emitted by a circular filament that surrounds this ionization cell. The electrons are accelerated and directed towards the ionization cell by a concentric cylindrical grid. Note that the grid voltage determines the electron energy which is strongly associated with the beam composition. C\textsubscript{60}\textsuperscript{+}, C\textsubscript{60}\textsuperscript{2+} and C\textsubscript{60}\textsuperscript{3+} are optimised at the grid voltage of 65 V, 95 V and 120V, respectively. All the C\textsubscript{60} ions are extracted and accelerated to 40 kV as they enter the optical
column, where the 40 keV C\textsubscript{60}\textsuperscript{+} ion beam is selected by a Wien filter, steered by two pairs of alignment plates, and focused using two Einzel lenses. In general, C\textsubscript{60}\textsuperscript{+} are successful at depth profiling as it breaks down into its individual C components when hitting the surface and deposits its initial kinetic energy near the surface, thus producing higher yields. In addition, the bombardment induced chemical damage can be removed by its own impact, leading to the creation of a steady state molecular ion signal.\textsuperscript{6}
Figure 2-4: Snapshots of $C_{60}$ ion source assembly.
2.3 J105 3D Chemical Imager

2.3.1 Operation Mechanism of J105 3D Chemical Imager

Figure 2-5: Front view of the J105 3D Chemical Imager: (A) glove box, (B) preparation chamber, (C) sample analysis chamber, (D) optical microscope, (E) RF only quadraouple, (F) Ar gas cluster ion beam, (G) electrostatic analyser, (H) C\textsubscript{60} ion source, (I) buncher, (J) first time focus and (K) harmonic field ToF reflectron.

The J105 3D Chemical Imager, as shown in Figure 2-5, is a novel SIMS instrument developed by Ionoptika Ltd. (Southampton, UK) and the Vickerman group at the University of
Manchester. The design of the instrument has been described previously.\textsuperscript{13,14} In brief, unlike conventional ToF-SIMS instruments that operate alternatively between data acquisition cycles in pulsed mode and erosion cycles in DC mode, the J105 uses a continuous primary ion beam to generate a continuous stream of secondary ions. The secondary ions are collisionally cooled and focused to the center of an RF only quadrupole, energy filtered by an electrostatic analyzer, collected in a buncher, and then accelerated into a harmonic filed ToF analyzer. This design allows for continuous data collection and ensures that no sample information is lost. In addition, the buncher-ToF configuration of the J105 decouples the mass analysis process from the sputtering process, allowing data acquisition to be performed at both high mass resolution and high spatial resolution. Note that in a conventional ToF-SIMS instrument, mass resolution is directly related to the length of the ion beam pulse, meaning that there is always a tradeoff between mass resolution and spatial resolution. A short pulse required for good mass resolution is often insufficient for high spatial resolution, since the effective spatial resolution in SIMS imaging is signal limited. In the J105 the restriction has been lifted, since now a DC beam is used, so the mass resolution is only dependent on how tightly the buncher packs the secondary ions. The instrument is able to provide submicrometer spatial resolution (approximately 300 µm) with a mass resolution $(m/\Delta m)$ above 5000.
2.3.2 20 kV Ar-GCIB ion source

The J105 3D Chemical Imager is currently equipped with two distinct ion sources. One is a 40 kV C₆₀ ion source, which is identical to the one described in section 2.2.2. The other one is a 20 kV Ar-GCIB system. The design and characteristics of the 20 kV Ar-GCIB system have been described in detail elsewhere. In brief, Ar gas is first introduced at high pressure (~18 bar) and then goes through a nozzle with a 30 µm aperture, expanding adiabatically into vacuum (the cluster formation chamber). Note that in the enclosed system, the gas cools itself down by converting a large part of its internal energy into kinetic energy. As a result, part of the cooled gas condenses to form neutral gas clusters, a process known as partial condensation. The neutral gas cluster size distribution can be affected by a number of parameters, such as the size of the nozzle, the shape of the nozzle and the input gas pressure. A conical skimmer with an opening

Figure 2-6: (a) A 20 kV Ar-GCIB ion column. (b) Schematic of gas cluster ion source.
of 0.5 mm in diameter is placed approximately 20 mm away from the nozzle and is collimated to allow neutral Ar clusters to flow into an ionization chamber, where the neutral clusters are ionized by electron bombardment. The acquired cluster ion beam can be mass-filtered by a Wien filter and then be focused in the ion optical column with an einzel lens. The distribution of cluster ion sizes can be checked by pulsing the ion beam and measuring the flight time of the primary ions between the pulser and the sample stage, as shown in Figure 2-7. The flight time spectrum can be used to determine the average cluster size of the beam via

\[
\text{Cluster size} = \frac{2 \times keV \times (T_m - T_o)^2}{L^2 \times m_{Ar}}
\]

where \(keV\) is the kinetic energy of the cluster ion, \(T_m\) is the measured flight time, \(T_o\) is signal delay time (5 \(\mu\)s), \(L\) is the flight distance (0.429 m) and \(m_{Ar}\) is the mass of Ar. For the example shown in Figure 2-7, the average cluster size is \(\sim 4000\). In general, Ar-GCIBs are remarkable new projectiles for SIMS depth profiling of organic materials, since they appear to yield better depth resolution and produce less chemical damage than \(C_{60}\), broadening the scope of this technology even further.\(^{17-20}\)
2.4 Thin Film Deposition Techniques

In this thesis, organic thin films are employed as model systems for fundamental studies of molecular depth profiling with cluster bombardment. Two thin film deposition methods, physical vapor deposition (PVD) and spin coating, will be discussed briefly below.

2.4.1 Physical Vapor Deposition
A home-built physical vapor deposition chamber attached to a Bio-ToF SIMS is shown in Figure 2-8. The deposition system has been described in detail elsewhere. In brief, 0.5 g of the material to be deposited is brought to sublime in vacuum by electrically resistive heating of a tungsten basket. The resulting gas travels through a diffusing grid placed above the crucible and lands onto cleaned Si wafers cooled to liquid nitrogen temperature to form uniform cholesterol thin films. The deposition rate is kept around 10 Å/s and the film thickness is monitored by a quartz crystal microbalance (QCM) during deposition and confirmed by atomic force microscopy measurements afterwards.

Figure 2-8: (a) Front view of the home-built PVD chamber. (b) Top view looking inside the PVD chamber.
2.4.2 Spin Coating

Spin coating is a very simple method to deposit thin films of uniform thickness. A typical spin coating process consists of (1) dissolving thin film material in a volatile solvent; (2) placing a droplet of the sample solution onto a substrate and (3) using a spin coater to spread the solution and allowing it dry to form a thin film. Trehalose thin films investigated in the thesis are prepared by this method. Note that trehalose molecules are very hydrophilic due to the -OH functional groups. Therefore, the Si substrates are piranha etched (3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution) to make their surfaces hydrophilic as well. As a result, trehalose aqueous solution becomes extremely compatible with the substrates and can be dispersed evenly to form uniform films, as shown in Figure 2-10. The film thickness can be adjusted by changing the spin speed and the concentration of the solution.

Figure 2-9: Schematic illustration of spin-coated trehalose thin films.
2.5 AFM

An AFM (Nanopics 2100, KLA-Tencor, San Jose, CA) is used to provide three-dimensional topographic information about a sample. This unique type of AFM can scan over large regions with up to 800 µm scan length, 20 µm Z range and a resolution of 2 nm at X- and Y-directions and 3 Å at Z-direction. There are two modes of operation of this AFM, as shown in Figure 2-10; (1) contact mode, where the deflection of the cantilever is kept constant while the tip scans over the sample surface; and (2) damping mode, where the cantilever is oscillated at the resonance frequency and the amplitude of the oscillation is kept constant.

![Figure 2-10: Schematic of the two modes of operation of a Nanopics 2100 AFM.](image)

In this thesis, the vertical and lateral dimensions of the sputtered craters are measured in contact mode and the crater depths are employed to determine the sputter yields of a variety of
organic compounds. The evaluation of sample surface roughness and thin film continuity is performed using damping mode.

2.6 References


(22) *Nanopics 2100 operation manual*; Seiko Instruments Inc., 2002.
Chapter 3

Depth Profiling of Metal Overlayers on Organic Substrates with Cluster SIMS


3.1 Introduction

Molecular depth profiling with energetic polyatomic ion beams\(^1\)\(^-\)\(^3\) has now been established for polymers\(^4\)\(^-\)\(^6\) and many types of organic molecules.\(^7\)\(^-\)\(^14\) Sophisticated protocols for optimizing these types of measurements using secondary ion mass spectrometry (SIMS) have been developed from both a practical\(^13\), \(^15\)\(^-\)\(^18\) and a theoretical\(^19\)\(^-\)\(^23\) point of view. In general, primary ions such as C\(_{60}\)\(^+\) are successful at depth profiling since the damage created during a single ion impact is largely removed by subsequent impacts, leading to the creation of a steady state molecular ion signal.\(^3\), \(^24\)\(^-\)\(^25\)

In view of the long-time success of the depth profiling of inorganic materials,\(^26\)\(^-\)\(^32\) there has been an obvious attempt recently to utilize cluster-SIMS for the characterization of hybrid materials containing both organic and inorganic components. A particularly important example involves the study of organic light emitting diodes (OLEDs)\(^33\)\(^-\)\(^34\) which contain a number of organometallic compounds as well as a metallic overlayer coating. This challenging system has not been successfully examined yet. So far, the Al metal overlayer must be removed
(delaminated) by physical means prior to analysis since the presence of this material prevents acquisition of a successful depth profile. After that, the remaining materials could be examined using C$_{60}^+$ but only when co-bombarding with low energy Ar$^+$ ions.$^{15,35}$ More successful results have been obtained using Ar clusters for erosion where molecular information with depth resolution of ~10 nm has been reported for a multilayer system.$^{36}$ The reasons behind the dramatic influence of a metal overlayer on molecular depth profiles are currently not known.

There have been few attempts to elucidate the mechanism behind the depth profiling of hybrid metal on organic systems. Using dynamic SIMS, Song et al.$^{37}$ have examined a model OLED structure and was able to observe diffusion of a Ag overlayer into the tris(8-hydroxyquinolinato) aluminium (Alq$_3$) substrate layer. Unfortunately, no useful molecular information was found due to the destructive nature of O$_2^+$ bombardment. Aluminium and Ag overlayers on trehalose have been studied using 20 keV C$_{60}^+$ bombardment with the resulting depth profile found to be severely degraded.$^{38}$ The results suggest that ion beam induced mixing of metal and organic materials complicate the erosion process, although no solutions were offered to fix this problem. These observations have been qualitatively confirmed by molecular dynamics (MD) computer simulations.$^{39}$ These studies utilized thin Ag layers on top of an octatetraene crystal as a model. The calculations show that the Ag atoms are indeed implanted into the organic substrate. Moreover, for thicker overlayer films, the implanted Ag is found in the form of large clusters. It is speculated that these implanted species are largely responsible for the increased damage observed in the experiments. In addition, the calculations show that the primary ion creates a hole in the metal overlayer when its thickness is on the order of 1 nm. The organic molecules are found to sputter from the sample by jetting through this opening.

To better disentangle the molecular-level details associated with the depth profiling of hybrid materials, here we examine a model system comprised of a thick cholesterol film with a gold overlayer of thickness varying from 1.4 to 3.5 nm. The results show that meaningful depth
profiles can be acquired for each of these model systems using 40 keV C\textsubscript{60}\textsuperscript{+} to erode through the metal-organic interfaces, but there are strong perturbations to yields, damage cross sections and altered layer thickness when compared to non-hybrid systems. The influence of the gold layer on the depth profile remains constant once the gold thickness exceeds 1.4 nm. From these observations, and by comparison to the MD simulations, we propose an approach to largely mitigate these perturbations.

3.2 Experiential Section

3.2.1 Description of the Model System.

A schematic of the model system used in this study is shown in Figure 3-1. In brief, 5 mm × 5 mm Si wafers (Ted Pella Inc., Redding, CA) serve as the initial building blocks. The substrates were sonicated in methanol for 15 minutes and rinsed with deionized water three times prior to use. Cholesterol (Avanti Polar Lipids, Alabaster, AL) was then deposited onto cleaned Si wafers to form single-component films in a previously described, home-built physical vapor deposition (PVD) chamber.\textsuperscript{40} The film thickness was monitored by a quartz crystal microbalance (QCM) during deposition and confirmed by atomic force microscopy (AFM) measurements afterwards. On top of single-component cholesterol samples, various thicknesses of gold thin films were deposited by ion beam sputtering to form chemically alternating metal-organic two-component films. During the sputter deposition processes, the sputter rate is kept low at 0.001 nm/s in order to allow thin gold films to be uniformly spread onto organic substrates while the thickness of the deposited Au layers is monitored by a QCM. The sputter deposition system has been described in detail elsewhere.\textsuperscript{41} In this study, structures with three different metal overlayers of thicknesses 1.4 nm, 2.8 nm, and 3.5 nm were constructed. The surface morphology
of these three samples as measured by an AFM indicated the films were continuous and pinhole free, as shown in Figure 3-2. In the end, the last building block, another cholesterol layer, was added to the two-component gold-cholesterol samples by PVD. A sandwich-like structure was formed, which contains thin gold delta layers between two cholesterol films. Cholesterol films on bare Si wafers were also made at the same time and were analyzed by AFM in order to get the thickness information of the new added building block.

Figure 3-1. Schematic illustration of the model system used in this study. (a) 5 mm × 5 mm Si wafers; (b) and (d) Chol/Si film; (c) Au/Chol/Si film; (e) Chol/Au/Chol/Si film. Cholesterol film was made by physical vapour deposition and gold layer was deposited by ion beam sputtering. Cholesterol film thickness of (b), bottom (c) and bottom (e) is the same and top cholesterol layer of (e) has the same thickness of (d).
3.2.2 Instrumentation.

Sample analysis was performed using a Bio-TOF IMS instrument, the design of which has been described previously.\textsuperscript{42} The mass spectrometer is equipped with a 40 keV C\textsubscript{60} primary ion source (Ionoptika Ltd., Southampton, U.K.), which is mounted at an angle of 40° with respect to the surface normal. The design and characteristics of the ion source have been described in detail elsewhere.\textsuperscript{3,43-44} In this study, singly charged C\textsubscript{60}\textsuperscript{+} primary ions were selected by a Wien filter and were focused to provide ~180-200 pA beam current with a 6-8 µm diameter. For depth profiling, the mass spectrometer was set to operate alternatively between erosion cycles and image acquisition cycles. During an erosion cycle, the C\textsubscript{60}\textsuperscript{+} ion beam was operated in DC mode to etch through the film at an area of 400 µm × 400 µm in 6 s intervals with an etch fluence of 4.0 × 10\textsuperscript{12} ions/cm\textsuperscript{2} per cycle. Between erosion cycles, SIMS images of 256 × 256 pixels and corresponding mass spectra were collected from a zoomed area of 200 µm × 200 µm within the

Figure 3-2. AFM image of original intact surface for (A) 1.4 nm Au/Chol/Si film; (B) 2.8 nm Au/Chol/Si film; (C) 3.5 nm Au/Chol/Si film. Roughness values are as labelled.
etched crater using the pulsed C$_{60}^+$ ion beam. The ion fluence applied during each acquisition cycle was kept below $1.0 \times 10^{10}$ ions/cm$^2$, ensuring negligible erosion even after collecting several hundred data points in the depth profile. The mass spectrometer was operated in a delayed extraction mode during data acquisition with a delay time of 60 ns between the primary ion pulse and the secondary ion extraction pulse. No sample charging was noticed in the positive SIMS mode and the acquired mass spectra have a mass resolution of 2000 at the molecule-specific peak of cholesterol, m/z 369. All the depth profiling experiments were performed at room temperature (RT).

3.2.3 Atomic Force Microscopy (AFM) Measurement.

Crater depth and size information were gathered by an AFM (Nanopics 2100, KLA-Tencor, San Jose, CA). This unique type of AFM offers a maximum scanning area of 0.8 mm × 0.8 mm in contact mode, allowing a convenient one-step measurement of the entire eroded crater. All AFM measurements in this study were taken immediately after the depth profiling experiment was completed. Surface relaxation after ion bombardment was not found in a previous study.$^8$ Samples were cleaned with N$_2$ gas before measurement to avoid particle artifacts and the resulting images were calibrated to correct surface tilt.

3.3 Results and Discussion

3.3.1 Single-component Films.

Before examining the hybrid metal-organic thin film structures shown in Figure 3-1, it is important to obtain depth profiles of the pure materials to act as controls. Two different
cholesterol films of different thicknesses were prepared by PVD to mimic the base film shown in Figure 3-1b, 3-1c and 3-1e (622 nm) and the overlayer film shown in Figure 3-1d and 3-1e (325 nm). The physical properties associated with the sputtering of a pure gold film have already been reported.\textsuperscript{45}

The depth profile of the underlying base cholesterol film is shown in Figure 3-3a. The secondary ion intensity of the cholesterol molecular ion peak (M-H)$^+$ at m/z 385, the quasi-molecular ion peak (M-OH)$^+$ at m/z 369, and substrate signal at m/z 28 for Si$^+$ are plotted as a function of C$_{60}^+$ ion fluence. Both of the cholesterol molecule related signals exhibit an initial drop in intensity, an intermediate steady-state erosion, and a loss of intensities at the film/Si substrate interface. The m/z 369 peak is chosen to represent the cholesterol molecule simply because it is of the highest intensity. A total ion fluence of $2.2 \times 10^{14}$ ions/cm$^2$ is used to etch through the 622 nm film before reaching the Si substrate. Note that the erosion rate of Si is significantly slower than that of cholesterol. Therefore, the removed Si thickness should be negligible. A similar depth profile is observed for the thinner 325 nm overlayer film as shown in Figure 3-3b. The average erosion rate of cholesterol in a single-component system is calculated from the known fluence and film thickness and is presented in units of sputtered material volume per incident ion. In our case, one C$_{60}^+$ primary ion removes $274 \pm 20$ nm$^3$ of material, a value consistent with earlier measurements.\textsuperscript{46}
Figure 3-3. Characterization of cholesterol building blocks in the model system. Depth profiles of (a) 1st batch and (b) 2nd batch cholesterol PVD films, sputtered and analyzed with 40 keV C$_{60}^+$ at 40° incidence. The inserted AFM images show the bombarded regions in three-dimensions and line scans taken across the craters showing the two cholesterol building blocks are 622 nm and 325 nm thick, respectively. (a) is the bottom cholesterol layer of Au/Chol and Chol/Au/Chol samples, while (b) is the top cholesterol layer of Chol/Au/Chol samples.

The other type of building block used in the hybrid system is a thin gold film. Recently, Yang et al.\textsuperscript{45} reported that the erosion rate is ~2.2 nm$^3$ of material per primary ion. Their system is equipped with a 20 kV C$_{60}^{2+}$ ion source and is equivalent in kinetic energy to the 40 keV C$_{60}^+$ ion beam employed here. Note that the erosion rate of cholesterol is >100 times that of gold.
3.3.2 Two-component Au-Cholesterol Films.

The next step is to investigate the behavior of the metal-organic interface under $C_{60}^+$ bombardment. The response of cholesterol films with varying thicknesses of Au overlayers to a total ion fluence of $2.0 \times 10^{14}$ $C_{60}^+$ bombardment are shown in Figure 3-4. The AFM measurements, as shown in Figure 3-2, show similar roughness values for all of the hybrid metal-organic thin films, indicating that the samples have similar surface features. Moreover, there is no evidence for pinholes or discontinuity from this characterization. It is clear that although the depth profiles are not identical, there are similarities and differences between the trends that merit special attention.

For the 1.4 nm Au film deposited on top of the cholesterol film, shown in Figure 3-4a, the cholesterol molecular ion and gold signal appear at the surface and start to degrade immediately with erosion. A steady state is reached for the cholesterol molecular ion. Here, $Au_3^+$ is chosen to represent gold simply because there is less interference in that mass range, although similar results are observed for $Au^+$. Samples with thicker gold layers result in distinctly different profiles. As shown in Figure 3-4b and 3-4c, depth profiles of both the 2.8 nm Au/Chol/Si film and the 3.5 nm Au/Chol/Si film contain three distinct regions. First, the gold signal appears without the presence of the cholesterol molecular ion. Second, both gold and cholesterol signals start to rise. Third, after reaching their peak value, both gold and cholesterol signals start to decline, and become similar to the behaviour of the 1.4 nm Au/Chol/Si structure.
Figure 3-4. Depth profiling of cholesterol films with varying thicknesses of Au overlayers. (a) 1.4 nm Au/Chol/Si film; (b) 2.8 nm Au/Chol/Si film; (c) 3.5 nm Au/Chol/Si film; Both (b) and (c) are divided into three regions: Region I in blue colour shows pure gold etching; Region II in pink colour represents the metal-organic interface with rising gold and cholesterol signals; In region III, the trends become similar to those in (a). Both metal and organic material signals start to decrease.

The observations described above are consistent with MD computer simulations of 15 keV C$_{60}$ bombarding an analogous silver-octatetraene hybrid system.$^{39}$ This modeling shows that when the metal overlayer is thick enough, it prevents the underlying organic molecules from disruption by absorbing the incident kinetic energy. Only metal atoms are ejected (Region I in Figure 3-4b and 3-4c). However, as the thickness of the layer is reduced to a critical value, energy deposition begins to occur in the organic phase. Moreover, the primary ion creates a hole in the metal overlayer which allows ejection of the underlying organic molecules via a jetting mechanism. It is this phenomena that we associate with the rising cholesterol signal in region II of Figure 3-4b and 3-4c. Note also that the cholesterol molecular ion intensity is enhanced at the interface and is associated with the presence of the Au film. The thicker Au overlayers are associated with a higher cholesterol intensity. In addition, the gold intensity also increases to approximately the same level as in the beginning of the depth profile, indicating that the Au$_{3}^{+}$ signal variation within the gold overlayer is mainly caused by matrix ionization effects. Presumably, oxides in the surface contaminants and the presence of oxygen in cholesterol increase the ionization probability of gold. The 1.4 nm and 2.1 nm gold films (Region I+II in Figure 3-4b and 3-4c) require $0.7 \times 10^{14}$ and $1.2 \times 10^{14}$ ions/cm$^{2}$ ion fluence, respectively, to remove the film. This fluence corresponds to an average erosion rate of $\sim 2.2$ nm$^{3}$ gold atoms per primary ion. Eventually, the metal overlayer becomes thin enough to allow primary ions to push
metal atoms into the organic layers. These implanted species are presumably associated with the decay of the metal signal (Figure 3-4a and Region III in Figure 3-4b and 3-4c). It is also clear that the presence of the Au overlayer significantly suppresses the cholesterol molecular ion information when compared to the pure cholesterol film.

3.3.3 The Cholesterol/Au/Cholesterol Structure.

The next level of complexity involves creating a sandwich-like sample which consists of a thin embedded Au layer of 1.4 nm thickness. Depth profiling of this sample is possible. After removal of the top cholesterol layer, the C$_{60}$ cluster penetrates through the thin gold layer and continues to etch away the buried organic layer. The cholesterol molecular ion remains detectable through the entire sample, as shown in Figure 3-5. The depth profile can conveniently be divided into two regions. The first region (green) encompasses the top 325 nm cholesterol film, while the second region (yellow) represents the bottom 622 nm layer.
The differences in the behavior of cholesterol within these two regions are clear. First, the absolute signal levels vary significantly. The molecular ion intensity of the buried cholesterol film at the steady state drops by a factor of 40, which is presumably due to the reduction of sputter yield and/or enhancement of fragmentation. The mass spectrum shown in the inset of Figure 3-5 indicates that the cholesterol molecular related information is retained. Second, the
erosion rate of cholesterol is reduced in the buried cholesterol area. From the data shown in Figure 3, we know that it requires \(\sim 2.2 \times 10^{14} \text{ ions/cm}^2\) to etch through a 622 nm cholesterol film. However, with the addition of the 1.4 nm thick gold layer, an ion fluence 4x larger is required to achieve the same erosion. Since the drop in erosion rate mimics the drop in total sputtering yield, the fragmentation must be enhanced in the buried cholesterol film.

The results for the depth profile through a thicker buried gold layer of 2.8 nm are shown in Figure 3-6. For this case, it is possible to extract information from the gold layer. In general, the cholesterol signal in the overlayer behaves in a normal fashion. There is a reduction of intensity at the surface, followed by a steady-state erosion period before reaching the Au layer. A quasi-steady state of the Au layer is observed with ionization enhancements at both metal/organic interfaces. After a short period of etching, the gold layer loses its ability to fully cover the bottom metal-cholesterol interface. Here, the cholesterol signal is observed via the jetting mechanism discussed previously. Significant amounts of Au continue to be mixed into the bottom cholesterol layer. Moreover, the ratio of the integrated area of the Au signal to the integrated area of the cholesterol signal in the bottom cholesterol layer is found to be independent on the thickness of the gold layer. The observation suggests that the amount of implanted Au is about the same in these cases.
The relative amount of the cholesterol fragment ion (m/z = 95) to the cholesterol molecular ion (m/z = 369) is plotted as a function of ion fluence in Figure 3-7. The origin of this characteristic fragment has been described previously. Note that the formation of these two cholesterol ions is simply dependent on proton transfer. Therefore, the presence of gold should not cause variations in ionization of these two ions. The fragment/molecular ion ratio profile exhibits the opposite trend of cholesterol molecular signal as shown in Figure 3-6. At steady state,
the cholesterol molecular ion intensity in the top cholesterol film is higher than it is in the bottom cholesterol film as shown in Figure 3-6. Hence, this ratio profile clearly shows that the presence of the gold layer increases the amount of cholesterol fragmentation. This finding is in agreement with some early static SIMS studies which state that sample metallization induces a dramatic increase of the fingerprint fragment ion yields of polymers. A similar ratio profile is also observed in the sample with 1.4 nm Au layer in-between two cholesterol films, as shown in Figure 3-8.
Figure 3-7. Ratio of the intensity of cholesterol fragment peaks at m/z 95 to the molecular signal of cholesterol at m/z 369 in the sample with 2.8 nm Au layer in-between two cholesterol films. (I) Top cholesterol film region; (II) Cholesterol-gold interface; (III) Gold-cholesterol interface; (IV) Bottom cholesterol film region. The figure is smoothed by a 10-point Adjacent-Averaging algorithm.
Figure 3-8. Ratio of the intensity of cholesterol fragment peaks at m/z 95 to the molecular signal of cholesterol at m/z 369 in the sample with 1.4 nm Au layer in-between two cholesterol films. (I) Top cholesterol film region; (II) Bottom cholesterol film region. The figure is smoothed by a 10-point Adjacent-Averaging algorithm.

3.3.4 Erosion Model.

Within the two separated cholesterol areas of the sandwich-like samples, the molecular ion signal exhibits a similar trend, namely a rapid decay into a steady state value. This behavior has been successfully interpreted in terms of a simple model\textsuperscript{19-20} describing the erosion and fragmentation dynamics in various systems.\textsuperscript{9, 13, 18-20, 50} Here, the same cholesterol molecular ion
displays different signal levels at both the initial state and the steady state. Therefore, the shapes of the molecular depth profiles in the two areas are different, as shown in Figure 3-9. We have employed the erosion dynamics model to investigate some important factors which could lead to the difference.

Figure 3-9. Erosion model fit (red line) for cholesterol molecular ion signal in the depth profile of 2.8 nm Au layer in-between two cholesterol films sample. Measured cholesterol molecular ion signals at the top cholesterol film are represented by black filled-squares (■), while blue filled-squares (■) correspond to cholesters at the bottom cholesterol film.
According to the model, the signal intensity at zero fluence \((S_0)\) decreases exponentially to a steady-state value \((S_{ss})\) as the depth profile evolves. The initial exponential decay in signal intensity is defined by disappearance cross section, described in detail elsewhere. Therefore, an exponential decay is fit to the cholesterol molecular ion signal in the low fluence region via

\[
S(f) = S_{ss} + (S_0 - S_{ss}) \exp \left[ -\left( \frac{Y}{d} + \sigma_D \right) f \right]
\] (3-1)

where \(Y\) is the total sputtering yield volume, \(d\) is the altered layer thickness, \(\sigma_D\) is the damage cross section, and \(f\) is the primary ion fluence. The acquired exponential slope represents the value of what appears in parentheses in the exponent of Eq. (3-1).

In addition, under steady-state conditions, the value of \(S_{ss}\) is related to \(Y\) and primary ion beam induced damage as

\[
S_{ss} = S_0 \frac{Y}{Y + d\sigma_D}
\] (3-2)

The ratio of \(Y\) to \(d\sigma_D\) is termed as “cleanup efficiency, \(\epsilon\),” which describes the ability of the projectile to remove chemical damage produced by its own impact. It is clear that under ideal conditions, \(Y \gg d\sigma_D\), the bombardment debris is removed efficiently during each impact and no chemical damage is accumulated.

Within the above equations, \(S_0, S_{ss}, Y\) and \(f\) are known from experiment. The remaining two variables, \(d\) and \(\sigma_D\), can then be extracted from Eq. (3-1) and (3-2). For our sample, at the top cholesterol layer, the value \(S_0\) is determined by extrapolating the erosion model fit to zero fluence. The fit excludes the first acquired data point, since we notice that the signal level at the first data point is variable, which may arise from different levels of surface contamination. Using, \(S_{ss}/S_0\) as \(\approx 0.5\), \(Y\) as \(\approx 259\) nm\(^3\) per \(C_{60}\) impact as measured for this sample, \(\sigma_D\) and \(d\) are calculated to be \(\approx 5\) nm\(^2\) and \(\approx 35\) nm, respectively. The cleanup efficiency is \(\approx 1.5\). The same method may be applied to calculate those parameters associated with the bottom cholesterol layer. In this case, \(S_0\) is determined by extrapolating the erosion model fit to the point where the cholesterol signal
starts to recover. With the presence of gold, Y for cholesterol is reduced to ~70 nm$^3$ per C$_{60}$ impact. The results show that the $\sigma_D$ value in the bottom cholesterol layer is similar as that in the top layer, however, the value of $d$ increases nearly fourfold. From the depth profile of the bottom cholesterol film, we notice that the cholesterol signal does not maintain a steady state after consuming ~3/4 of its total erosion ion fluence. This result indicates that during erosion of the last 170 nm of the bottom cholesterol film, the supply of undamaged material ends, a finding which is in accordance with the altered layer thickness determined from the erosion dynamics model. Owing to the reduced sputter yield, the cleanup efficiency in the bottom layer is reduced to ~0.1, reaching the lower limit required to obtain useful information from molecular depth profiling.

3.4 Conclusion

Molecular depth profiling of hybrid metal-organic structures is shown to be feasible using 40 keV C$_{60}$ erosion, although the sputter yield, altered layer thickness and cleanup efficiency of the organic molecule is severely degraded by the presence of metal. For the specific case of cholesterol/Au/cholesterol, we find that a Au layer thickness of 1.4 nm or greater induces these deleterious effects. The mechanism for this degradation, as deduced from molecular dynamics computer simulations and our experimental observations, involves the continuous mixing of Au atoms and clusters that are implanted into the organic phase by the eroding cluster beam. Despite these difficulties, however, steady state signals are observed in all layers, and depth profiling of the entire hybrid structure occurs in a meaningful fashion. We anticipate that the protocols developed here will be useful in elucidating the behavior of other hybrid systems using different metal compounds.
It is of interest to speculate about developing approaches to improve the quality of depth profiles for these types of systems, especially when considering the importance of producing reliable protocols for characterizing OLED materials. The major issue appears to be the implantation of metal into the organic phase. Molecular dynamics computer simulations have been employed to provide insight into the experimental observation that characteristic secondary ion intensities are enhanced on organic surfaces coated with metallic nanoparticles. In fact, this strategy is referred to as metal-assisted SIMS (MetA-SIMS), which is particularly effective when employing atomic ion bombardment. A key point associated with the mechanism of this effect is that metal atoms associated with the cluster are sputtered away from the surface with only a small percentage being implanted into the organic sample. In our case, a low energy atomic ion - perhaps 300 eV Ar+ - could be employed to remove the metallic layer without significant metal-implantation, while the C60 projectile could be employed to remove the underlying organic material.

3.5 Acknowledgments

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3.6 References


Chapter 4

Molecular Depth Profiling with Argon Gas Cluster Ion Beams


4.1 Introduction

Secondary ion mass spectrometry (SIMS) has been used as an in-depth characterization method for inorganic materials, particularly semiconductors, for many years.\textsuperscript{1-3} To expand the scope of this technique into the investigation of organic samples, there has been a growing emphasis on the development of cluster ion sources, such as Au\textsubscript{3},\textsuperscript{4,5} Bi\textsubscript{3},\textsuperscript{6} SF\textsubscript{5},\textsuperscript{7} and C\textsubscript{60}.\textsuperscript{4} These probes, particularly C\textsubscript{60}, are more effective than the traditional atomic ion sources, because less chemical damage is accumulated during the interaction of the projectiles with the solid. Molecular depth profiling of a variety of organic materials is now possible,\textsuperscript{8-11} providing an important new characterization modality for SIMS. Recently, argon gas cluster ion beams (Ar-GCIBs)\textsuperscript{12} have generated a great deal of excitement, because they appear to yield better depth resolution and produce less chemical damage than C\textsubscript{60},\textsuperscript{13-16} broadening the scope of this technology even further.

There is flexibility associated with the implementation of GCIBs. For example, the nature of the chemical composition of these clusters can be varied from consisting of water clusters,\textsuperscript{17,18} Ar clusters doped with other species such as CO\textsubscript{2} \textsuperscript{15} and CH\textsubscript{4},\textsuperscript{19} or other molecules
such as N$_2^{20}$ and C$_2$H$_5$OH$^{21-22}$. The idea behind many of these experiments is to increase the ionization efficiency of the target molecules by providing a source of protons for making [M + H]$^+$ ions. Other dopants such as CO$_2$ appear to provide a stabilizing effect on the cluster, yielding better focusing properties for imaging.$^{15}$

At a more basic level, however, it is also possible to vary the cluster size, mass and kinetic energy over wide ranges. There have been attempts to predict how the sputtering yield and the ionization probability depend upon these parameters using both fundamental$^{23}$ and empirical$^{24-25}$ approaches that have helped to begin to organize available data in a consistent fashion. In addition, there have been several Ar-GCIB studies that have focused on how the depth resolution obtained during molecular depth profiling of multilayer structures depends upon cluster size and kinetic energy.$^{26-27}$ To achieve a molecular depth profile in the shortest time, with the best ionization efficiency and with the fewest sputter-induced artifacts, there surely exists a complex interplay between these parameters that has yet to be worked out.

Here, we examine depth profiles of 150 nm spin-cast thin films of trehalose deposited onto Si wafers. The profiles were obtained under various conditions using the Ar-GCIB projectile for sputtering and for analysis. We limited the study to pure Ar-GCIBs to avoid chemical effects associated with reactive species. Trehalose is chosen as a model substrate because it has been extensively used by us to determine appropriate conditions for C$_{60}$ depth profiling and it has been successfully characterized with an erosion dynamics model to measure the thickness of the altered layer at the surface, depth resolution, sputtering yield, and damage cross section.$^{28-30}$ Following this methodology, we examine depth profiles obtained using kinetic energies of 10 and 20 keV with cluster sizes of Ar$_{1000}$, Ar$_{2000}$, Ar$_{3000}$ and Ar$_{4000}$. With this approach, it is possible to quantitatively determine how the important parameters affect the shape and the intensity of the depth profile. Perhaps most importantly, this study suggests that the best situation results from using the highest kinetic energy and the largest possible cluster with an E/n
value slighter larger than 5 eV/atom. This finding is in agreement with recently published studies in the static SIMS regime, which state that high energy and larger clusters are beneficial for increasing the molecular ion yield of organic materials.\textsuperscript{15,18}

4.2 Experimental Section

4.2.1 Material and Sample Preparation

Pre-sliced 5 mm × 5 mm Si wafers (Ted Pella Inc., Reading, CA) were used as substrates for all films. The substrates were piranha etched (3:1 H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2}) for 20 min and rinsed with deionized water three times to remove contaminants from the substrates and make the substrate surface hydrophilic. \textit{(Extreme caution must be exercised when using piranha etch. An explosion-proof hood should be used.)} Trehalose (Sigma-Aldrich Co., St Louis, MO) films were prepared by spin casting 50 µL of a 0.5 M aqueous trehalose solution in 10 µL aliquots onto the cleaned Si wafers. Each aliquot was allowed to spin for 30 seconds at 5000 rpm before the subsequent aliquot was applied. A uniformly colored film with a glassy appearance is normally obtained. The freshly prepared films were immediately transferred to the ToF-SIMS instrument for measurement to minimize surface contamination.

4.2.2 Instrumentation

Sample analysis was performed using a J105 3D Chemical Imager (Ionoptika Ltd., Chandlers Ford, UK), the design of which has been described previously.\textsuperscript{31} The instrument is equipped with a 40 kV C\textsubscript{60} primary ion beam and a 20 kV Ar-GCIB system. Unlike conventional ToF-SIMS instruments that operate alternatively between data acquisition cycles in pulsed mode
and erosion cycles in DC mode, this J105 instrument uses a continuous primary ion beam to generate a continuous stream of secondary ions. The secondary ions are collected in a buncher and then accelerated into a ToF analyzer. This design allows for continuous data collection and ensures that no sample information is lost. In this study, trehalose films were first investigated with a 40 keV \( \text{C}_{60}^+ \) ion beam. SIMS images of 64 × 64 pixels and corresponding mass spectra were collected from an area of 500 \( \mu \text{m} \times 500 \mu \text{m} \) with an ion fluence of \( \sim 1.3 \times 10^{12} \text{ions/cm}^2\) per image. Depth profiles and ion intensity measurement were collected from the central 13 × 13 pixels of each image, thus eliminating the crater edge effects. The gathered sputter yield and beam-induced chemical damage information were compared to earlier measurements that were carried out on a traditional ToF-SIMS instrument. The design and characteristics of the 20 kV Ar-GCIB system have been described in detail elsewhere. In the Ar-GCIB experiments, the cluster size distribution can be checked by pulsing the ion beam and measuring the flight time of the primary ions between the pulser and the sample stage, as shown in Figure 4-1. From the known flight distance and kinetic energy, the flight time spectrum can be used to determine the average cluster size of the beam and a Wien filter is used for selecting cluster ions of the desired size. In this study, we have \( \text{Ar}_{1000}, \text{Ar}_{2000}, \text{Ar}_{3000} \) and \( \text{Ar}_{4000} \) cluster ions at kinetic energies of 10 and 20 keV, respectively. For each gas cluster, the primary ion beam current was measured using a Faraday cup and the beams used were all adjusted to provide \( \sim 90 – 120 \text{pA} \) beam currents. The experimental setup was the same as described above except that the ion fluence applied here was higher, \( \sim 5.5 \times 10^{12} \text{ions/cm}^2 \) per image. Note that in this study all of the depth profiling experiments were performed in negative ion mode at room temperature and no sign of sample charging was noticed.
Figure 4-1. Measured (a) flight time spectra and (b) cluster size distributions of 10 kV and 20 kV Ar$_{n}^{+}$ ion beams.
4.2.3 Atomic Force Microscopy (AFM) Measurements

The trehalose film thickness was measured by an AFM (Nanopics 2100, KLA-Tencor, San Jose, CA, USA). This unique type of AFM offers a maximum scanning area of 0.8 mm × 0.8 mm in contact mode, allowing a convenient one-step measurement of the entire eroded crater. An AFM image of a trehalose film eroded by a 40 keV C_{60}^{+} ion source is illustrated in Figure 4-2. The AFM measurement indicates a 0.7 nm root-mean-square (rms) film roughness and a 150 nm film thickness. Note that the erosion rate of Si is significantly slower than that of trehalose. Therefore, the removed Si thickness should be negligible. This AFM was also employed to determine sputtering yields via the formation of a wedge-shaped crater.\textsuperscript{32}
Figure 4-2. AFM images of a trehalose film bombarded by a 40 keV C\textsubscript{60}\textsuperscript{+} ion beam. Image a shows the bombarded region of the film in three-dimensions. Image b shows that the unbombarded region of the film has a 0.7 nm r.m.s roughness. Image c shows a line scan taken across the bombarded region of the film, which indicates that the film has a thickness of 150 nm.

4.3 Results and Discussion

4.3.1 Negative Secondary Ion Depth Profiles of Trehalose Films Bombarded by C\textsubscript{60}

The negative secondary ion depth profile for a 150 nm trehalose film on Si bombarded by 40 keV C\textsubscript{60}\textsuperscript{+} is shown in Figure 4-3a, where the trehalose molecular ion [M – H] at m/z 341 and substrate signal at m/z 168 for Si\textsubscript{6}\textsuperscript{-} are plotted as a function of C\textsubscript{60}\textsuperscript{+} ion fluence. A total ion fluence of ~1.05×10\textsuperscript{14} ions/cm\textsuperscript{2} is used to etch through the film before reaching the Si substrate. The sputter yield volume of trehalose is calculated from the known fluence and film thickness.
and is presented in units of sputtered material volume per projectile ion. In this case, one C_{60}^+ primary ion removes 143 nm$^3$ of material, a value consistent with earlier measurements.\textsuperscript{30} In addition, an erosion model developed by Cheng et al.\textsuperscript{29} is used to fit the trehalose molecular ion decay profile to quantify the ion beam bombardment induced chemical damage, as shown in Figure 4-3b. According to the model, the dependence of the secondary ion signal $S$ on ion fluence $f$ is governed by

$$S(f) = S_{ss} + (S_0 - S_{ss}) \exp \left[ -\left( \frac{Y}{d} + \sigma_D \right) f \right] \quad (4-1)$$

where $S_0$ is the signal intensity at zero fluence, $S_{ss}$ is the signal intensity at steady state, $Y$ is the sputter yield volume, $d$ is the altered layer thickness, $\sigma_D$ is the damage cross section, and $f$ is the primary ion fluence. The value of $S_{ss}$ is also related to $Y$ and primary ion beam induced damage as

$$S_{ss} = S_0 \frac{Y}{Y + d\sigma_D} \quad (4-2)$$

The two variables associated with chemical damage, $d$ and $\sigma_D$, can then be extracted from Eq. (4-1) and (4-2). For our sample, $d$ and $\sigma_D$ are calculated to be $\sim$25 nm and $\sim$30 nm$^2$, respectively. These values are slightly higher than our earlier report,\textsuperscript{30} which is probably associated with the intrinsic water content of the deposited films, as explained by Lu et al.\textsuperscript{33} Trehalose films with less water content have a larger ratio value between the initial and steady state signal, indicating an enhanced damage cross section during the ion bombardment, which is the case for the trehalose films investigated in this study. Note that in the previous work, trehalose thin films were all analyzed in positive ion mode, where the trehalose molecular ion peak [M + H]$^+$ at m/z 343 is of low intensity and two most abundant trehalose molecule related peaks are quasi-molecular ions [M-OH]$^+$ at m/z 325 and the sodium adduct [M + Na]$^+$ at m/z 365. There is less interference of trehalose molecular ion information in negative ion mode, where the only predominant peak of trehalose molecule is [M – H] at m/z 341.
Figure 4-3. (a) Depth profile of a 150 nm trehalose film obtained with a 40 keV $\text{C}_{60}^+$ ion beam. The secondary ion intensities of the trehalose molecular ion peak at m/z 341 $[\text{M} - \text{H}]$ and substrate signal at m/z 168 for $\text{Si}_6^-$ are plotted as a function of $\text{C}_{60}^+$ ion fluence. (b) Erosion model fit (red line) for the trehalose molecular ion signal in the depth profile of a 150 nm trehalose film bombarded by 40 keV $\text{C}_{60}^+$. 
4.3.2 Negative Secondary Ion Depth Profiles of Trehalose Films Bombarded by Ar-GCIBs

Eight negative secondary ion depth profiles of the trehalose films obtained using different kinetic energies (E) and Ar cluster sizes (n) are presented in Figure 4-4. Depth profiles shown in Figure 4-4, panels a-c and e exhibit a similar shape to the one obtained with C\textsubscript{60}\textsuperscript{+}, namely the trehalose molecular ion falls quickly into a steady state value. The depth profiles shown in Figure 4-4, panels d and f-h, however, are distinctly different. In these cases, the trehalose signal initially decreases and then slowly increases to reach a steady state. Note that these unusual depth profiles appear only when E/n ≤ 5 eV/ atom. Speculation about the reasons behind this behavior is discussed below.
Figure 4-4. Depth profiles of the 150 nm trehalose films obtained with 10 kV and 20 kV Ar⁺ ion beams.
Values of the trehalose sputter yield volume at different kinetic energies and Ar cluster sizes are summarized in Table 4-1. These results clearly indicate that the sputter yield volume is affected by a combination of kinetic energy and Ar cluster size. Briefly, as shown in Figure 4-5, the trehalose sputter yield volume decreases with increasing Ar cluster sizes at a given kinetic energy. Moreover, for the same cluster size, the sputter yield volume increases with increasing kinetic energy. Seah\(^2\) has introduced a universal equation for Ar gas cluster sputtering yields to organize the experimental data and to allow rational comparisons to be made. The universal equation that describes the relationship between sputter yield volume per atom \((Y/n)\) and the kinetic energy per atom \((E/n)\) is defined as

\[
\frac{Y}{n} = B \frac{(E/An)^q}{[1 + (E/An)^q]^{q-1}} \quad (4-3)
\]

where the parameters B, A and q can be determined by fitting Eq. (4-3) to the experimental data.

Our results show that \(Y/n\) exhibits a nearly linear dependence on \(E/n\) and the parameters B, A and q have values of 0.018 nm\(^3\), 4.8 eV and 2.0, respectively. These values are close to the ones reported for other organic materials.\(^{24,34}\)

---

**Table 4-1.** Measured Trehalose Sputter Yield Volume for Different Kinetic Energies and Cluster Sizes of Ar-GCIBs.

<table>
<thead>
<tr>
<th>Clusters Size</th>
<th>(\text{Ar}_{1000}^+)</th>
<th>(\text{Ar}_{2000}^+)</th>
<th>(\text{Ar}_{3000}^+)</th>
<th>(\text{Ar}_{4000}^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 kV</td>
<td>61 nm(^3)</td>
<td>53 nm(^3)</td>
<td>45 nm(^3)</td>
<td>39 nm(^3)</td>
</tr>
<tr>
<td>10 kV</td>
<td>24 nm(^3)</td>
<td>20 nm(^3)</td>
<td>15 nm(^3)</td>
<td>10 nm(^3)</td>
</tr>
</tbody>
</table>
Using a more fundamental approach, Paruch et al.\textsuperscript{23} have recently suggested taking cohesive energy ($U_0$) of the analyte into consideration. Therefore, our data was replotted as $y/(E/U_0)$ versus $(E/U_0)/n$, as shown in Figure 4-6b. Note that $y$ is the sputter yield in units of sputtered material molecules per projectile ion and $U_0$ is defined as the energy needed to free a molecule from the substrate. For trehalose, it is mainly the intermolecular hydrogen bond attractions that hold the substance together, and its cohesive energy is estimated to be $\sim$0.8 eV for a trehalose molecule. The estimation is based on the assumption that the cohesive energy is equal
to the heat of sublimation. The plot shows that in the low \((E/U_0)/n\) portion, the sputter yield is low and increases with increasing energy; while when it passes the threshold value \(((E/U_0)/n = 5/U_0)\), the sputter yield remains almost constant. The low sputter yield in the low \((E/U_0)/n\) portion is probably associated with the unusual depth profiles shown in Figure 4-d and f-h. We will come back to this issue below.
Figure 4-6. (a) Dependence of Y/n on E/n for Ar$_n^+$ cluster bombardment of trehalose films. The red line represents a fit to the universal equation (Eq. 4-3) for argon gas cluster sputtering yields proposed by Seah.\textsuperscript{24} (b) Dependence of y/(E/U$_0$) on (E/U$_0$)/n for Ar$_n^+$ cluster bombardment of trehalose films.
The next step is to gain a better understanding of the molecular sputtering process of the trehalose films under Ar\textsubscript{n}\textsuperscript{+} cluster bombardment, specifically regarding the creation of chemical damage. The erosion model mentioned earlier can be successfully applied to those normal trehalose molecular ion depth profiles shown in Figure 4-4a-c and e. The calculated d and \sigma\textsubscript{D} values are \~ 5 nm and 17 nm\textsuperscript{2}, 17 nm and 17 nm\textsuperscript{2}, 13 nm and 19 nm\textsuperscript{2} and 10 nm and 23 nm\textsuperscript{2} for 10 kV Ar\textsubscript{1000}\textsuperscript{+}, 20 kV Ar\textsubscript{1000}\textsuperscript{+}, 20 kV Ar\textsubscript{2000}\textsuperscript{+}, and 20 kV Ar\textsubscript{3000}\textsuperscript{+}, respectively. It appears that for the same cluster (Ar\textsubscript{1000}\textsuperscript{+}), higher kinetic energy yields a higher d value, whereas \sigma\textsubscript{D} remains nearly constant. Moreover, the results show that the d value is decreasing with increasing cluster size at 20 kV (Ar\textsubscript{1000}\textsuperscript{+} < Ar\textsubscript{2000}\textsuperscript{+} < Ar\textsubscript{3000}\textsuperscript{+}), whereas \sigma\textsubscript{D} is increasing with increasing cluster size. It seems that \sigma\textsubscript{D} is related to the actual size of the cluster. Therefore, a larger cluster will have a higher \sigma\textsubscript{D} value. The d value is mainly associated with E/\textit{n}. At the same kinetic energy, a larger cluster has a lower value of E/\textit{n}, so the energy is deposited closer to the surface which results in a smaller d value.

The intensity of the first data point of each depth profile acquired with Ar\textsubscript{n}\textsuperscript{+} is shown in Figure 4-7 as a function of E/\textit{n}, and one finds that Ar\textsubscript{n}\textsuperscript{+} with a smaller E/\textit{n} value has a smaller fragment to molecular ion ratio, which indicates less damage. This finding can be further confirmed from the trehalose molecular ion depth profiles shown in Figure 4-4, where the span between trehalose molecular ion intensity at the first data point and the steady state becomes narrower as the E/\textit{n} value decreases. Note that the signal level of the first acquired data point on the freshly prepared trehalose film is quite reproducible and no significant fluctuation is observed. In principle, the unusual shape of the profiles shown in Figure 4-4d and f-h can also be interpreted in terms of the erosion dynamics model, if the assumption of a constant total sputter yield is dropped.\textsuperscript{37} If the yield variation is slow, the system will follow Eq. (4-1) into a quasi-steady-state regime, where the molecular ion signal follows a gradual change of \textit{Y} via Eq. (4-2). The observed signal rise would then correspond to an increasing sputter yield, which leads to a
faster removal of the fragmentation debris produced by a projectile impact. As a consequence, the accumulated damage should be reduced and one should observe a decreasing signal of fragments as compared to the molecular ion. The ratio of the intensity of the trehalose fragment at m/z 179 to the trehalose molecular ion at m/z 341 as a function of primary ion fluence is displayed in Figure 4-8. It is evident that the ratio increases with increasing fluence, indicating the buildup of more damage while the molecular ion signal increases. To examine the role of possible sputter yield variations further, a wedge crater was eroded as shown in Figure 4-9. Briefly, the wedge crater was created by repeating the raster as many times as there are pixels in one line or lines in one raster frame. In each of these raster frames, one more line was skipped. In our case, the beam was scanned across a 500 μm × 500 μm area using a 64 × 64 pixel raster. The raster was repeated 64 times, scanning 64 lines in the first frame, 63 lines in the second frame, etc., until the last scan was only over a single line. One set of these wedge frames therefore consists of 64 rasters. The dwell time on each pixel was set to about 20 μs, which is the minimum dwell time that ensures stable beam position on a pixel. The number of wedge frame sets during a sputter erosion step was calculated such that the set total sputtering time in an erosion cycle was reached. As outlined in detail elsewhere, a fluence-dependent sputter yield variation manifests itself as a curved crater bottom in such an experiment. Because all craters observed in Figure 4-9 exhibit a straight line profile, the unusually shaped depth profiles are not caused by a variation in sputter yield.
Figure 4-7. Dependence of the ratio of the intensity of the trehalose fragment at m/z 179 to the trehalose molecular ion at m/z 341 from the first data point of each depth profile as a function of E/n.
Figure 4-8. Ratio profiles of the intensity of the trehalose fragment (m/z 179) to the intensity of trehalose molecular ion (m/z 341) as a function of ion fluence under different Ar$_n^+$ bombarding conditions.
Figure 4-9. AFM image of the wedge crater eroded into a 150 nm trehalose film by (a) a 20 kV Ar$^{2000+}$ ion beam and (b) a 10 kV Ar$^{2000+}$ ion beam. Note the slope of the bevel remains as a straight line before the crater reaches the Si substrate.

Now, the remaining question is what factor leads to the two different shapes of trehalose molecular ion depth profiles shown in Figure 4-4. If sputter yield changes are excluded possible explanations for the observed increase of the molecular ion signal are that there is an increasing survival probability against fragmentation or that there is an enhanced ionization of the sputtered molecules. In order to examine this further, the ratio of the intensity of two characteristic trehalose fragments (m/z 143 to m/z 161) is plotted as a function of ion fluence for each Ar$_n^+$ bombarding condition, as presented in Figure 4-10. For those normal trehalose molecular ion depth profiles shown in Figure 4-4a-c and e, this ratio remains virtually constant, see Figure 4-10a-c and e, which confirms that a true steady state is reached under these conditions. Note that
for all of these conditions, \( E/n > 5 \text{ eV/atom} \). However, for the unusual depth profiles shown in Figure 4-4d and f-h, the ratio between the two fragments increases throughout the same fluence interval where the molecular ion signal increases, until it finally reaches a steady state, as shown in Figure 4-10d and f-h. In connection with Figure 4-8, this finding indicates that the observed increase of the molecular ion signal is accompanied by increasing fragmentation as well. Hence, this signal increase must be attributed to an increasing ionization probability of the emitted molecules. Note that the mass difference (\( \Delta m \)) between the two fragments is 18, which indicates that there could be a water content change during the depth profiling. The extra water can cause trehalose ionization probability to increase during the experiments.\(^{33}\)

Figure 4-10. Ratio profiles of the intensity of two characteristic trehalose fragments (m/z 143 to m/z 161) as a function of ion fluence under different Ar\(_n^+\) bombarding conditions.
Finally, it is possible to acquire information about the useful yield of trehalose under different \( \text{Ar}_n^+ \) bombarding conditions. Here, the useful yield is defined as the ratio of the number of detected molecular ions to the number of the sputtered molecule equivalents, and its value is estimated via

\[
\text{Useful Yield} = \frac{S_1}{[f \times A \times y]} \quad (4-4)
\]

where \( S_1 \) is the molecular ion signal intensity at the first data point, \( f \) is the primary ion fluence used to take the spectra, \( A \) is the data analysis area, and \( y \) is the sputter yield in units of sputtered molecule equivalents per projectile ion. Note that the amount of signal transmission loss in the mass spectrometer is not considered here. As shown in Figure 4-11, the useful molecular ion yield of trehalose increases with increasing kinetic energy but remains almost the same with increasing Ar cluster sizes at a given kinetic energy, indicating that the useful yield is dependent only upon kinetic energy.
Figure 4-11. Dependence of useful molecular ion yield of trehalose on E/n for Ar\textsubscript{n}\textsuperscript{+} cluster bombardment of trehalose films.

4.4 Conclusion

The effect of projectile size and kinetic energy of Ar-GCIBs on the molecular depth profiling of trehalose thin films has been investigated with the purpose of finding the optimal cluster size and cluster energy to improve the quality of depth profiles for organic materials. Our results suggest that when E/n > 5 eV/atom, normal depth profiles could be obtained with relatively high sputter yield, whereas when E/n ≤ 5 eV/atom, unusual depth profiles, which show
ionization efficiency variation, are acquired with low sputter yield. However, this observation does not imply that E/n values should be as high as possible. In fact, the E/n value should be kept above but close to the threshold value (5 eV/atom in our case), because ion beam bombardment induced chemical damage is limited.

Although this study has focused upon using trehalose as a model system, we believe the conclusions can be generalized for many other organic materials. In preliminary studies, as shown in Figure 4-12, we have found similar behavior for other organic thin films including sucrose, dipalmitoylphosphatidylcholine (DPPC), and Gly-Gly-Tyr-Arg (GGYR). It will be of interest to determine how much the threshold value for creating depth profiles without artifacts changes with molecule type. In general, however, our study shows that high kinetic energy increases the useful molecular ion yield of trehalose. Hence, a combination of high kinetic energy and large cluster size will ultimately optimize molecular depth profiling experiments with SIMS.
Figure 4-12. Depth profiles of secondary ion intensity versus 20 kV Ar$_{4000}^+$ ion fluence of (a) sucrose film. The sucrose film was prepared with a 0.5 M aqueous sucrose solution; (b) DPPC film. The DPPC film was prepared with a 0.5 M DPPC in chloroform solution; (b) GGYR film. The GGYR film was prepared with a concentration of 1:100 in trehalose, where the concentration of the trehalose solution is 0.5 M.

4.5 Acknowledgement

We appreciate the contributions of Dr. Hua Tian in optimizing the instrumentation in these studies. This study was financially supported by National Institutes of Health Grant 9R01 GM113746-20A1. In addition, infrastructure support from the National Science Foundation under Grant CHE-0908226 and by the Division of Chemical Sciences at the Department of Energy Grant DE-FG02-06ER15803 is acknowledged.

4.6 References


Chapter 5

Chemical Imaging of Interfacial Reactions in Ionic Liquids with ToF-SIMS

This chapter has been adapted from Kan Shen and Nicholas Winograd, “Chemical Imaging of Interfacial Reactions in Ionic Liquids with ToF-SIMS”, manuscript in preparation.

5.1 Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a well-known surface analysis technique that maps detailed chemical information of the surface at a submicron lateral resolution. With the development of cluster primary ion beams, molecular depth profiling of polymer and organic thin films has become common.\(^1\,^6\) With the power of chemical imaging and depth profiling, it seems reasonable to speculate that SIMS will develop into a tool for characterization of chemical synthesis or biological samples: to unveil the identity and structure information of reaction product embedded in a reaction medium or to map the distribution of biomolecules in biological systems. However, this is not the case yet. SIMS has not been reported as a tool that can look directly into chemical reactions; although there are a few attempts to investigate single cells with SIMS, the samples have to be chemically fixed\(^7\,^8\) or frozen\(^9\,^12\). These difficulties are due to that the analytes of interest oftentimes do not live in a vacuum-compatible environment, which are necessary for SIMS analysis.

To go beyond the limitation of vacuum conditions, there are two possible options. One is to use desorption electrospray ionization (DESI)\(^13\), a complementary technique to SIMS, that allows characterization of samples at ambient pressure. Direct analysis of liquid samples by DESI has also been reported.\(^14\) However, DESI cannot provide the same spatial resolution as
SIMS does, which prevents its use for imaging on the cellular and subcellular level. The other option is to use ionic liquids. Ionic liquids are salts in which the ions are weakly coordinated with each other. Two unique features of these liquids are that their properties can be tuned by proper selection of the component ions and they have negligible vapor pressure. The combination of SIMS and ionic liquids can be mutually beneficial: Ionic liquids can be used as reaction medium and/or matrix to preserve analytes of interest in vacuum condition for SIMS analysis, which can greatly extend the scope of SIMS applications; SIMS can direct analyze samples in ionic liquids without the need for separation or purification. However, currently, ionic liquids have only been investigated as a matrix to enhance the signals in SIMS experiments.

In this study, we perform depth profiling and chemical imaging with SIMS to detect reactions which occur in ionic liquids. The model system is comprised of TiO$_2$ microspheres with diameters of 5-30 µm formed by interfacial sol-gel reactions in an ionic liquid. The results show that 40 keV C$_{60}^+$ is able to erode through the reaction medium and map the distribution of those embedded TiO$_2$ microspheres. In addition, the results also show that SIMS is capable of detecting surface modification of these microspheres as well as probing into the interior of the spheres. In general, we have developed a protocol for direct analysis of reactions that use ionic liquids as an embedding medium with SIMS.

5.2 Experiential Section

5.2.1 Preparation of Hollow TiO$_2$ Microspheres.

A slightly modified version of the hollow metal oxide microspheres synthesis method described by Nakashima et al. was employed in preparation of the hollow TiO$_2$ microspheres. A schematic illustration of the hollow TiO$_2$ microspheres formation process is shown in Figure 5-
1. In brief, 1 mL of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF$_6$) (Matrix Scientific, Columbia, SC) was added into a 20 mL glass scintillation vial, dried in an oven at 120 °C for 2 h and then allowed to cool down to room temperature in a desiccator prior to use. 0.2 mL anhydrous toluene solution containing 0.3 M titanium tetra-n-butoxide (Ti(OBu)$_4$) (Acros Organics, Fair Lawn, NJ) was then added dropwise into the ionic liquid under vigorous stirring at room temperature. The mixture was stirred at a rate of 800 rpm for 5 min. Hollow TiO$_2$ microspheres with a diameter of 5-30 µm were formed via interfacial hydrolysis and condensation reactions between Ti(OBu)$_4$ dissolved in toluene droplets and trace water adsorbed in BMIM-PF$_6$.21
Figure 5-1. Schematic of the hollow TiO₂ microspheres formation process. (a) Structure of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. BMIM-PF₆ served as the reaction medium in this study; (b) Ti(OBu)₄ dissolved in toluene droplets reacted with trace water adsorbed in BMIM-PF₆ at the interface. Hollow TiO₂ microspheres were obtained via the interfacial sol-gel reaction;²¹ (c) An optical micrograph of the synthesized TiO₂ microspheres.
5.2.2 Preparation of Fluorescent Dyed Hollow TiO$_2$ Microspheres.

For synthesis of fluorescent dyed hollow TiO$_2$ microspheres,$^{21}$ 1 mL of BMIM-PF$_6$ was first treated in the same way as described above. The glass vial containing the ionic liquid was then wrapped in aluminum foil and kept in the dark. Next, 0.1 mg fluorescein isothiocyanate (FITC) (Fisher Scientific, Pittsburgh, PA) and 0.2 mL anhydrous toluene solution containing 0.3 M Ti(OBu)$_4$ was added sequentially into the ionic liquid under vigorous stirring at room temperature. The resulting mixture was stirred at a rate of 800 rpm for 5 min. Hollow TiO$_2$ microspheres coated with fluorescent dyes were formed, as shown in Figure 5-2a. A possible binding mechanism, as depicted in Figure 5-2b, is that the carboxyl group of FITC dyes can simultaneously interact with the surface of TiO$_2$ microspheres by bidentate chelation or bridge as the hollow TiO$_2$ microspheres form.$^{22,23}$
Figure 5-2. Surface modification of hollow TiO$_2$ microspheres by fluorescent dye FITC: (a) a fluorescent micrograph of the FITC dyed hollow TiO$_2$ microspheres. The image was taken with an Olympus IX70 fluorescence microscope; (b) the binding mechanism of FITC dye with the surface of hollow TiO$_2$ microspheres.$^{22,23}$
5.2.3 SIMS and SEM Analyses.

Sample analysis was performed using a J105 3D Chemical Imager (Ionoptika Ltd., Southampton, U.K.), the design of which has been described in detail elsewhere. The instrument is equipped with a 40 kV C\textsubscript{60} primary ion beam. Singly charged C\textsubscript{60}\textsuperscript{+} primary ions were selected by a Wien filter and were focused to provide approximately 1 pA beam current with a 1 µm beam diameter. The beam was directed toward the sample surface at an angle of 40º relative to the surface normal. All the experiments were performed at room temperature (RT).

To characterize synthesized microspheres, 10 µL of the reaction solution was spread onto a 5 mm × 5 mm Si wafer by spin coating. The C\textsubscript{60}\textsuperscript{+} ion beam was used to depth profile through a small region of the sample (approximately 100 µm × 100 µm) and SIMS images of 256 × 256 pixels and corresponding mass spectra were recorded for each layer. No sample charging was noticed in the positive SIMS mode and the acquired mass spectra have a mass resolution of 5000 (m/Δm).

In addition, the instrument is equipped with an electron detector, allowing the acquisition of scanning electron microscope (SEM) images of 512 × 512 pixels. For the SEM measurement, 10 µL of reaction solution was first diluted 100-fold with methanol and then centrifuged at 2000 rpm for 5 minutes. The resulting pellet was resuspended in 100 µL methanol and then spin cast onto a 5 mm × 5 mm Si wafer. This sample preparation procedure removes most of the IL and helps identify the locations of the microspheres.
5.3 Results and Discussion

5.3.1 SEM Image of TiO$_2$ Microspheres.

A representative SEM image of the TiO$_2$ microspheres synthesized in the ionic liquid is shown in Figure 5-3. It is clear that spheres in a range of discrete sizes from 5 µm to 30 µm could be detected with the C$_{60}^+$ primary ion beam. Note that the edges of the spheres appear brighter than the rest parts in the SEM image. The phenomenon is known as the edge effect, where more secondary electrons could escape from the edges of an sample than from flat areas.$^{25}$ The inset SEM image shows a sphere with a hole in it. Note that there are no secondary electrons coming out of the hole. This observation suggests that the microsphere has a hollow core.$^{21}$

Figure 5-3. SEM image (512 × 512 pixels) of the synthesized TiO$_2$ microspheres taken by 40 keV C$_{60}^+$ primary ion source. The inset shows a TiO$_2$ microsphere with a hole on its shell.
5.3.2 Visualization of TiO\textsubscript{2} Microspheres Embedded in BMIM-PF\textsubscript{6} with Image Depth Profiling of ToF-SIMS.

With the 40 keV C\textsubscript{60}\textsuperscript{+} primary ion beam, a total ion fluence of $1.0 \times 10^{15}$ ions/cm\textsuperscript{2} was applied to depth profile though an area of 70 µm × 70 µm. The data set contains 20 images in total and all the images were taken at 256 × 256 pixels. The mass spectra corresponding to the first and the last image are shown in Figure 5-4 and they look distinctly different. At the beginning, the mass spectrum is dominated by peaks at m/z 83 and 139, which are the characteristic peaks of BMIM-PF\textsubscript{6}. There is no sign indicating the existence of TiO\textsubscript{2} microspheres. However, after etching 20 layers, the intensity of the IL signals was decreased to a great extent. Peaks at m/z 48, 64, 128, 144, and 208 for TiO\textsubscript{2} and peaks at m/z 112 and 168 for Si substrate become the main components of the mass spectrum.
Figure 5-4. Image depth profiling though a region of interest with a total ion fluence of $1.0 \times 10^{15}$ ions/cm$^2$ C$_{60}^+$ bombardment: (a) and (b) are the mass spectra correspond to the first and the last image, respectively.
A chemical image of m/z 139 in red for BMIM\(^+\), m/z 144 in green for Ti\(_2\)O\(_3\)\(^+\) and m/z 168 in blue for Si\(_6\)\(^+\) was then constructed for each layer to help visualize the change of the distributions as a function of C\(_{60}\)\(^+\) ion fluence, as shown in Figure 5-5. The results show that at the beginning, the reaction solution was spread over the substrate, and the majority of the Si substrate was covered by IL. Through erosion, BMIM-PF\(_6\) was gradually etched away and Ti\(_2\)O\(_3\)\(^+\) signal started to appear from the reaction medium. At the end of the depth profile, Ti\(_2\)O\(_3\)\(^+\) signal was only distributed in four spherical-shaped areas and the rest of the image area was Si substrate signal. IL around the microspheres has been almost completely etched away. In addition, as seen in Figure 5-6, the distribution of m/z 48 for Ti\(^+\), m/z 64 for TiO\(^+\), m/z 128 for Ti\(_2\)O\(_2\)\(^+\), and m/z 208 for Ti\(_3\)O\(_4\)\(^+\) were colocalized with that of m/z 144 for Ti\(_2\)O\(_3\)\(^+\), which confirms that the microspheres are made of TiO\(_2\).
Figure 5-5. RGB overlay of BMIM$^+$ (m/z 139, red), Ti$_2$O$_3$$^+$ (m/z 144, green) and Si$_6$$^+$ (m/z 168, blue) to show the change of their distributions during the depth profiling process. All images are taken from a 70 µm × 70 µm area.
5.3.3 Hollow Core of the TiO$_2$ Microsphere.

The next step is to investigate the internal structure of the TiO$_2$ microsphere. The bottom sphere of the four available ones, as shown above, is chosen to be the target of the analysis. Since it is known that the sputtering rate of inorganic materials is much slower than that of organic materials, the 40 keV C$_{60}^+$ ion beam was chosen to etch through a small part (5 µm × 5 µm) of the sphere in DC mode and the etching process was stopped immediately after the disappearance of Ti$_2$O$_3^+$ signal. The total etching ion dose applied is approximately $10^{17}$ ions/cm$^2$. Note that from the optical image shown in Figure 5-1c, it is observed that the shell thickness of the sphere
is approximately 1/10 of the diameter of the sphere. In this case, the diameter of the sphere is around 20 µm. Therefore, the thickness of the shell is approximately 2 µm and the average erosion rate of the TiO₂ microsphere is approximately 2 nm³/C₆₀⁺ primary ion, a value close to the reported erosion rates of some other inorganic materials.²⁷

In addition, three consecutive images were taken before and after the etching process with the same ion fluence, approximately 10¹³ ions/cm² per image. One image of each is shown in Figure 5-7, along with the Ti₂O₃⁺ signal level in the bombarded area. The data in Figure 5-7 shows that the Ti₂O₃⁺ signal was in a steady state before the bombardment. It rules out the possibility that the Ti₂O₃⁺ signal will decay with erosion and demonstrates that SIMS is able to analyze a spherical structure in a layer by layer fashion if it has a solid core structure. However, after the bombardment, the signal from Ti₂O₃⁺ disappeared in the crater area. It seems reasonable to speculate that the beam started to hit the shell on the opposite side, but the emitted secondary ion cannot be extracted out of the core as a result of the presence of the top of the shell. This observation reinforces that the microsphere has a hollow core.

Issues and concerns inherent in this method lie in the complexities of analyzing 2D images of a 3D object, an example is shown in Figure 8. In which, Figure 8a shows the SIMS image of an intact TiO₂ microsphere, where m/z 128 for Ti₂O₂⁺ and m/z 168 for Si₆⁺ are represented in green and blue, respectively. Note that the 2D SIMS image was distorted that the TiO₂ sphere was elongated into an egg-shape as a result of the incoming beam angle. Next, as described above, the ion beam was left in DC mode to erode a small hole on the surface of the sphere. A SIMS image of the resulting TiO₂ microsphere was taken, as shown in Figure 8b. Now part of the ion beam could go through the hole and hit the inside wall of the sphere, but the resulting secondary ions cannot escape since the extraction field was blocked. As a result, there is a black hole in the TiO₂ sphere image. Finally, the DC beam was used to continue the etching process and as a result, part of the material was ripped off from the sphere and a previous shadow
area (marked in pink) was revealed and exposed for analysis, as shown in Figure 8c. A 256 pixel SIMS image was taken afterwards. The interesting finding here is that the peak of m/z 128 for Ti$_2$O$_2^+$ split into two regions, the distribution of the left side of the peak was still localized in the sphere region, same as in Figure 8b. However, the distribution of the right side of the peak was localized in the black hole area. The speculation for the origin of the splitting of the peak is that during the DC etching, part of the eroded materials fell into the flat pink area. Therefore, the flight time of the same material would be slightly different due to the sample height difference. Overall, this example shows that the 2D image of a 3D object no longer delivers the accurate information of the sample in terms of the exact spatial distributions of chemicals. It is clear that this kind of problem needs to be addressed for the advancement of this technique and its applications.
Figure 5-7. Ti$_2$O$_3^+$ signal level in marked region of interest (ROI) before and after the bombardment. The ROI is 5 µm × 5 µm.
Figure 5-8. Schematic illustration of acquiring SIMS images of TiO$_2$ microspheres. (a) an intact microsphere; (b) a microsphere with a hole on it. Ti$_2$O$_2^+$ (m/z 128, green) and Si$_6^+$ (m/z 168, blue) were used to construct the SIMS images for (a) and (b); (c) a cracked microsphere. The pink color marked the newly revealed area. The inset image shows the split of the Ti$_2$O$_2^+$ (blue) peak in comparison to the one obtained in condition (a) (black). Left and right part of the split m/z 128 peak (green and red) and Si$_6^+$ (m/z 168, blue) were used to construct the SIMS image.

5.3.4 Surface Modified TiO$_2$ Microspheres.

Finally, it is of great interest to characterize the fluorescent dyed hollow TiO$_2$ microspheres. Similar to the sample transfer procedure described above, 10 µL of its reaction solution was spin-cast onto a 5 mm × 5 mm Si wafer, following which the substrate was rinsed with methanol three times. The extra washing step was used to remove as much IL as possible, since now the focus of the study is simply the surface of the microspheres embedded within the IL. An ion fluence of $2.0 \times 10^{13}$ ions/cm$^2$ was used to take the SIMS image of the fluorescent dyed sample. The results shown in Figure 5-9 clearly demonstrate that SIMS imaging can be used directly to detect the fluorescent dye present on the TiO$_2$ microspheres. The distribution of the molecular ion for FITC dye at m/z 390 is colocalized with that of Ti$_2$O$_3^+$ at m/z 144. As shown in Figure 5-2b, upon contacting with the TiO$_2$ microspheres, the FITC dye could only react at the surface of the spheres. Therefore, it is only a monolayer of dye molecules attached to the surface of TiO$_2$ microspheres, which explains the low level signal observed for the FITC dye. Overall, the finding here is of great importance since the model study indicates that SIMS has the potential to map specific markers at single cell level.
5.4 Conclusion

We have successfully demonstrated that ToF-SIMS could be used to characterize hollow TiO₂ microspheres formed by interfacial sol-gel reactions embedded in an ionic liquid. With the protocols developed here, we look forward to expanding the scope of such analysis towards other systems that use ionic liquids as an embedding medium. One of the ongoing projects in our lab is to characterize liposomes in ionic liquids. Some preliminary data showed that ionic liquids could be used to help maintain the structures of such fragile biological samples under high vacuum conditions and imaging mass spectrometry could even capture an interesting phenomenon that liposomes burst under primary ion bombardment, as shown in Figure 5-10. These findings may lead to the development of a drug release model system for ToF-SIMS study. In addition, we have also shown some problems associated with imaging SIMS in this study, where complexities
arise from projecting a 3D object into a 2D image plane. More fundamental studies on this hollow microsphere model probably can provide a clue of how to address these problems.

Figure 5-9. (a) SEM image (512 × 512 pixels) of the prepared liposomes taken by 40 keV C\textsubscript{60}+ primary ion source. The field of view for the image is 150 µm × 150 µm. SIMS images were then taken from a 50 µm × 50 µm area of it. The ROI is marked in orange. (b) Two consecutive SIMS images of the liposomes. In the 1st SIMS image, there is no DPPC signal; while in the 2nd SIMS image, m/z 184 appears in the marked area in red. In addition, the distribution of ionic liquid also changes in the two SIMS images. This is due to that when the primary ion beam etches away the ionic liquid on the surface of the liposome and starts to hit directly on it, the fragile lipid vesicle breaks and all the ionic liquid containing inside is released.
5.5 References


Chapter 6

Conclusions and Future Directions

6.1 Conclusions

The objective of the thesis is focused on improving fundamental understandings of ion-solid interactions and expanding applications of cluster ToF-SIMS in molecular depth profiling and chemical imaging.

The first part of the thesis demonstrates that by erosion with a 40 keV $C_{60}^+$ beam, reliable depth profiles can be acquired on hybrid metal on organic systems, as indicated by the presence of a steady state molecular ion signal of the organic molecule. During the erosion process, however, clear diffusion of metal atoms into the underneath organic solid is observed. The metal implantation imposes a negative effect on the underlying organic substrate, namely causing a reduced sputter yield, an increase in the amount of fragmentation and an increase in the ion-induced altered layer thickness. It also shows that the influence of the metal film on the depth profile remains constant once the metal thickness exceeds a critical value. The experiment results are in agreement with molecular dynamics computer simulations on $C_{60}$ bombardment of a silver-octatetraene hybrid system\(^1\) and the two together provide better understanding on the subject of molecular depth profiling of hybrid materials.

The second part of the thesis presents a detailed study of the sputtering characteristics of a model organic system under Ar gas cluster ion beams. Ar-GCIBs are a new development for molecular depth profiling of organic materials that is generating much interest in the SIMS community. However, detailed studies of its characteristics are lacking. In this study, new observations into different depth-profiling regimes are made and interpreted in the context of...
sputter yields and ionization efficiencies. For the specific case of trehalose model system, normal depth profiles are obtained with relatively high sputter yields when \( E/n > 5 \text{ eV/atom} \); while distorted depth profiles in the steady state region are observed which exhibit a low sputter yield and variable ionization efficiency when \( E/n \leq 5 \text{ eV/atom} \). There are also important implications for quantitative analysis and optimal use of new gas cluster ion beams for depth profiling studies. This study suggests that high kinetic energy increases the useful molecular ion yield of trehalose and \( \text{Ar}_n^+ \) clusters with a small \( E/n \) value minimizes ion beam bombardment induced chemical damage.

The third part of the thesis focuses on the extension of the ToF-SIMS technique into the field of characterization of micron-scaled objects. Our results show the first successful example of using ToF-SIMS to depth profile through an ionic liquid and identify TiO\(_2\) microspheres with diameters of 5-30 \( \mu \text{m} \) formed by interfacial sol-gel reactions embedded in that solvent. In addition, we demonstrate that the surface and the internal structure of inorganic microspheres can be investigated with this technique. In general, the protocol developed in the study offers an alternative approach to characterize materials synthesized in ionic liquids.

### 6.2 Ongoing and Future Research

The use of ToF-SIMS to depth profile single-component organic thin films, even complex multilayer organic structures, has progressed rapidly with the development of cluster ion sources. It seems reasonable to predict that the same technique to be used for characterization of binary thin films will come naturally. However, this is not the case yet due to the presence of matrix effects, where the secondary ion yield of an analyte in the sample may strongly be enhanced/suppressed by the presence of another compound.\(^{2,4}\) An example is shown in Figure 6-1, which is part of a VAMAS interlaboratory study of organic depth profiling of mixed
materials led by NPL. The thin films are made from binary mixtures of Irganox 1010 and Fmoc-pentafluoro-L-phenylalanine (Fmoc-PFLPA) in which the composition is known as a function of the depth. The result clearly demonstrates that the presence of Fmoc-PFLPA suppresses the detection of Irganox 1010, as indicated by the signal level of m/z 1175 in region D-H is much lower than that in region B. Therefore, it becomes necessary to evaluate the matrix effect and to find a method to extract reliable compositional information from depth profile data. Our laboratory is pursuing the application of laser post-ionization (LPI) to secondary neutral mass spectrometry (SNMS) for detection of the sputtered neutral molecules. The key feature of the technique has been described in detail elsewhere.\textsuperscript{5,6} In brief, a femtosecond infrared laser is used to ionize sputtered neutral particles from the sample surface. The benefits of doing so are twofold. First, since the majority of the secondary particles are neutrals, there can be more molecular ions generated with LPI. Second, since now the emission and ionization of the sputtered particles are separated from each other, matrix effects of SIMS are eliminated. Together, it provides a more sensitive and quantitative approach for surface analysis.
Figure 6-1: Depth profile of an MMF sample obtained with 10 kV Ar$^{1000+}$ primary ion beam. Regions A and C are 100 nm of Irganox 1010; region B is 100 nm of Fmoc-pentafluoro-L-phenylalanine; regions D, E and F are 100 nm of three different mixtures of Irganox 1010 and Fmoc-pentafluoro-L-phenylalanine (25:75; 75:25; 50:50); region G is 200 nm of Irganox 1010 with 3 nm marker layer of Fmoc-pentafluoro-L-phenylalanine; region H is 200 nm of Fmoc-pentafluoro-L-phenylalanine with 3 nm marker layer of Irganox 1010.
To improve the accuracy and quality of SIMS images is another important future research direction. Figure 6-2 shows polymer domains formed by spin casting a polystyrene/poly(methyl methacrylate) (PS/PMMA) mixture from a toluene solution onto a silicon oxide surface. Details of the sample preparation procedure can be found elsewhere. In brief, the solubility of PS in toluene is better than PMMA, therefore, PMMA solidifies first during spin coating, leading to the formation of PMMA islands, as shown in Figure 6-2a and b. However, corresponding SIMS and SEM images, as shown in Figure 6-2c and d, are simply a projection of a non-flat surface onto a flat 2D image plane. Tarolli et al. has introduced image fusion to the SIMS community, by which a hybrid image that combines the high spatial resolution of SEM image and the specific chemical information from SIMS image could be generated. The resulting higher resolution chemical image could then be registered with an AFM image by image registration, a method is currently in development. Registering the fused image with AFM data would allow for accurate depth information to be correlated to each pixel. In that way, accurate 3D ToF-SIMS visualization of non-flat samples can come to the realization.
Figure 6-2: (a) AFM line scan and (b) 3D representation of a polymer blend thin film. The scan area is 20 × 20 µm²; (c) SED image and (d) SIMS image of a polymer blend thin film with 40 keV C₆₀⁺. Dark red represents PS at m/z 152 and light blue represents PMMA at m/z 69.

6.3 References


Appendix

Preparation of Liposomes in Ionic Liquids

Liposomes in ionic liquids were prepared by a slightly modified version of the method reported by Gayet et al.\textsuperscript{1} In brief, 8 µmol of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) (Avanti Polar Lipids, Alabaster, AL) and 2 µmol of 1,2-dipalmitoyl-sn-glycero-3-phospho-(1′-rac-glycerol) (sodium salt) (DPPG) (Avanti Polar Lipids, Alabaster, AL) was first dissolved in 1 mL of chloroform/methanol (9:1, v/v) in a 50 mL round-bottom flask. The organic solvent was then removed by a rotatory evaporator to yield a lipid film. The lipid film was dried in a desiccator for 2h and then 1 ml of BMIM-PF\textsubscript{6}/H\textsubscript{2}O (1:1, v/v) was added into the flask containing the dried lipid film. The flask was kept in a 100°C water bath and the mixture inside the flask was stirred at 1000 rpm for 30 min. The resulting solution contained micron-sized liposomes in high concentration.

References

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Kan Shen was born in Jiaxing, Zhejiang Province, China on April 21, 1985 to Jianxin Shen and Lihua Zhou. He attended Sichuan University in Chengdu in 2003 and earned a Bachelor of Science degree in Pharmacy in 2007. In August of 2008, he began his graduate study in Chemistry at South Dakota State University. He transferred to The Pennsylvania State University in July 2010 where he joined the research group of Professor Nicholas Winograd. He conducted his research in the area of analytical chemistry and received his Doctor of Philosophy in 2015.