MOLECULAR DEPTH PROFILING AND WEDGE-CRATER BEVELING
WITH TOF-SIMS AND CLUSTER ION BEAMS

A Dissertation in
Chemistry
by
Dan Mao

© 2011 Dan Mao

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2011
The dissertation of Dan Mao was reviewed and approved* by the following:

Nicholas Winograd  
Evan Pugh Professor of Chemistry  
Dissertation Advisor  
Chair of Committee

Christine Dolan Keating  
Associate Professor of Chemistry

Tae-Hee Lee  
Assistant Professor of Chemistry the Huck Institutes of the Life Sciences

John Golbeck  
Professor of Biochemistry and Biophysics

Barbara J. Garrison  
Shapiro Professor of Chemistry  
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
The development of cluster ion beams ($\text{SF}_5^+$, $\text{C}_{60}^+$, $\text{Ar}^{(500-2000)}^+$, etc.) have opened up a new interest in molecular depth profiling of organic and biological materials with Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Molecular depth profiling is the foundation for the ultimate goal of a three dimensional (3-D) characterizations of organic and biological samples. However, it is a complicated process with many variations on outcomes including surface topography developments, erosion rate variations and depth resolution degradations. There are also many experimental factors affecting these depth profile results including sample temperature, impact angle, primary ion beam kinetic energy and sample rotation, etc. The process of depth profiling is far from being fully understood and all these fundamentals need to be investigated before achieving a successful 3-D image of complex samples like single cells.

The work presented in this thesis is aimed toward developing wedge-crater beveling of molecular depth profiling, a useful tool that provides valuable and unique information to understand the depth profiling process. Irganox multilayer standard samples obtained from National Physical Lab (NPL, UK) with delta layers are used to evaluate the wedge strategy under bombardment of a 40-keV $\text{C}_{60}^+$ cluster ion beam. Protocols have been setup to acquire information of surface topography roughness, erosion rate and depth resolution by combing the wedge-crater SIMS results with atomic force microscopy (AFM) surface scans. Experimental conditions are optimized to improve the depth profile results, such as, sample temperature, primary ion beam energy and incident angles. The results are comparable to conventional depth profiling. In
general, the optimal experimental conditions for the purpose of 3-D imaging molecular depth profiling include cryogenic temperature sputtering, low kinetic energy cluster ion beams and a glancing angle impact. The temperature effects are also investigated in details from multiple wedge-shaped craters formed at different temperatures. Overall, it is demonstrated that the wedge-crater beveling is an important tool for elucidating the factors that are important for molecular depth profiling experiments.
TABLE OF CONTENTS

LIST OF FIGURES ..................................................................................................... vii

LIST OF TABLES ....................................................................................................... xiii

ACKNOWLEDGEMENTS .................................................................................. xiv

Chapter 1 Introduction .......................................................................................... 1

1.1 Overview of ToF-SIMS .................................................................................. 2
1.2 Development of Cluster Ion Sources .............................................................. 4
1.3 Molecular Depth Profiling ............................................................................ 8
1.4 Instrumentations and Methods ....................................................................... 14
   1.4.1 BIOTOF Instrument ............................................................................. 14
   1.4.2 Nanopics 2100 AFM ............................................................................ 15
   1.4.3 Wedge-Crater Beveling Sputtering Scheme ......................................... 16
   1.4.4 Irganox Multilayered Samples ............................................................. 18
1.5 Thesis Overview ............................................................................................. 19
1.6 Reference ........................................................................................................ 21

Chapter 2 Developing Wedge-Crater Beveling Depth Profiling ......................... 27

2.1 Introduction ..................................................................................................... 27
2.2 Experimental Section .................................................................................... 29
2.3 Results and Discussion .................................................................................. 32
2.4 Conclusions ................................................................................................... 42
2.5 Acknowledgement .......................................................................................... 43
2.6 Reference ........................................................................................................ 43

Chapter 3 Molecular Depth Profiling by Wedged Crater Beveling .................... 46

3.1 Introduction ..................................................................................................... 46
3.2 Experimental Section .................................................................................... 49
3.3 Results and Discussion .................................................................................. 53
   3.3.1 Surface Roughness .............................................................................. 53
   3.3.2 Erosion Rate ....................................................................................... 57
   3.3.3 Depth Resolution ............................................................................... 59
3.4 Conclusions ................................................................................................... 71
3.5 Acknowledgement .......................................................................................... 72
3.6 References ...................................................................................................... 72

Chapter 4 Investigations of Temperature Effects by Wedge-Crater Beveling ........ 76
LIST OF FIGURES

Figure 1-1: Cross-sectional views of the temporal evolution of a typical collision event leading to ejection of atoms due to 15 keV Ga\(^+\) and C\(_{60}\)^+ bombardment of Ag (111) surface at normal incidence. The dimensions of the solid are 10 \(\times\) 10 \(\times\) 10 nm\(^3\), microcrystallite containing 612,000 atoms. The atoms are colored by original layers in the substrate. The projectile atoms are black.\(^{30}\) ............................................................................................................7

Figure 1-2: Secondary ion signal intensities versus accumulated C\(_{60}\)^+ ion fluence during depth profiling of a trehalose film doped with 1% GGYR (263 nm).\(^{4}\) ....10

Figure 1-3: (a) Chemical structure of the alternating LB film of AA and DMPA deposited on piranha-etched silicon substrate and the depth profiles measured at (b) liquid nitrogen temperature using 40-keV C\(_{60}\)^+ projectiles.\(^{51}\) .....................11

Figure 1-4: (a) Schematic drawing of LB20-6 and the DMPA blocks are represented by green, AA blocks are represented in red and Si in blue and (b) the chemical structure rebuilt from the SIMS depth profile images with green showing the DMPA signal, red showing the AA signal, and blue showing Si signal.\(^{56}\) .................................................................................................................12

Figure 1-5: Nanopics results of a wedge-shaped crater. Top panel shows the 2-D and 3-D images of this crater and lower panel shows a line scan along the y direction of the wedge crater .................................................................16

Figure 1-6: This figure shows the manufacturing process of Irganox 1010/3114 delta layers. Two sample holders filled with Irganox 1010 (blue) and Irganox 3114 (yellow) are alternatively heated to evaporate the materials. A quartz crystal microbalance (QCM) is used to monitor the thickness of deposited materials. The resulting multiplayer samples on silicon wafer (light green) have accurate thickness of within \(\pm\)0.1 nm.................................................................................................................19

Figure 2-1: In order to erode a wedge-shaped crater, the raster area was varied from frame to frame by sequentially skipping more and more lines in the y-direction. As shown in the top figure, the ion beam first rastered the whole crater area from 1 to 8. Then the ion beam skipped area 1 and rastered a smaller area in the crater from 2 to 8. The ion beam continued to skip lines in the y-direction until the end of crater is reached. This way, the crater area along the y-direction received an increasing ion dose. In real experiments, by increasing the sputtering time per cycle, pixels along y-direction can receive linear increasing ion fluence .....................................................................................30
Figure 2-2: Optical images of the wedge crater formed on Irganox delta layers samples with 12 steps wedge-beveling. Due to the light reflect index, Irganox sample with different thickness shows different colors under microscope.

Figure 2-3: During the wedge depth profile, when the deepest side of the crater reached 150 nm. The red line across the wedge crater represents the actual SIMS imaging surface during this sputter cycle. Then image of m/z 42 from this surface is shown as below representing the signal from Irganox 3114. Dark Green: Irganox 1010; Orange: Irganox 3114; Light Green: Si.

Figure 2-4: AFM image of wedge crater eroded into a 350 nm Irganox 1010 film on Si doped with 4 delta layers of Irganox 3114. The upper panel represents a top view with the dark blue vertical lines representing the expected positions of the delta layers. The horizontal light blue line denotes the position of a line scan shown in the bottom panel. In the bottom panel, the position of the delta layers is also shown. With the wedge angle reported as 0.0483°, the 3 nm delta layer is expected to appear to be 3.55 µm to the interrogating C_{60}^{+} probe. Note the decrease in the slope of the bevel as the crater reaches the Si substrate, designated in gray.

Figure 2-5: This figure shows a topography scan across the wedge crater along the line indicated in Figure 2-4 (orange) along with line scans of the SIMS signals representing the Irganox 3114 delta layers (m/z 42, blue) and SiO_{2} substrate interface layer (m/z 60, green). The erosion rate is shown in magenta, with smoothed values given by square grey points. The grey line represents the roughness fluctuations around the average height (see text).

Figure 2-6: A line scan of m/z 42 can be obtained across the crater. From the line scan data, we know the distance between the 1st and 2nd Irganox 3114 layer signal on this m/z 42 SIMS imaging is 170 µm (whole crater 450 µm). And from the structure of the film, we also know the depth distance between the 1st and 2nd layer is 47 nm. We can get the FWHM value of each layer from the figure below by locating them in the x axis. They can be converted into a depth scale to get the depth resolution of each layer.

Figure 2-7: Top panel: this figure shows a line scan of Irganox 3114 signal m/z 42 across a wedge crater in y direction, a profile of m/z 42; lower panel: this figure shows an AFM line scan of a wedge crater in y direction, a relationship profile between depth and scan length.

Figure 2-8: This figure shows both AFM and SIMS line scans as the function of scan length. The red line is a fitting of black dots of SIMS signal m/z 42 and the purple line is the AFM depth information.
Figure 2-9: This figure shows a depth profile result of Irganox 3114 m/z 42 based on real depth scale by interpolating depth data from AFM line scan. .................40

Figure 2-10: This figure shows the smoothed data taken from the bottom panel but converted to a depth scale appropriate to represent the cross-section of the 350 nm Irganox film. ........................................................................................................42

Figure 3-1: The top cross-section view of the wedge crater process. A C$_{60}^+$ primary ion source is used to remove material in a rastered area divided into 256 pixels $\times$ 256 pixels. A wedge-shaped crater is eroded by applying an increasing ion fluence along the $y$ direction of the raster area. The resulting crater contains information from zero to $2 \times f_0$ projectile ion fluence. Depth profile information is obtained by taking a SIMS image of the resulting crater bottom. In this case, the $y$ dimension of the crater is 600 $\mu$m, and the maximum depth is 400 nm. Note that the angle of the wedge with respect to the surface is $\theta = \sin^{-1}(400 \text{nm} / 600 \mu\text{m}) = 0.038^\circ$..................................................52

Figure 3-2: AFM topography scan along the wedge shaped crater eroded into a 400-nm Irganox 1010 film doped with four Irganox 3114 delta layers by a 40-keV C$_{60}^+$ ion beam impinging at 40° with respect to the surface normal. Upper panel: ion erosion with the sample at room temperature. Lower panel: ion erosion performed at liquid nitrogen temperature. The red and blue curves represent the roughness fluctuations around the average crater profile calculated by smoothing the AFM scan data as described in the text. ...............55

Figure 3-3: RMS roughness ($R_q$ value, see text) as a function of eroded depth during sputtering of the Irganox 1010/3114 delta layer film with a 40-keV C$_{60}^+$ ion beam impinging under 40° with respect to the surface normal. The data were obtained at two different sample temperatures during ion bombardment. ........................................................................................56

Figure 3-4: Erosion rate (see text) as a function of eroded depth during bombardment of the Irganox 1010 / 3114 delta layer film at two different sample temperatures, 100 K (blue dots) and 300 K (red dots). Both wedge craters were created by a 40-keV C$_{60}^+$ ion beam impinging at 40° with respect to the surface normal. .................................................................58

Figure 3-5: Left panel: schematic illustration of the wedge shaped crater imaging technique used to identify the Irganox 3114 delta layers (yellow) embedded into the Irganox 1010 matrix (blue) film deposited on a silicon substrate (green). Right panels: SIMS images of the Irganox 3114 specific secondary ion signal at m/z 42 taken on the wedge shaped crater bottom for two different beveling angles as indicated by the red lines. ...............................................60
Figure 3-6: SIMS images of the Irganox 3114 specific secondary ion signal at m/z 42 (inserts) and line scans of the respective signal intensity along the lines indicated by the arrows as obtained after erosion of a wedge shaped crater under different experimental conditions. Top panels: ion erosion at room temperature under 40° incidence; Middle panels: ion erosion at 100 K under 40° incidence; lower panels: ion erosion at 100 K under 71° incidence with respect to the surface normal. The left and right columns refer to two different or beveling angles characterized by the maximum eroded depth \( z_{max} \) at the deepest side of the wedge shaped crater. Left panels: partial with \( z_{max} \sim 120 \) nm (between 2\(^{nd}\) and 3\(^{rd}\) delta layer); Right column: wedge erosion down to the silicon substrate with \( z_{max} \sim 450 \) nm. All wedged craters were eroded under bombardment with a 40-keV \( \text{C}_{60}^+ \) ion beam.

Figure 3-7: Measured width (FWHM) of the m/z 42 secondary ion signal peak representing the uppermost Irganox 3114 delta layer in the line scans as depicted in Figure 5 as a function of beveling angle characterized by maximum crater erosion depth \( z_{max} \) as indicated in Figure 3-5. Black dots: experimental data; Solid line: least square fit of Eq. 3.6 to the experimental data; Open circles: calculation according to Eq. 3.5 by setting the fitting parameter \( B \) to zero.

Figure 3-8: Depth profile of 1\(^{st}\) and 2\(^{nd}\) Irganox 3114 delta layers obtained using the wedge crater imaging technique at low temperature and oblique ion incidence. Crater erosion was performed at 100 K with a 20-keV \( \text{C}_{60}^+ \) primary ion beam impinging at 71° with respect to the surface normal. Insert: image of the m/z 42 secondary ion signal acquired at this experimental condition. The plot was derived from a line scan as indicated in the image with the depth scale being calibrated from AFM data as described in the text. Measured depth resolution (FWHM) for 1\(^{st}\) and 2\(^{nd}\) layer: 8.2 and 7.9 nm, respectively.

Figure 3-9: AFM line scans of stepped wedge craters formed at room temperature (top panel) and liquid nitrogen temperature (lower panel). The craters were eroded into an Irganox 1010 film doped with four Irganox 3114 delta layers using a 40-keV \( \text{C}_{60}^+ \) ion beam at a 40° impact angle.

Figure 4-1: This figure shows the temperature controlled sample stage. A variable autotransformer is used to heat up condensed liquid nitrogen, forming a constant ratio of gas/liquid mixture to achieve temperatures between liquid nitrogen temperature and room temperature.

Figure 4-2: The optical images of a wedge crater from an Irganox delta layered sample. Top panel (a): wedge crater with the deepest side at 150 nm. Lower panel (b): wedge crater with the deepest side at 400 nm.
Figure 4-3: Conventional sputter depth profiles of Irganox 1010/3114 multilayers sample at 300 K, 250 K, 150 K and 90 K with C\textsubscript{60}\textsuperscript{+} at 40° incident angle. The Irganox 1010 matrix signal (C\textsubscript{2}H\textsubscript{3}O\textsubscript{2}\textsuperscript{−} m/z 59) is normalized to surface intensity. And Irganox 3114 delta layer signal (C\textsubscript{33}H\textsubscript{46}N\textsubscript{3}O\textsubscript{5} m/z 564, CNO\textsuperscript{−} m/z 42) is normalized to maximum intensity of the entire depth profile...

Figure 4-4: Depth profiles of Irganox 1010/3114 multilayers sample at 300 K (top panel) and 90 K (lower panel) with 40-keV C\textsubscript{60}\textsuperscript{+} at 40° incident angle. Each Irganox 1010 matrix signal is normalized to surface intensity.

Figure 4-5: Calculated erosion rate from conventional depth profiles by dividing ion fluence from known volume between each layer.

Figure 4-6: AFM topography scan along the wedge shaped craters eroded into a 380-nm thick Irganox 1010 film doped with four Irganox 3114 delta layers by a 40-keV C\textsubscript{60}\textsuperscript{+} ion beam impinging at 40° with respect to the surface normal at 90 K, 130 K, 160 K, 210 K, 250 K and 300 K temperature. The blue curves represent the roughness fluctuations around the average crater profile calculated by subtracting the original data from the smoothed AFM scan data (black curves).

Figure 4-7: RMS roughness (R\textsubscript{q} value, see text) as a function of eroded depth during sputtering of the Irganox 1010/3114 delta layer film with a 40-keV C\textsubscript{60}\textsuperscript{+} ion beam impinging under 40° with respect to the surface normal. The data were obtained at six different sample temperatures during ion bombardment at Top panel: 90 K (black), 130 K (orange), 160 K (magenta) and 210 K (olive); Lower panel: 250 K (blue) and 300 K (red).

Figure 4-8: Erosion rate as a function of eroded depth during bombardment of the Irganox 1010 / 3114 delta layer film at; Top panel: 90 K (black), 130 K (orange), 160 K (magenta) and 210 K (olive); Lower panel: 250 K (blue) and 300 K (red). All six wedge craters were created by a 40-keV C\textsubscript{60}\textsuperscript{+} ion beam impinging at 40° with respect to the surface normal.

Figure 5-1: Erosion rate as a function of eroded depth during bombardment of the Langmuir-Blodgett film (AA). Left panel: Average erosion rate of 90 K, 140 K, 165 K and 205 K results; Right panel: erosion rate obtained at 265 K (magenta triangle) and 300 K (red circle). All six wedge craters were created by a 40-keV C\textsubscript{60}\textsuperscript{+} ion beam impinging at 40° with respect to the surface normal.

Figure 5-2: Langmuir-Blodgett film (AA) and Si substrate interface width as the function of temperature including 90 K, 135 K, 165 K, 205 K, 265 K and 300 K. All wedge craters were created by a 40-keV C\textsubscript{60}\textsuperscript{+} ion beam impinging...
at 40° with respect to the surface normal. The black curve shows the average width from 3 line scans along y direction in SIMS results of wedge craters with error bar shows the reproducibility of line scans. The red curves shows the calibrated interface width from two strategies with the error bar shows the agreement between two strategies. The picture insert shows a Si signal at the Si-LB film interface and line scans is used to calculate the interface width. .......113
LIST OF TABLES

Table 3-1: Structure of Irganox Delta Layer Samples .........................................................49
Table 3-2: Depth Resolution Under All Conditions .............................................................64
Table 4-1: Structure of Irganox Delta Layer Samples (1nm) ............................................81
Table 4-2: Nitrogen Flow and Variable Autotransformer Value ...........................................85
ACKNOWLEDGEMENTS

Work on my Ph.D. and this thesis would not have been possible without encouragement and support from many people.

Most of all I would like to express my deep thanks to my research advisor, Professional Winograd, for not only giving me the opportunities to work on such exciting and cutting edge research projects, but also his guidance, understanding and patience. His excitement about science and creative thinking have always inspired me. I owe special thanks to Professor Andreas Wucher from University of Duisburg-Essen, Germany, for the inspiring idea on wedge-crater beveling and insightful discussions to make this technique possible. I would also like to thank Professor Barbara Garrison for her thoughtful advice and support during these years. My appreciation also goes to other faculty members, Professor Tae-Hee Lee, Professor Christine Dolan Keating and Professor John Golbeck, for serving on my committee.

Thanks must go to the present and past members, colleagues of the Winograd group, for all the help and support over years, especially Dr. Juan Cheng, Dr. Tony Carado, Dr. Caiyan Lu, Dr. Joseph Kozole, Dr. Jung-Hwan Kim, Dr. Michael Kurczy, Dr. Alan Piwowar, Dr. Shawn Parry, Dr. David Willingham, Dr. Leiliang Zheng, Daniel Brenes, Lauren Jackson, Andrew Kucher, Jordan Lerach, Melissa Passarelli, Kan Shen and Jay Tarolli. Specially, I would like to thank our staff assistant Sabrina Glasgow for her kindly help over years.

I also want to thank my parents, Yunian Mao and Huiying Zhang for their supports, faith and inspiring on my life and education.
Finally, I would like to express my deeply thanks to my beloved wife Jin Qian, for her tremendous support and unconditional love has been since high school, and will always be.
Chapter 1

Introduction

Every so often a major breakthrough expands a mature field into a remarkable new direction. The development of a cluster ion beam source used in time-of-flight secondary ion mass spectrometry (ToF-SIMS) has transformed this well-established two-dimensional (2-D) surface characterization technique into a three-dimensional (3-D) chemical imaging powerhouse and commonly referred to as cluster ToF-SIMS. These cluster ion beam sources serve as the energetic primary ion beam that is focused to a particular spot size to impact the sample target, resulting in the emission of secondary ions. Reduced topography and damaged cross sections\(^1\text{-}^4\), coupled with enhanced ion yields and sensitivities\(^5\text{-}^7\) make molecular depth profiling as well as submicron spot size mass spectral imaging feasible. Cluster ToF-SIMS is still in its infancy when characterizing complex organic and biological materials in a 3-D fashion\(^8\text{-}^10\) but has led to new discoveries of buried chemical interactions. There many fundamental factors that involves in the depth profiling process including sputter yield, surface topography developments, etc. Fully understandings of these factors pile up the foundations for three dimensional mass spectral imaging. The objective of the work presented is focused on developing a new strategy of sputtering to understand chemical changes as well as physical developments during molecular depth profiling with cluster ToF-SIMS. In this chapter, the fundamentals of ToF-SIMS, the recent developments of cluster ion sources
and the basic concepts of molecular depth profiling will be introduced. The general instrumentations and wedge sputtering methods will also be described.

1.1 Overview of ToF-SIMS

Secondary ion mass spectrometry (SIMS) is a well-established surface analytical technique used for obtaining elemental and molecular chemical information. SIMS directs a primary beam at the target and causes desorption and ionization of secondary ions, electrons, photons, neutrals, etc. by ion bombardment. This ionization process delivers a unique advantage over electrospray ionization (ESI)\textsuperscript{11} mass spectrometry and matrix-assisted laser desorption ionization (MALDI)\textsuperscript{12} because no sample evaporations happen nor matrix materials is needed.

In ToF-SIMS, a pulsed beam of energetic primary ions is used to bombard the sample surface. As a result of the bombardment process secondary particles including positive ions, negative ions, electrons and neutrals are desorbed into the ultra high vacuum (UHV) environment. Both the positive and negative ions are used for further mass analysis. After the secondary ions are emitted, with respect to the charged state of the secondary ion either a positive or negative voltage is applied to the sample stage. Selected charged ions are extracted and accelerated into a time-of-flight (ToF) mass spectrometer with the same kinetic energy. However, due to different mass-to-charge ratios the secondary ions will travel with different velocities. These secondary ions are then detected at a detector by measuring their flight times from the sample surface to the detector. Resulting signals are collected and converted into a mass spectrum. The
delivery of the next pulse of primary ions is commenced once all secondary ions have been detected within the mass analyzer. Mass spectra acquired can be used to determine the elemental and molecular species on the sample surface.

There are two typical modes of SIMS analysis, dynamic SIMS and static SIMS. Dynamic SIMS is widely used in semiconductor industry for quantitative element trace analysis. In semiconductor industry, dynamic SIMS involves continuously etching away the inorganic sample surface with an atomic ion beam. It delivers a fast sputtering rate and produces a high ion yield. This technique can be used to reveal chemical information underneath the surface as the function of depth, and it is recognized as depth profiling. However, this technique cannot be used on organic or biological materials because the continuous sputtering generates an ion fluence that surpasses a limit known as the static limit where no molecular chemical information can be preserved with an atomic ion beam.

In contrast, in static SIMS the primary ion beam is operated in a short pulse (~ ns) when impinging the top surface of a sample and delivered with an ion fluence kept below $10^{12}$ ions/cm$^2$ commonly referred to as the static limit. Operating below the static limit ensures that the impacts do not overlap and the mass spectrum only represents the top surface layer of material. Most static SIMS instruments are equipped with a ToF mass analyzer due to its substantially high transmission efficiency. With a traditional atomic primary ion beam, it is important to keep ion fluence under the static limit to prevent the loss of molecular specificity due to chemical damage caused by the energetic ion bombardment process. However, with the recent development of cluster ion sources, which will be discussed in detail in the next section, the static limit is no longer
applicable which permits that analysis of organic and biological systems that were once not achievable with atomic ion beams.

Mass spectral images can be acquired to visualize the distribution of sample surface constituents. An image is acquired by rastering a finely focused ion beam over the sample surface. The entire mass spectral information is obtained for every pixel in the images that describe the chemical distribution as a function of location. Because samples can be analyzed without further treatment, SIMS has become a useful imaging tool to map chemical information for biological samples. Because of the low chemical damage induced by cluster ion beams, SIMS depth profiles can be used to determine the distribution of different chemical species as a function of depth from the surface. This type of analysis attracts a tremendous amount of interest because there are very few analytical techniques that are capable of characterizing buried interfaces with nm depth resolution.

1.2 Development of Cluster Ion Sources

Before the development and application of cluster ion beams in a SIMS analysis, energetic atomic projectiles were employed to desorb intact molecules but proved to be problematic in some cases. These atomic ion beams including Ga\(^+\), In\(^+\), Cs\(^+\), Ar\(^+\), etc. induce high levels of material disruption below the sample surface with very little material removed.\(^{1,12}\) The disruption results in the ability to preserve important molecular specificity of organic thin films under atomic ion beam bombardment. The potential of polyatomic projectiles was not discovered until 20 years ago by Appelhans et
It was observed early on that an increase in secondary ion efficiency and a decrease in sample damage during a SIMS analysis using SF$_6^0$ cluster ion beam, later to be replaced by SF$_5^+$ were achievable. Although polyatomic projectiles were not widely accepted by the SIMS community at that time due to performance issues including low current, large beam width and short lifetimes, it lights up a promising future and a bright direction for the development of cluster ion sources.

The general acceptance of cluster ion sources was initiated by the dramatic developments of commercially available liquid metal ion gun (LMIG) sources such as Au$_3^+$, Bi$_3^+$, and a C$_{60}^+$ gas ion source. In a C$_{60}$ source, the gas phase of C$_{60}$ is generated by heating up C$_{60}$ powder and conventional electron impact strategies are used to ionize C$_{60}$ gas vapor. The resulting ions of C$_{60}^+$, double charge C$_{60}^{2+}$ and triple charge C$_{60}^{3+}$ are extracted into a wien filter where a certain type of C$_{60}$ charged ions can be selected based on its mass-to-charge-ratio. The selected ion beams is further focused through apertures and electrostatic lenses onto the sample surface with a width as low as 300 nm.

The C$_{60}^+$ cluster ion beam behaves very differently from a traditional atomic ion beam when used to analyze materials via a SIMS analysis. A computer simulated impact of 15 keV Ga and C$_{60}$ onto a silver single crystal surface is shown in Figure 1-1. In this simulation, a large amount of primary energy during Ga bombardment is deposited well below the sample surface, causing material disruption under the surface. During a single C$_{60}$ bombardment, because the 15 keV kinetic energy of the C$_{60}$ cluster is evenly distributed among all 60 carbon atoms, each carbon atom carries a kinetic energy of 250 eV, which is substantially higher than the carbon-carbon bond energy. The C$_{60}$ molecule
dissociates during the bombardment and each carbon atom creates a cascade of moving atoms. The energy from C\textsubscript{60} projectile deposited into the sample surface remains closer to the surface. The number of atoms removed by a single buckyball impact is increased more than 15 folds over Ga, while the depth of damage is much smaller.\textsuperscript{30} The yields of material removed with high mass (> 500 Da) are increased by several orders of magnitude when using a C\textsubscript{60} projectile. These advantages of C\textsubscript{60} bombardment do not compromise lateral resolution achieved. With adjustments of apertures and electrostatic focusing lenses, the beam width can be as low as 300 nm, making cluster SIMS a powerful tool to map the chemical distribution of small targets like biological molecules and single cells.

There are still a few drawbacks of using C\textsubscript{60} as the primary ion source although it has been recognized as a very effective beam for analysis of numerous organic samples. One drawback is the concern of carbon deposition. Although samples are in “As-Is” condition without further treatment, evidences of carbon deposition have been observed during the past years for low incident energies of (\leq 10\text{ keV}) C\textsubscript{60}\textsuperscript{+} sputtering.\textsuperscript{31-34} There are suggestions that carbon deposition might be the reason of surface roughening during depth profiling.\textsuperscript{31} Another area that needs improvement is the secondary ion yield for ultra high mass range (> 1500 Da). Most biological molecules are still not detectable using C\textsubscript{60}\textsuperscript{+} ion source.
Figure 1-1: Cross-sectional views of the temporal evolution of a typical collision event leading to ejection of atoms due to 15 keV Ga$^+$ and C$_{60}^+$ bombardment of Ag (111) surface at normal incidence. The dimensions of the solid are $10 \times 10 \times 10$ nm$^3$, microcrystallite containing 612,000 atoms. The atoms are colored by original layers in the substrate. The projectile atoms are black.$^{30}$
A recent member introduced to the cluster ion source family is the Argon (Ar) gas cluster ion beams (GCIBs). This ion source was originally designed for sample surface cleaning.\textsuperscript{35} It was modified for applications in SIMS by Matsuo \textit{et al.}\textsuperscript{36} The Ar cluster ion beam contains an average Ar cluster size of 2000 atoms. It is suggested from computer simulations that Ar cluster ion beams have can potentially increase the sputter yield, increase secondary ion signals and reduce surface topography when compared to a C\textsubscript{60}\textsuperscript{+} ion source.\textsuperscript{36} Recently, Ar cluster ion beams used in SIMS applications have shown promising results in the characterization of organic and biological materials.\textsuperscript{37-43} However, it carries some drawbacks as well. For instance, the cluster size produces a large spot size, the decay in ionization efficiency with increasing Ar cluster size, and uneven erosion during bombardment.\textsuperscript{38} Although it is still unclear how Ar GCIBs can influence the SIMS community at this stage, exploration of novel ion sources with improved performance continues moving forward.

### 1.3 Molecular Depth Profiling

The aim of depth profiling is to acquire information of composition variation as the function of depth below the initial surface. Before the introduction of cluster ion beams, depth profiling of organic materials was impossible due to loss of molecular specificity induced by chemical damage.\textsuperscript{21,30,44-46} Cluster ion beams, on the other hand, have a different sputtering behavior where its high sputtering rate allows any chemical damage to be removed as quickly as it is created.\textsuperscript{4,5,47,48} Earliest attempts of organic depth profiling were performed at the National Institute of Standards and Technology
(NIST) with an SF$_5^+$ ion beam. With ion fluences well beyond the static limit, researchers were still able to obtain the molecular ion signal of glutamate. Research interests of molecular depth profiling on organic and biological materials exploded with C$_{60}^+$ cluster ion source becoming the most commonly mounted primary ion beam on a ToF-SIMS instrument. One of the earliest examples of a successful depth profile was obtained from a peptide doped trehalose film using a 20-keV C$_{60}^+$ beam. It suggests that the depth profile of the molecular ion consists of an initial exponential decay, a plateau at a steady state, and terminates with a fast signal decrease when reaching the substrate. An analytical erosion model has been created to describe the molecular ion intensity as a function of ion fluence by using obtained information, such as molecular sputtering yield, damage cross section, and the thickness of a surface layer altered by the projectiles. Since then, molecular depth profiling with energetic polyatomic primary ions has been demonstrated to be feasible for a vast number of model systems consisting of thin films of lipids, metabolites, polymer additives and polymers. A typical successful depth profile of a trehalose thin film is presented in Figure 1-2. Depth profiling was performed on a 263 nm trehalose film doped with 1% Gly-Gly-Tyr-Arg (GGYR) peptides. The initial decline of the signal before steady state is attributed to the buildup of chemical damage on the surface. Eventually, chemical damage is induced and removed by sputtering in equilibrium and a steady state is observed. Once the eroded crater is characterized by an atomic force microscope (AFM), the ion fluence can be converted into a depth scale and a depth profile is obtained.
Another example of dual components depth profile is shown in Figure 1-3. The structure of a Langmuir-Blodgett (LB) film consisting of six building blocks of either alternating barium arachidate (AA) or barium dimyristoyl phosphatidate (DMPA) multi-layers is shown in Figure 1-3 (a). In Figure 1-3 (b), a SIMS depth profile at a cryogenic temperature shows that the ion signal from each molecule continue to alternate in intensity until the Si interface is reached, precisely reflecting the chemically alternating structure of the film.

Figure 1-2: Secondary ion signal intensities versus accumulated $C_{60}^+$ ion fluence during depth profiling of a trehalose film doped with 1% GGYR (263 nm).
Molecular depth profiling has become a practical strategy now but continues to be probed for a complete understanding in its fundamentals. There is interest in determining the factors that yield the highest quality result. For example, one key factor is to maximize the depth resolution observed when eroding through interfaces. In a thick multilayered system, the depth resolution is determined by measuring the width of 16% ~ 84% of the maximum signal. In a delta layered system where the layer thickness is negligible, a full width half maximum (FWHM) is used to evaluate the depth resolution. The first widely used organic delta layered system was manufactured by National Physical Laboratory (NPL) in the United Kingdom using two types of Irganox materials. Within our lab an LB film standard was developed that is also based on a delta layered system and proven to be successful for depth resolution investigations. 

Figure 1-3: (a) Chemical structure of the alternating LB film of AA and DMPA deposited on piranha-etched silicon substrate and the depth profiles measured at (b) liquid nitrogen temperature using 40-keV $C_{60}^+$ projectiles.
Research in the past few years has revealed many factors that affect the outcomes of molecular depth profiling. It has been found that the sputter yield increases linearly with beam energy,\textsuperscript{24,48} however the depth resolution decreases.\textsuperscript{24} Studies of incident angles have shown that the interface width is reduced with glancing angle impact. It is suggested that the energy deposition is varied by changing the angle of impact.\textsuperscript{54} Sample rotation has been recently applied to molecular depth profiling and demonstrated to reduce the surface roughening and interface width.\textsuperscript{25} Depth resolution has been proposed to be related to topography formation during erosion.\textsuperscript{24}

Figure 1-4: (a) Schematic drawing of LB20-6 and the DMPA blocks are represented by green, AA blocks are represented in red and Si in blue and (b) the chemical structure rebuilt from the SIMS depth profile images with green showing the DMPA signal, red showing the AA signal, and blue showing Si signal.\textsuperscript{56}
Amongst all these interesting observations the one observation that captures the most interest and attraction is the effect of the sample temperature on a molecular depth profile. It has been widely reported that by lowering the sample temperature a true steady state, reduced ion signal decay, erosion rate decay and surface roughening can be obtained.\textsuperscript{20,21,25,26,51,55} High quality depth resolution images can be acquired with sample cooling without sacrificing the lateral resolution of the image.

These types of investigations with model systems build a foundation and provide the opportunities for 3-D imaging. In depth profiling experiments, a SIMS image is taken after every few nanometers of materials are removed. For a homogeneous sample with a uniform sputter rate, simply combining the chemical images from each cycle with calibration of the depth from the AFM scans before and after the sputtering will build a real 3-D image from top to bottom. An example of LB film 3-D depth profiling image is show in Figure 1-4.\textsuperscript{56} It shows the ion signal from DMPA (green) and AA (red) continue to alternate in intensity until the Si interface (blue) is reached. However, with many 3-D imaging protocols proposed,\textsuperscript{9,10,57} none can be applied on a complex biological samples where the erosion rate is not uniform in both lateral and vertical directions. In order to obtain 3-D mass spectral images for biological systems, surface topography information has to be obtained simultaneously within a SIMS acquisition. Most of the surface detection devices have to be mounted at 90\textdegree relative the sample surface where the space is occupied by a TOF analyzer. Currently, there is no such long-range in-situ surface topography detection strategy that works at an angle like 45\textdegree for current ToF-SIMS instruments. However, with improvements of surface analysis technique and new ToF-SIMS instrumentation design, in-situ measurement of surface physical information at the
same time when SIMS chemical information is acquired will be achievable in a foreseeable future.

1.4 Instrumentations and Methods

1.4.1 BIOTOF Instrument

The ToF-SIMS instrument used in this thesis work is a home-designed system called BIOTOF and the details are described elsewhere. Additional components have been continuously added to this instrument including latest designs in cluster ion sources. Currently, it is equipped with a 25-keV Au LMIG and a 40-keV C\textsubscript{60} source. The work presented in this thesis was performed using the C\textsubscript{60} ions source at 20 keV and 40 keV. The 40-keV C\textsubscript{60} source is mounted at 40° incident angle relative the sample surface normal. This sophisticatedly designed ion source, with help from selectable apertures and dedicated focusing lens, delivers an ion beam which can be focused to as small as 300 nm. In order to perform glancing angle experiments, a specially made wedge sample block with a beveling angle of 31° is used to hold the sample in the stage, resulting in a 71° impacting angle. Another feature of this BIOTOF instrument is the high performance sample cooling system which was original designed for handling freeze fractured biological samples. The sample stage has the capability of being cooled and stabilized to 90 K using liquid nitrogen as the coolant. Modification was added to the cooling part to achieve temperatures between 90 K and 300 K by adding a variant to heat against the cooled liquid nitrogen flow. Temperatures within ± 5° from a set point can be
achieved by adjusting the current of the variant. Conventional depth profile and wedge-crater beveling experiments presented in this thesis can be automatically operated by the software with preset sputtering schemes.

1.4.2 Nanopics 2100 AFM

In wedge-crater beveling experiments, investigations of physical parameters of eroded surface are as important as the acquired SIMS results. Conventional atomic force microscope (AFM) has an analysis area limited to ~100 µm which is not enough for characterizations of wedge craters.

An AFM device, Nanopics 2100 (KLA-Tencor, CA) atomic force profilometer is employed to obtain topographical information. The Nanopics 2100 is a compact system that combines the high resolution of an AFM with scanning speed and ease of the use of a surface profiler. It delivers high-speed, high-resolution scans of surface roughness, step height, surface contour and most importantly it supports an analysis area up to 1 mm × 1 mm. The contact scanning mode is used to obtain surface topographical information, when a contact scanning tip is dragged along the surface while collecting data. The software used to analyze scanning results has many functions to calibrate the surface tilt. Extreme care is taken to calibrate the wedge craters to prevent artifacts. A typical wedge-shaped crater under Nanopics is shown in Figure 1-5, where the line scan along the \( y \) direction of the crater can be taken to analyze the surface development as a function of ion fluence. Also, the crater dimensions can be obtained to calculate the ion fluence and determine the incident angle.
1.4.3 Wedge-Crater Beveling Sputtering Scheme

During conventional sputtering cycles, the ion beam is operated in a direct current (DC) mode and digitally controlled to raster over 256 x 256 pixels covering a surface.
area. A sputter time per cycle (s) is set in the experimental software. And sputtering time on each pixel can be calculated from Eq. 1.1. For example, if the ion beams has a dwell time of about 30 µs on each pixel for a 2 s sputter time per cycle set in the instrument it will take the ion beam 10 µs to move from one pixel to the next one. In such a case, the ion beam will spend at a minimum of 20 µs at a on each pixel to prevent the beam operating in a non-stop moving situation.

\[
(SputteringTimePerPixel)t = \frac{(TimeSetInSoftware)t_{set}}{256 \times 256} 
\]

1.1

In order to erode a wedge-shaped crater, the raster area is varied from frame to frame by sequentially skipping more and more lines in the y-direction, beginning with the line closest to the ion source. In this way, the resulting wedge crater consists of up to 256 steps. The software uses the set sputter time per cycle to decide how many steps to form in sputtering. So the wedge raster scheme is set up as a sequence of fast frames with a relatively short dwell time of about 10 µs on one pixel and 10 µs to move the beam to the next pixel. It takes 1.31 s to raster a 256 x 256 pixels area. The time needed to erode \( n \) steps in a wedge crater can be calculated according to equation Eq. 1.2. In reverse, the software use the set time per sputtering cycle to calculate how many steps to the wedge crater should have.

\[
(TimeNeededToErode(n)Steps)t = \frac{(1 + n) \times n}{2 \times n} 
\]

1.2

Because of the unique advantage of wedge-crater beveling only a few cycles are needed to reach the desired depth and SIMS data acquisition is not required during the
formation of a crater. Also, a decrease of ion beam current can be obtained by focusing the beam to a smaller spot. This delivers a high performance of SIMS images and easy-controlled wedge beveling. For the results presented in this thesis, wedge craters were formed with over 100-steps sputtering scheme where the width per step is smaller than ion beam width. It is safe to consider that the ion fluence along the $\gamma$-direction of the wedge crater is linear.

### 1.4.4 Irganox Multilayered Samples

A series of Irganox multilayered samples were investigated in this thesis as the model system. They were manufactured by NPL with a standard procedure described in detail elsewhere.\textsuperscript{24,25} The illustration of this manufacturing procedure is shown in Figure 1-6.

A single crystal silicon wafer with (100) orientation was cleaved to a $\sim$ 10 mm $\times$ 10 mm square. Any particulates on the surface were removed by soaking overnight in isopropanol prior to drying by nitrogen blow. Once cleaned, the silicon wafer is transferred into an Edwards AUTO 360 vacuum coater, with each wafer (light green) faced down for physical vapor deposition. A quartz crystal microbalance (QCM) was placed to the side of the vapor deposition holder and used to monitor the thickness of each Irganox layer deposited. The multilayer system of Irganox samples was achieved by the alternate evaporation of Irganox 1010 (blue) and Irganox 3114 (yellow) on the silicon wafers. Irganox 3114 layers with a thickness of 0.9 $\sim$ 3.0 nm serve as the delta layers
buried between Irganox 1010. This system has a long shelf life and is ideal for obtaining depth resolutions of different experimental conditions.

---

**Figure 1-6:** This figure shows the manufacturing process of Irganox 1010/3114 delta layers. Two sample holders filled with Irganox 1010 (blue) and Irganox 3114 (yellow) are alternatively heated to evaporate the materials. A quartz crystal microbalance (QCM) is used to monitor the thickness of deposited materials. The resulting multiplayer samples on silicon wafer (light green) have accurate thickness of within ±0.1 nm.

---

### 1.5 Thesis Overview

Tremendous efforts have been devoted into fundamental research of molecular depth profiling in the past few years. There is considerable interest in determining the factors that yield the highest quality result. However, the depth profiling process is far from being fully understood. There are many conditions that have been observed to
influence the outcome of the depth profile, but these conditions are still in the preliminary stage of investigations. Also, because of lacking in-situ physical measurement of surface topography information, some factors cannot be elucidated in considerable detail. With the introduction of new cluster ion sources, methodologies and areas of applications in this rapidly developing phase, more fundamental research is needed in order to lay a solid foundation to achieve the ultimate goal of 3-D mass spectral imaging.

The overall objective of thesis is to develop and investigate wedge-crater beveling as a tool for acquiring fundamental information about molecular depth profiling with $C_{60}^+$ cluster ToF-SIMS. Specifically, a protocol of wedge-crater beveling is developed in Chapter 2. The sputtering scheme is modified to erode a wedge-shaped crater into the samples. Preliminary results show that the important parameters can be easily measured by coupling the SIMS results with AFM measurements. However, it remains unclear whether the beveling process itself introduces artifacts that might prevent the results from being directly employed to elucidate normal molecular depth profiles. These concerns are examined in detail in Chapter 3. This chapter demonstrates that a standard organic delta layer system (Irganox delta layers) can be successfully characterized by combining wedge molecular depth profiling with AFM. Experimental conditions are altered to investigate the quality of profiles. Fundamental parameters associated with molecular depth profiling that are obtained from this strategy are comparable with conventional depth profiling. In Chapter 4, wedge-crater beveling is expanded and applied to investigate the effects of the sample temperature in a molecular depth profile. For the first time, a wealth of information regarding depth profiling process as the function of temperatures is presented instead of a simple comparison of SIMS results at two different
temperatures. In Chapter 5, information gathered from a conventional depth profile of the Irganox delta layer sample is comprehensively compared to information obtained from wedge-crater beveling. Finally, future directions of molecular depth profiling and wedge-crater beveling are discussed in Chapter 6. Overall, the development of a wedge-crater beveling strategy presented in this thesis delivers a better understanding of the fundamental processes that govern a molecular depth profile.

1.6 Reference


(49) Mahoney, C. M.; Roberson, S. V.; Gillen, G. *Analytical Chemistry* **2004**, *76*, 3199-3207.


Chapter 2
Developing Wedge-Crater Beveling Depth Profiling

This chapter has been reproduced and adapted with permission from D. Mao, A. Wucher and N. Winograd, *Analytical Chemistry* (2010). This paper was submitted as a letter paper for Analytical Chemistry and has been expanded for further clarification in this chapter.

2.1 Introduction

Since it was first reported that cluster ion beams minimize the accumulation of beam-induced damage in a wide variety of organic materials,\(^1\) secondary ion mass spectrometry (SIMS) experiments have been focused upon the implementation of molecular depth profiling and 3-dimensional (3-D) imaging as unique characterization tools in materials science. Depth information with a resolution to 10 nm has been achieved by correlating the amount of material removed, using tools such as the atomic force microscope (AFM), with the magnitude of the incident ion current and the time of bombardment.\(^2\) Considerable information has been published recently regarding the ultimate achievable depth resolution.\(^3,4\) Factors such as topography, ion beam mixing, temperature, incident beam angle and variations in the erosion rate have all been implicated in influencing the outcome of these experiments.\(^5,6\) Although the parameters for molecular depth profiling are often very different than those associated with inorganic
depth profiling of atomic species, some of the formalism developed more than 20 years ago is still applicable to these new systems.

An interesting strategy involves the sculpting of a wedge shaped crater using a focused ion beam (FIB) source. Beveling with very small slope angles has been employed to achieve laterally magnified cross-sections of ion milled multilayer structures for many years using atomic solids. More recently, Gillen and coworker utilized cluster bombardment and beveling to elucidate the structure of buried polymer interfaces, demonstrating, for the first time, the feasibility of using this idea for organic materials. It was suggested that a depth feature of 1 nm could easily be resolved with a 5 µm SIMS probe for lateral homogenous samples.

The creation of wedge-shaped craters for the study of 3-dimensionally complex materials is certainly intriguing from an imaging perspective, but here we suggest that by combining wedge technology with AFM measurements, fundamental information about the molecular depth profile may be acquired. To illustrate, we employ a C_{60}^{+} projectile to prepare a shallow wedge type structure in an organic thin film of Irganox 1010 doped with four delta layers of Irganox 3114. This sample has been studied extensively by Shard and coworkers, and has been utilized as a standard reference material for a round-robin VAMAS study of molecular depth profiling. The wedge experiments not only reveal a complementary strategy for determining interface widths, but also provide direct information about topography and sputtering yield at every point in the depth profile from a single measurement. These data are essential to acquire in order to find optimum parameters for 3-dimensional imaging, and for making accurate calculations of the ultimate achievable depth resolution.
2.2 Experimental Section

The experiments were performed using a ToF-SIMS spectrometer\textsuperscript{13} equipped with a fullerene ion source delivering a focused (~ 7 μm diameter) 40-keV C\textsubscript{60}\textsuperscript{+} ion beam of about 200 pA. A 50 ns primary beam pulse incident at 40° was employed to acquire SIMS spectra. Images were created with a digitally controlled raster over 256 × 256 pixels covering a surface area of 450 × 360 μm\textsuperscript{2}. During ion erosion cycles, the beam was operated in a dc mode and rastered across the same field of view as employed for data acquisition. The raster scheme was set up as a sequence of fast frames with a relatively short dwell time of about 10 μs on each pixel. This protocol minimizes material re-deposition effects well known from FIB technology.\textsuperscript{7} In order to erode a wedge-shaped crater, the raster area was varied from frame to frame by sequentially skipping more and more lines along the direction of the wedge y, beginning with the line closest to the ion source. Each time the number of skipped lines reached the total value of 256, the complete raster frame was restored and the sequence repeated as shown in Figure 2-1. This way, the applied ion fluence varies linearly with (y) as Eq. 2.1

\[
f(y) = 2 f_0 \frac{y}{L_y}
\]

Where \(L_y\) is the crater dimension in the y-direction (450 μm) and \(f_0\) is the average applied ion fluence. Since the angle of the beveled structure with respect to the sample surface is always less than 0.05°, the angle of incidence of the primary ion beam remains essential fixed during the measurement. Wedge craters’ optical images show the color change due to light reflection, just as shown in Figure 2-1. Optical image of a 12 steps wedge craters are shown in Figure 2-2 and it looks similar to illustration Figure 2-1.
After completion of the crater erosion and data taken with SIMS of the wedge surface as shown in Figure 2-3, the topography of the bombarded surface was investigated using a wide-area AFM (KLA Tencor Nanopics 2100). The system was operated both in contact mode to characterize the erosion crater and non-contact mode to determine the rms surface roughness. Care was taken to correct the obtained images for curvature effects by making sure that line scans taken outside of and parallel to the y-direction.
eroded crater were flat. Measurements were recorded immediately after the wedge was created.

Figure 2-2: Optical images of the wedge cater formed on Irganox delta layers samples with 12 steps wedge-beveling. Due to the light reflect index, Irganox sample with different thickness shows different colors under microscope.

A 350 nm thin film of Irganox 1010 on Si and doped with four delta layers of Irganox 3114 with thicknesses of ranged from 3.0 to 3.7 nm served as the model system for these experiments. The sample was manufactured at the National Physical Laboratory (NPL) in the UK and was used as received without any further preparation. The four delta layers of Irganox 3114 were created 47 nm, 97 nm, 194 nm and 293 nm below the surface.
2.3 Results and Discussion

Implementation of a wedge-shaped erosion pattern, combined with the topological precision of AFM, allows the fundamental parameters associated with molecular depth profiling to be acquired with an unprecedented level of detail. To illustrate, the AFM image of the eroded crater for the Irganox model film is shown in Figure 2-4 and the combined AFM/SIMS information is summarized in Figure 2-5. The data show that it is

Figure 2-3: During the wedge depth profile, when the deepest side of the crater reached 150 nm. The red line across the wedge crater represents the actual SIMS imaging surface during this sputter cycle. Then image of m/z 42 from this surface is shown as below representing the signal from Irganox 3114. Dark Green: Irganox 1010; Orange: Irganox 3114; Light Green: Si
possible to acquire information about depth resolution using the laterally magnified cross-sections during SIMS acquisitions, as well as about erosion rates and topography as a function of primary ion fluence from AFM measurements, all from a single experiment. These parameters are essential to characterize the quality of the depth profile using the previously developed erosion dynamics model.

The AFM pictures depicted in Figure 2-4 show the top view and a line scan of the beveled crater after erosion is complete. Since the rastering scheme ensures a linear fluence variation according to Eq. 2.1, the slope of the crater bottom along this line reflects the erosion rate at the corresponding crater depth. Since this line does not decrease in a linear fashion, it is clear that the erosion rate is decreasing with erosion depth, approaching nearly zero at the Irganox/Si interface. Moreover, the topography data exhibit a short-scale fluctuation which increases with increasing depth.

Combined SIMS data and AFM data are illustrated in Figure 2-5. It shows the uncorrected AFM data for the wedge crater as well as SIMS lines scans using the characteristic delta layer SIMS ion at m/z 42 and the SiO₂ ion at m/z 60. Figure 2-10 consists of smoothed AFM topography data and erosion rate information that has been converted to a depth scale directly associated with the cross section of the Irganox film. The SiO₂ SIMS signal is also included for reference purposes.
There are a number of interesting features associated with Figure 2-5 and Figure 2-10. Although the first two Irganox delta layers at a depth of 47 nm and 97 nm are not resolved as seen in the Figure 2-5, the 3rd and 4th layers are clearly separated. The FWHM of the 3rd delta layer is found to be ~ 30 nm by utilizing lateral to depth scale
conversion as shown in Figure 2-6. It is in reasonable agreement to the value of 25 nm reported previously, acquired using 30 keV C$_{60}^+$ bombardment.$^{10}$ The first two delta layers are easily separated, however, by reducing the beveling angle to effectively increase the lateral magnification.

Figure 2-5: This figure shows a topography scan across the wedge crater along the line indicated in Figure 2-4 (orange) along with line scans of the SIMS signals representing the Irganox 3114 delta layers (m/z 42, blue) and SiO$_2$ substrate interface layer (m/z 60, green). The erosion rate is shown in magenta, with smoothed values given by square grey points. The grey line represents the roughness fluctuations around the average height (see text).

An advantage of wedge-crater beveling is depth profile results based on real depth scale can be obtained in a single crater. A protocol is developed to get real time depth
scale depth profile results, which is extremely hard to obtain by regular depth profiling. In order to get covert SIMS line scan which is in lateral scale of μm into vertical depth scale of nm, both SIMS and AFM line scan along the y direction are needed.

Figure 2-6: A line scan of m/z 42 can be obtained across the crater. From the line scan data, we know the distance between the 1st and 2nd Irganox 3114 layer signal on this m/z 42 SIMS imaging is 170 µm (whole crater 450 µm). And from the structure of the film, we also know the depth distance between the 1st and 2nd layer is 47 nm. We can get the FWHM value of each layer from the figure below by locating them in the x axis. They can be converted into a depth scale to get the depth resolution of each layer.

First, a line scan of SIMS across a formed wedge crater in y direction is taken for the target signal, as shown in top panel of Figure 2-7. This generates a profile of the SIMS signal as the function of scan length. Next, an AFM line scan of the same wedge crater is taken in y direction, as shown in lower panel of Figure 2-7. This gives a relationship between the depth scale and scan length. Interestingly, both line scans are as function of the scan length.
In SIMS, the starting point and ending point of the wedge crater can be found by pinpointing the half intensity of signal peak on the edge of the craters. And in AFM, the starting point of the wedge crater is the point when depth starts to increase and ending point is the half way of the edge on the deeper side. So both AFM and SIMS starting point and ending point of the crater can be found and match. A combined figure consists

Figure 2-7: Top panel: this figure shows a line scan of Irganox 3114 signal m/z 42 across a wedge crater in y direction, a profile of m/z 42; lower panel: this figure shows an AFM line scan of a wedge crater in y direction, a relationship profile between depth and scan length.
of both AFM and SIMS with matching crater scan length can be plotted as shown in Figure 2-8.

Then the depth information for each ion intensity data point of m/z 42 SIMS signal profile can be interpolated from AFM scan. A depth profile of m/z 42 signal is obtained based on real depth scale, as shown in Figure 2-9. This type of depth information for depth scale is tedious because of the drawback of lacking topography information for conventional depth profiling.

By using this protocol, we can obtain depth resolution information from the wedge crater experiments. Note that, all of these figures and results represent one SIMS imaging cycle during the whole wedge depth profile. The wedge crater width in the y direction stays the same at 450 µm. At this point, the deepest side is 150 nm and the angle of the wedge can be calculated as 0.019°. With continued wedge depth profile, the wedge crater will become deeper and angle will become larger till the substrate is reached corresponding to an angle of 0.050°.

Although these preliminary data suggest that the beveling process yields data directly comparable to depth profiling using flat-bottomed craters, more experiments with different conditions will be required to ensure that subtle differences do not exist.

Next, it is possible to calculate the erosion rate from the numerical derivative of the topographical line scan data. Due to the overlaid roughness fluctuations, the resulting magenta curve is quite noisy. Since topography variations generally occur over several nm of depth, the fluctuations were smoothed using a 10 point Fourier transform filter (cutoff frequency 0.046). The resulting data are plotted in Figure 2-10 (magenta squares) and show that the erosion rate drops by roughly a factor of two during removal of the
Irganox film. This finding is in good agreement with previous data\textsuperscript{10} for a similar sample bombarded with 30-keV C\textsubscript{60}\textsuperscript{3+} ions.

![Graph](image.png)

**Figure 2-8:** This figure shows both AFM and SIMS line scans as the function of scan length. The red line is a fitting of black dots of SIMS signal m/z 42 and the purple line is the AFM depth information.

The interface to the underlying substrate is clearly visible by the rise of the substrate related signal shown for both panels of Figure 2-10 in green. Inspection of the positive secondary ion spectrum in this region reveals a series of strong peaks at m/z 16, 60, 76, 136 and 196, which are interpreted as (SiO\textsubscript{2})\textsubscript{n}O\textsuperscript{-} secondary cluster ions originating from the native oxide layer between the molecular film and the silicon substrate. At the
interface, the erosion rate is found to abruptly drop to nearly zero, reflecting the fact that the sputter yield of SiO$_2$ is significantly lower than that of the organic film.

The data presented in Figure 2-10 can be used to settle a long standing question regarding the erosion rate variation across various interfaces. It is seen that an initial, rather abrupt stoppage of the erosion occurs at the point where the SiO$_2$ ion signal has reached about 25% of its maximum value. Interestingly, the erosion rate appears to pick up again within the interface oxide layer, until it stops when the Si substrate is reached. The average erosion rate throughout the removal of the interface oxide layer is about 20%
of that of the Irganox film immediately before reaching the interface. A linear interpolation based on the variation of the substrate signal, as is often used to correct for interface variations, would result in a value of approximately 50% and therefore lead to a slight overestimation of the actual interface width.

In order to evaluate the development of surface roughness, the topography scan is first smoothed by a 36-point Savitzky-Golay algorithm. The resulting data represent the average height of the crater bottom at each point along the scan. Subtracting this curve from the original line scan data then yields the height fluctuations which represent the surface roughness. These data are shown as the grey trace in Figure 2-10 and reveal that the surface roughness increases with increasing crater depth. Starting from an initial surface value below 1 nm, the roughness increases only slightly up to an eroded depth of about 200 nm. At this point, which interestingly coincides with the removal of the third Irganox 3114 delta layer, the roughness suddenly builds up. At the same time, relatively large fluctuations of the topography are observed, which appear to be correlated with corresponding fluctuations of the erosion rate as well. After erosion to a depth of about 395 nm, a roughness value of about 4 nm is reached. This type of information would be extremely tedious to obtain from conventional depth profiling experiments since AFM measurements would be required at many depths and multiple depth profile would be obtained.
2.4 Conclusions

In summary, we show that the wedge crater provides a simple means to obtain valuable information about depth resolution, topography, and the depth dependence of the erosion rate in molecular sputter depth profiling. This information is required to allow an accurate calibration of the depth scale in such experiments. There are important implications associated with this preliminary study. For biomaterials such as single cells...
and tissue, the beveling approach may provide a better means for directly observing the bilayer associated with cell membranes. Moreover, dramatic changes in topography and erosion rate are expected for such complex systems, complicating the construction of three-dimensional mass spectral information. A direct point by point determination of the factors that influence the depth scale would provide a direct means of correcting for these important effects.

2.5 Acknowledgement

Financial support from the National Institute of Health under grant no. 2R01 EB002016-16 and LipidMaps consortium GM 069338-07, the National Science Foundation under grant no. CHE-0908226 and the Department of Energy grant no. DE-FG02-06ER15803 is acknowledged.

2.6 Reference

(1) Mahoney, C. M.; Roberson, S. V.; Gillen, G. Analytical Chemistry 2004, 76, 3199.


Chapter 3

tnolecular Depth Profiling by Wedged Crater Beveling

This chapter has been reproduced and adapted with permission from D. Mao, C. Lu, A. Wucher and N. Winograd, *Analytical Chemistry* (2011). This paper has been expanded for further clarification in this chapter.

3.1 Introduction

Molecular depth profiling with energetic polyatomic primary ions has now been demonstrated to be feasible for a number of model systems consisting of thin films of lipids, metabolites, polymer additives and polymers.\textsuperscript{1-7} By combining depth profiling with imaging, 3-dimensional information can also be achieved as shown using both model systems and biological cells.\textsuperscript{8-10} The basic idea is to bombard the sample with a fluence of polyatomic ions that is sufficient to remove up to several microns of material from the sample surface, typically requiring $10^{13}$ to $10^{15}$ ions-cm$^{-2}$ of primary ion fluence. With atomic ions and cluster ions that contain a small number of atoms, this amount of fluence typically leads to chemical damage accumulation which destroys the fundamentally important molecular specificity.\textsuperscript{11-14} For larger polyatomic projectiles such as C$_{60}$ and Ar$_{1500}$, however, the characteristic high sputtering rate allows any chemical damage to be removed as quickly as it is created.\textsuperscript{15-18}
Now that molecular depth profiling appears to be a practical strategy, there is considerable interest in determining the factors that yield the highest quality result. For example, it is desirable to minimize damage accumulation and maximize the depth resolution observed when eroding through interfaces.\textsuperscript{3} So far, the makeup, kinetic energy and angle of incidence of the primary particle as well as the target temperature have been shown to influence these factors.\textsuperscript{4,6,19-22} Depth resolution has been proposed to be related to topography formation during erosion.\textsuperscript{3} Many of these issues have been discussed in connection with a standard sample of Irganox 1010 constructed to contain buried delta layers of Irganox 3114.\textsuperscript{3,22,24,25} This sample was prepared at the National Physical Laboratory (Middlesex, UK) and studied by 12 different laboratories in round-robin fashion.\textsuperscript{26}

Recently we have acquired molecular depth profiles by using a wedge crater sputtering strategy.\textsuperscript{27} With this scheme, a beveled structure is cut into the organic thin film by adjusting the incident cluster ion beam fluence to remove more material from one end of the crater than the other.\textsuperscript{28,29} Typically, the wedge is created from a 500 \(\mu\)m by 500 \(\mu\)m crater with a beveling angle measured with respect to the surface of about 0.03\(^\circ\). This small angle leads to lateral amplification of buried structures so that nm features can be resolved using conventional SIMS imaging. From a detailed characterization of the surface of the wedge using atomic force microscopy (AFM), the sputtering rate, topography and depth resolution can be obtained continuously at every point in the depth profile.\textsuperscript{27} Hence, this configuration provides a wealth of information that is useful in obtaining a fundamental understanding of the important phenomena associated with
molecular depth profiling, and in determining the parameters needed to optimize depth resolution and minimize chemical damage accumulation.

Although these preliminary results show that the important parameters can be easily measured, it remains to be shown whether the beveling process itself introduces artifacts that might prevent the results from being directly employed to elucidate normal molecular depth profiles. Here, we examine this issue in considerable detail. The results show that the depth resolution acquired by SIMS imaging on the bevel in some circumstances do indeed provide an excellent model for the erosion process, and provide a convenient platform for elucidation of the factors that degrade depth profiles. We show, for example, that the depth resolution at organic interfaces can be reduced to 8 nm when utilizing glancing incident angles and low temperature, even after erosion through several hundred nanometers into a buried interface. This value appears not to be influenced by topography formation since the AFM data show the surface roughness remains less than 1 nm throughout the bevel. These studies also suggest that temperature effects are exceedingly important in inhibiting chemical damage and topography. The wedge strategy reveals that several different mechanisms appear to be contributing to this observation. In general, we suggest that wedge crater sputtering is a unique and powerful way to characterize molecular depth profiling and will be an important asset in performing 3-dimensional imaging experiments, particularly on biological samples.
3.2 Experimental Section

The samples were manufactured at The National Physical Laboratory, U.K.\textsuperscript{3} Silicon substrates of 10 mm × 10 mm were cleaned and treated before insertion into an Edwards AUTO306 vacuum coater with Irganox 1010 and Irganox 3114 (CIBA, Macclesfield, U.K.) held in crucibles. A quartz crystal microbalance (QCM) was used to monitor the thickness of the layers during vapor deposition. Delta layers of Irganox 3114 were embedded into the Irganox 1010 coated Si substrates. The thickness accuracy of each delta layer is ± 0.3 nm.\textsuperscript{22} The film thicknesses of each layer from surface to substrate are listed in Table 3-1.

<table>
<thead>
<tr>
<th>Layer*</th>
<th>Type</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Irganox 1010</td>
<td>47.6 nm</td>
<td>48.2 nm</td>
</tr>
<tr>
<td>2</td>
<td>Irganox 3114</td>
<td>3.0 nm</td>
<td>3.0 nm</td>
</tr>
<tr>
<td>3</td>
<td>Irganox 1010</td>
<td>48.2 nm</td>
<td>48.8 nm</td>
</tr>
<tr>
<td>4</td>
<td>Irganox 3114</td>
<td>3.1 nm</td>
<td>3.1 nm</td>
</tr>
<tr>
<td>5</td>
<td>Irganox 1010</td>
<td>95.1 nm</td>
<td>96.2 nm</td>
</tr>
<tr>
<td>6</td>
<td>Irganox 3114</td>
<td>3.7 nm</td>
<td>3.8 nm</td>
</tr>
<tr>
<td>7</td>
<td>Irganox 1010</td>
<td>95.6 nm</td>
<td>96.7 nm</td>
</tr>
<tr>
<td>8</td>
<td>Irganox 3114</td>
<td>3.7 nm</td>
<td>3.8 nm</td>
</tr>
<tr>
<td>9</td>
<td>Irganox 1010</td>
<td>95.1 nm</td>
<td>96.2 nm</td>
</tr>
</tbody>
</table>

Structure of the Irganox 1010/3114 delta layer sample manufactured by NPL in the course of a recent VAMAS interlaboratory study\textsuperscript{22,26} Four Irganox 3114 delta layers are embedded into an Irganox 1010 matrix film of approximately 400 nm thickness deposited on a silicon substrate.

Experiments were performed using ToF-SIMS instrumentation previously described.\textsuperscript{30} For the studies presented here, the instrument is equipped with a 40 keV-C\textsubscript{60}\textsuperscript{+} primary ion source (IOG 40-60, Ionoptika, Southampton, UK). The beam produced by this source is directed toward the sample surface at an angle of 40° relative to the
surface normal. The beam is mass selected via a Wien filter and is focused to a spot size ranging from 5 ~ 8 µm for a DC beam and 7 ~ 12 µm for pulsed beam after passing through a 300 µm beam-defining aperture. The dc current measured at a Faraday cup is typically 20–200 pA depended on focus. Some experiments were performed at 20 keV by reducing the extraction voltage from the source.

The mass spectrometer itself was operated in delayed extraction mode with a 50-ns delay time between the primary ion pulse of 50 ns and the secondary ion extraction pulse. This procedure allows the ion impact to occur with the sample at ground potential and in a field-free region. We have found that under these circumstances, charge compensation is not necessary as long as more than one positive ion is emitted from the sample for each \( C_{60}^+ \) impact. The sample block could be cooled by passing liquid nitrogen directly through the sample holder. The sample temperature during this cooling process was typically 100 K, as determined by a thermocouple measurement.

To change the angle of incidence of the primary ion beam, a special sample holder was fabricated with a beveled angle of 31°, yielding an impact angle of 71° during sputter erosion. Since this configuration distorts the extraction field during SIMS analysis, the craters were subsequently imaged using the standard flat sample mount with the \( C_{60} \) beam incident at 40°.

For crater erosion, the \( C_{60}^+ \) ion beam is rastered in dc mode over a 550 µm x 420 µm area with a resolution of 256 × 256 pixels. The dwell time on each pixel was restricted to 10 µs during each pass to minimize any possible redeposition of material into nearby regions. The protocol for wedge creation has been described in some detail
previously in connection with inorganic depth profiling experiments. The idea is to control the ion beam fluence at each pixel such that a beveled crater bottom is produced.

Creation of the wedge-shaped crater is easily accomplished using a simple algorithm to determine which pixels are bombarded by the C$_{60}^+$ beam and for how long. Our protocol, as illustrated in Figure 3-1, involves setting up a series of frames. For the first frame, each of the 256 × 256 pixels receives the same ion fluence. In the second the frame, the first line corresponding to 256 pixels in the y direction is skipped, with the same fluence being applied to the remaining pixels. Subsequent frames are acquired with an additional line of y pixels skipped each time. In this way, the lines of pixels along the y direction receive linearly increasing ion fluence. For the entire crater, the applied ion fluence is shown in Eq. 3.1.

$$f(y) = 2f_0 \frac{y}{L_y}$$

3.1

Where $L_y$ is the crater dimension in the y direction (550 µm) and $f_0$ is the average applied ion fluence on the entire crater. The SIMS images are acquired in pulsed mode, with negligible ion fluence and a raster field-of-view covering the entire erosion area.

Surface topography, crater depth and size were characterized using AFM (Nanopics 2100, KLA-Tencor, San Jose, CA). Measurements were performed by removing the sample from the SIMS instrument and immediately placing it in the AFM for analysis. There is some question as to whether material moves as a function of time, although our measurements yielded identical results for up to many hours after crater formation. The 1 mm × 1 mm maximum scanning area of AFM in contact mode allows a convenient one-step measurement of the entire wedge-shaped sputter crater with both
microscopic and macroscopic topographical information. Extreme care was taken to correct the obtained images for curvature effects by making sure that line scans taken outside of and parallel to the eroded crater were flat.

Figure 3-1: The top cross-section view of the wedge crater process. A $C_{60}^+$ primary ion source is used to remove material in a rastered area divided into 256 pixels $\times$ 256 pixels. A wedge-shaped crater is eroded by applying an increasing ion fluence along the $y$ direction of the raster area. The resulting crater contains information from zero to $2 \times f_0$ projectile ion fluence. Depth profile information is obtained by taking a SIMS image of the resulting crater bottom. In this case, the $y$ dimension of the crater is 600 $\mu$m, and the maximum depth is 400 nm. Note that the angle of the wedge with respect to the surface is $\theta = \sin^{-1}(400$nm / 600$\mu$m) = 0.038°.
3.3 Results and Discussion

Previous studies have shown that by utilizing the topological precision of AFM to characterize a beveled crater, direct information about surface roughness and sputtering yield can be obtained at every point in the depth profile from a single measurement. The topographical line scan along the y direction of the wedge crater can be converted into roughness and erosion rate curves. Briefly, the macroscopic lateral derivative of the eroded depth reflects the depth dependent erosion rate, whereas the microscopic fluctuations reflect the surface roughness. The purpose of this work is to fully utilize the wedge strategy to examine the factors that influence surface topography and the erosion rate, with the goal of gaining fundamental insights into the factors that are involved. At the same time, the strategy provides an opportunity to optimize the depth resolution by investigating the effect of temperature, incident angle and primary ion beam energy on the shape of the resulting wedge-crater.

3.3.1 Surface Roughness

To evaluate the surface roughness as a function of the eroded depth, the microscopic height fluctuations obtained from the AFM data are analyzed as previously described. In order to eliminate the macroscopic depth variations, the AFM topography scan is first smoothed by a 36-point Savitzky-Golay algorithm, resulting in a curve representing the average height of the depth for each point in the crater. By subtracting this curve from the unsmoothed AFM data, the microscopic height fluctuations representing the surface roughness can be obtained. The results acquired at room
temperature and liquid nitrogen temperature are shown in Figure 3-2. The roughness build-up during the removal of the Irganox film is obvious if the ion bombardment is performed at room temperature. Height fluctuations at room temperature (red curve) are less than 1 nm on the initial surface, increase to ~ 3 nm at roughly 200 nm depth, and continue to increase until reaching the Si substrate. At liquid nitrogen temperature (blue curve), the roughness remains constant throughout the removal of the entire organic layer. After reaching the Si interface, the height fluctuations dropped at both room and liquid temperature.

For a more quantitative assessment, we determine the rms roughness value $R_q$ as shown in Eq. 3.2, a running average taken over $2N$ data points around a specific point $(i)$ in the line scan.

$$R_q(i) = \sqrt{\frac{1}{2N} \sum_{k=i-N}^{i+N} [\Delta h(k)]^2}$$  \hspace{1cm} 3.2$$

Using $N = 20$, these values are plotted as a function of eroded depth in upper panel of Figure 3-3. The error bars reflect the standard deviation of $R_q$ determined with the center points $(i)$ being displaced by up to five points to each side of a plotted data point. The roughness starts low at the initial surface with $R_q$ values less than 1 nm at both room temperature and liquid nitrogen temperature, in agreement of the reported value after the sample was made. The roughness remains low during erosion of the entire film at liquid nitrogen temperature. At room temperature, on the other hand, the roughness starts to increase at ~200 nm eroded depth and keeps increasing until reaching the Si substrate, resulting in $R_q$ over ~ 3 nm at this point. The comparison of roughness
development trends between room temperature and liquid nitrogen temperature clearly show the differences.

Figure 3-2: AFM topography scan along the wedge shaped crater eroded into a 400-nm Irganox 1010 film doped with four Irganox 3114 delta layers by a 40-keV C$_{60}^+$ ion beam impinging at 40° with respect to the surface normal. Upper panel: ion erosion with the sample at room temperature. Lower panel: ion erosion performed at liquid nitrogen temperature. The red and blue curves represent the roughness fluctuations around the average crater profile calculated by smoothing the AFM scan data as described in the text.
One interest finding is that during the first 100 nm erosion, the roughness of both experimental conditions remains low. However, according the previous reported depth resolution value, the depth resolution already started to degrade at this point and the cause of this degrade was attributed to the surface topography development. However, the result obtained on wedge crater show more information and it suggests the degradation of depth resolution is not caused only by the surface roughening.

Figure 3-3: RMS roughness ($R_q$ value, see text) as a function of eroded depth during sputtering of the Irganox 1010/3114 delta layer film with a 40-keV C$_{60}^+$ ion beam impinging under 40° with respect to the surface normal. The data were obtained at two different sample temperatures during ion bombardment.
These roughness data are extremely valuable because they are obtained as a function of real eroded depth at every point of the beveled crater. These data would be difficult to acquire in a conventional depth profile since separate carters would be required at each depth for subsequent AFM analysis.

### 3.3.2 Erosion Rate

Due to the linear relation between scan length $y$ and ion fluence as given in Eq. 3.1, the erosion rate can be calculated from the AFM data,\textsuperscript{27} as the numerical derivative of the smoothed topographical line scan.

To show the erosion rate variation as a function of eroded depth, the average of the derivative was calculated for sets of 40 data points, and the resulting value was plotted at the depth corresponding to the center of each of these intervals. The erosion rate for room temperature (red solid dots) and liquid nitrogen temperature (blue solid dots) are shown in the lower panel of Figure 3-4, where the error bars reflect the standard deviation of the straight line slope fits determined for each interval.

In general, the sputter yield volume ranges from 120 ~ 300 nm$^3$/impact for a 40-keV C$_{60}^+$ ion beam. At room temperature, the erosion rate starts to drop after removal of about 150 nm and continues to drop throughout the erosion of the rest of the organic film, where it has finally decayed to about 60% of the original surface value before reaching the Si substrate. While at liquid nitrogen temperature, the erosion rate remains fairly constant during the removal of the entire 400 nm film. The small fluctuation of the data points is induced by surface roughness calibration.
Interestingly, the decay of the erosion rate begins rather abruptly and appears to be correlated with the buildup of surface roughness. If the analysis is performed at liquid nitrogen temperature, the erosion rate remains at the same level as the initial rate, and no decrease is observed during the removal of the entire Irganox film.

Figure 3-4: Erosion rate (see text) as a function of eroded depth during bombardment of the Irganox 1010 / 3114 delta layer film at two different sample temperatures, 100 K (blue dots) and 300 K (red dots). Both wedge craters were created by a 40-keV $C_{60}^+$ ion beam impinging at 40° with respect to the surface normal.
3.3.3 Depth Resolution

Depth resolution during molecular depth profiling is one of the most important parameters since the value ultimately determines the range of applications for this methodology. The sample investigated here consists of a 395 nm thin film of Irganox 1010 doped with four delta layers of Irganox 3114 with thicknesses ranging from 3.0 to 3.7 nm located at depths of 47, 97, 194, and 293 nm below the surface. The sample was manufactured by the UK National Physics Laboratory (NPL) and served as a model system for depth resolution measurements in a recent VAMAS interlaboratory study on molecular sputter depth profiling\textsuperscript{22,26}. In wedge experiments of laterally homogenous layers, a depth profile can be obtained by taking a single SIMS image of the eroded beveled crater. This concept is illustrated in Figure 3-5, which shows the imaging plane of two wedges eroded to different maximum depth $z_{\text{max}}$ as red lines.

In the SIMS image, the delta layers can be identified as stripes of the Irganox 3114 specific signal at m/z 42, one of the strongest secondary ion signal, which is shown for two different beveling angles (A and B) in the upper and lower right panels of Figure 4, respectively. It is obvious that the lateral width of these stripes must be connected to the beveling angle and the apparent vertical width $\Delta z$ of the layer. The full width half maximum (FWHM) of the 1\textsuperscript{st} and 2\textsuperscript{nd} stripe can be measured by means of a line scan across such an image, and the apparent depth resolution is calculated from this width as shown in Eq. 3.3.

$$
\Delta z = \frac{\text{stripe width } \Delta y (\text{FWHM})}{\text{crater dimension } L_y} \cdot z_{\text{max}} \quad 3.3
$$
In the experiments performed here, the images were taken using a slightly larger rastering area than used during sputter erosion. Hence, the scan length entering Eq. 3.3 is the same as the respective crater dimension in Eq. 3.1, and therefore both $L_y$ and $z_{\text{max}}$ can be determined from the AFM measurement of the eroded crater.

Figure 3-5: Left panel: schematic illustration of the wedge shaped crater imaging technique used to identify the Irganox 3114 delta layers (yellow) embedded into the Irganox 1010 matrix (blue) film deposited on a silicon substrate (green). Right panels: SIMS images of the Irganox 3114 specific secondary ion signal at m/z 42 taken on the wedge shaped crater bottom for two different beveling angles as indicated by the red lines.

Calculation of the depth resolution from Eq. 3.3 implicitly assumes there is a linear relation between depth and ion fluence (i.e., the $y$ coordinate along the line scan), which in turn relies on the assumption of a constant erosion rate. An advantage of the
wedge depth profiling experiment is that this assumption is not necessary, since the
determination of the depth resolution can be based on the actual depth scale taken from
the AFM data. For that purpose, a scan across the AFM crater data is made along the
same line as that performed across the SIMS image, thereby allowing us to determine the
actual eroded depth $z$ at every point $y$ along the line scan. From the resulting $z(y)$ data, the
SIMS line scan can then be converted into a true depth profile even in cases where the
erosion rate strongly varies as a function of eroded depth.

The improvements of depth resolution have been reported by optimizing the
experimental conditions, including lowering sample temperature, reducing primary ion
beam energy, and increasing impact angle.\textsuperscript{4,22,31} In order to investigate the wedge depth
profiling strategy and compare it to standard depth profiling results, similar conditions
were investigated and analyzed.

The SIMS images of the Irganox 3114 signal including line scans along the
indicated arrows obtained under four different sets of experimental conditions are shown
in Figure 3-6. The data in the upper row were measured at room temperature with the ion
beam impinging at $40^\circ$ with respect to the surface normal. The data displayed in the
middle row were obtained at low temperature using the same impact angle, and the lower
panels refer to an increased impact angle of $71^\circ$ eroded at low temperature. The left and
right columns refer to two different beveling angles by eroding the wedge to different
depths $z_{\text{max}}$. 
Figure 3-6: SIMS images of the Irganox 3114 specific secondary ion signal at m/z 42 (inserts) and line scans of the respective signal intensity along the lines indicated by the arrows as obtained after erosion of a wedge shaped crater under different experimental conditions. Top panels: ion erosion at room temperature under 40° incidence; Middle panels: ion erosion at 100 K under 40° incidence; lower panels: ion erosion at 100 K under 71° incidence with respect to the surface normal. The left and right columns refer to two different or beveling angles characterized by the maximum eroded depth $z_{\text{max}}$ at the deepest side of the wedge shaped crater. Left panels: partial with $z_{\text{max}} \sim 120$ nm (between 2nd and 3rd delta layer); Right column: wedge erosion down to the silicon substrate with $z_{\text{max}} \sim 450$ nm. All wedged craters were eroded under bombardment with a 40-keV C$_{60}^+$ ion beam.
All three sets of experiments were performed with a 40-keV C$_{60}^+$ ion source, wedge crater sizes ranging from 500 to 600 µm and typical erosion times from 10 to 60 minutes depending upon the value of $z_{max}$ and primary ion beam current. The apparent depth resolutions, $\Delta z$ for the four delta layers determined under those conditions are shown in Table 3-2.

There are important trends apparent in the data. First, as already noted the depth resolution clearly improves when performing the experiment at 100 K rather than at room temperature and is further improved by sputtering at glancing impact angle. Second, the apparent width of the delta layer peaks visible in Figure 3-6 increases with increasing layer depth at room temperature, whereas it remains practically the same for all four layers if the erosion is performed at low temperature. Inspection reveals that this effect is entirely caused by the depth dependent decrease of the erosion rate. The depth resolution remains constant within error limits if the nonlinear fluence-to-depth conversion is taken into account (see Table 3-2). The third key observation is that the depth resolution measured for the 1$^{st}$ and 2$^{nd}$ delta layer at the smaller beveling angle (i.e., when the wedge shaped craters were eroded to only about 120 nm maximum depth) is similar to that obtained using a regular depth profiling protocol under otherwise identical experimental conditions.

Another central criterion needed to evaluate the effectiveness of our protocol is to determine whether the measured depth resolution obtained from wedge craters is identical to that obtained by direct depth profiling experiments$^{3,6,32}$ under all conditions or whether other factors need to be considered. At this point, the answer to this question is not straightforward. In general, we find that for small beveling angles and for small
values of $z_{\text{max}}$, very good agreement is found between the two approaches as seen by comparing the first and regular depth profile column of Table 3-2. As the beveling angle is increased, however, the measured depth resolution becomes considerable larger than that obtained by conventional means.

Table 3-2: Depth Resolution Under All Conditions

<table>
<thead>
<tr>
<th>Depth Resolution</th>
<th>300 K 40 keV</th>
<th>100 K 40 keV</th>
<th>100 K 40 keV</th>
<th>100 K 20 keV</th>
<th>Regular DP</th>
<th>Beveling Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_{60}^+$ 40° Impact</td>
<td>C$_{60}^+$ 40° Impact</td>
<td>C$_{60}^+$ 71° Impact</td>
<td>C$_{60}^+$ 71° Impact</td>
<td>300K, 40°</td>
<td>40 keV C$_{60}^+$</td>
</tr>
<tr>
<td>1st Layer</td>
<td>20 nm</td>
<td>16 nm</td>
<td>10 nm</td>
<td>8 nm</td>
<td>18 nm</td>
<td>0.01°</td>
</tr>
<tr>
<td>2nd Layer</td>
<td>27 nm</td>
<td>17 nm</td>
<td>10 nm</td>
<td>8 nm</td>
<td>23 nm</td>
<td>0.01°</td>
</tr>
<tr>
<td></td>
<td>40 nm</td>
<td>25 nm</td>
<td>13 nm</td>
<td>18 nm</td>
<td>0.04°</td>
<td></td>
</tr>
<tr>
<td>3rd Layer</td>
<td>45 nm</td>
<td>27 nm</td>
<td>15 nm</td>
<td>23 nm</td>
<td>0.04°</td>
<td></td>
</tr>
<tr>
<td>4th Layer</td>
<td>48 nm</td>
<td>31 nm</td>
<td>15 nm</td>
<td>30 nm</td>
<td>0.04°</td>
<td></td>
</tr>
</tbody>
</table>

Apparent depth resolution (FWHM) determined from line scans across SIMS images of the Irganox 3114 specific secondary ion signal at m/z 42 as described in the text. The data refer to different experimental conditions regarding the sample temperature, the incidence angle and energy of the bombarding C$_{60}^+$ ion beam and the beveling angle of the eroded wedge shaped crater. Upper rows: crater eroded to maximum depth between 2nd and 3rd delta layer ($z_{\text{max}} \sim 120$ nm); lower rows: crater eroded down to silicon substrate ($z_{\text{max}} \sim 400$ nm).
The apparent depth resolution is observed to be significantly worse when the beveling angle is increased by eroding the wedge shaped crater to 400 nm maximum depth. Since the ion fluence applied to expose a particular delta layer is independent of the beveling angle, this apparent broadening cannot be induced by a vertical broadening of the delta layer response caused, for instance, by ion induced interlayer mixing effects. It must therefore be caused by a peculiarity of the conversion from lateral to vertical resolution via the wedge shaped crater. The thickness of each Irganox 3114 delta layer is about 3 nm. In the absence of vertical broadening effects, the lateral width of the delta layer exposed by the beveled cross section can be calculated as shown in Eq. 3.4.

\[ ExposedWidth = \frac{3\text{nm}}{\tan(\text{BevelingAngle})} = \frac{3\text{nm} \times \text{CraterLength}}{Z_{\text{max}}} \]  

3.4

Taking the data obtained at liquid nitrogen temperature and 40° impact for example, for a 580 µm crater, when the wedge was eroded to 120 nm, the 1st layer exposed width is 14.5 µm and the line scan results shows a 94 µm FWHM, corresponding to 19 nm depth resolution. When the wedge is eroded to 400 nm, the 1st layer exposed width should be 4.35 µm, and hence the 1st layer FWHM should be 28 µm according to the calculation from Eq. 3.4. However, the measured FWHM is much larger (51 µm), which converts to an apparent depth resolution of about 40 nm after depth scale calibration.

Apparently other factors besides fluence dependent interlayer mixing are causing the broadening of the measured strip width in the SIMS image with increasing beveling angle. In principle, this observation is expected, because the lateral resolution during acquisition of the SIMS image must enter the measured FWHM, which is ultimately
restricted by the primary ion beam width. In order to understand the role of this restriction, a series of experiments were carried out where the erosion of the wedged shaped crater was stopped at different depths and SIMS images were taken from the resulting crater in a way similar to a standard imaging depth profile.

![Diagram showing beveling angle and measured vs calculated width]

**Figure 3-7:** Measured width (FWHM) of the m/z 42 secondary ion signal peak representing the uppermost Irganox 3114 delta layer in the line scans as depicted in Figure 5 as a function of beveling angle characterized by maximum crater erosion depth $z_{max}$ as indicated in Figure 3-5. Black dots: experimental data; Solid line: least square fit of Eq. 3.6 to the experimental data; Open circles: calculation according to Eq. 3.5 by setting the fitting parameter $B$ to zero.

The experiment was performed under 40° incidence at low temperature, and data acquisition was started when the first delta layer showed up in the image and ended when
the entire film was removed at the deep side of the crater. The lateral width (FWHM) of the 1\textsuperscript{st} Irganox 3114 delta layer was determined and plotted as the function of eroded maximum depth $z_{\text{max}}$ in Figure 3-7. The dark squares are the measured FWHM of the 1\textsuperscript{st} Irganox 3114 delta layer. It is seen that the FWHM of the 1\textsuperscript{st} layer starts from 150 µm and decreases to about 50 µm with increasing beveling angle, where it appears to become constant. Since the experiment was performed under conditions where the erosion rate remains constant, Eq. 3.4 should hold and the measured FWHM strip width should be given as

This relation is plotted as a dotted line in Figure 6, and it is obvious that it does not describe the experimental data correctly. Fitting a function

$$\Delta y = \frac{\Delta z}{z_{\text{max}}} \cdot L_y$$ \hspace{1cm} 3.5

Fitting a function to the data, we obtain parameters $A = \Delta z \cdot L_y$ and $B$ as indicated in the Figure which can then be used to determine the actual vertical broadening $\Delta z$ of the delta layer response function as the ultimate depth resolution achievable in this experiment. From the known scan length $L_y = 580$ µm, we obtain $\Delta z \sim 15$ nm, which is very close to the values measured at $z_{\text{max}} = 120$ nm. If the same experiment is performed under oblique ion incidence at 71° impact angle and at a reduced impact energy of 20 keV during erosion, we obtain the data displayed in Figure 3-8, which translate into an apparent depth resolution of about 8 nm.

$$\Delta y(z_{\text{max}}) = \sqrt{\left(\frac{A}{z_{\text{max}}}\right)^2 + B^2}$$ \hspace{1cm} 3.6
If the wedge is eroded deeper, the measured apparent depth resolution is worsened by the constant width $B$, which is of the order of 40 µm in this example. At present, it is not clear what may cause this additional lateral broadening, which is significantly larger than the imaging ion beam width of about 12 µm (FWHM). A similar analysis of the data obtained under 71° incidence (again at 100 K) reveals $\Delta z \sim 8$ nm and
$B \sim 21 \mu m$, respectively, measured with an imaging ion beam width of 8 $\mu m$ (FWHM).

Interestingly, both $\Delta z$ and $B$ appear to be reduced by approximately the same factor as compared to the 40° impact angle measurement.

![AFM line scans](image)

Figure 3-9: AFM line scans of stepped wedge craters formed at room temperature (top panel) and liquid nitrogen temperature (lower panel). The craters were eroded into an Irganox 1010 film doped with four Irganox 3114 delta layers using a 40-keV $C_{60}^+$ ion beam at a 40° impact angle.

At present, we can only speculate about possible reasons for the observed lateral broadening. In principle, surface roughness could lead to such an effect, but the resulting broadening would be independent of $z_{\text{max}}$ only if the rms roughness value would increase linearly with the crater beveling angle. However, the AFM data provide no indication of such an effect, which would also be difficult to explain since the ion fluence (or erosion depth) needed to expose a delta layer is independent of the beveling angle. Another possible cause of image broadening would be the lateral relocation of surface material
during the ion beam erosion. Although computer simulations suggest that lateral movement is indeed possible, the modeling suggests that the magnitude of the effect is on the order of a few hundred nanometers, much less than the tens of microns suggested by the data in Figure 3-10. Determination of origin of this effect could provide important insight into the sputtering process, since it is currently not predicted by any theory. The wedge protocol may hence provide an interesting platform for examining the dynamics of material motion.

Another possible cause of image broadening would be the lateral relocation of surface material during the ion beam erosion. The wedge crater strategy can in principle be employed to investigate such an effect. For that purpose, the applied ion fluence is ramped up in few, discrete steps instead of rather continuously along the y-direction of the wedge, and the resulting erosion pattern is mapped by AFM. In this case, lateral relocation of surface material would act to smear out the step edges. In order to look at possible temperature effects, craters of 12 steps were produced at both room temperature and liquid nitrogen temperature.

The resulting AFM data are shown in Figure 3-9. In both cases, the steps are clearly visible. Analyzing the height gradients at the step edges, one obtains 84%-16% widths of 15 – 18 µm, which are comparable to the eroding ion beam width measured in the direction perpendicular to the steps. At low temperature, this structure is well preserved down to about 400 nm depth. At room temperature, on the other hand, the structure becomes more and more smeared out with increasing eroded depth and the last few steps below approximately 270 nm are not clearly discernible any more. Hence, we have to conclude that significant lateral relocation of material is occurring during the ion
erosion process, which leads to transport of surface particles over distances on the micrometer scale. This finding is interesting in view of recent molecular dynamics simulations of silicon sputtering, where it was found that even under multi-impact $C_{60}$ bombardment surface atoms are only relocated over distances of the order of 100 nm before being removed from the surface by sputtering. Apparently, long range transport processes must contribute to the material relocation observed here, which must be thermally activated since they can be influenced by the sample temperature. Interestingly, these transport processes become strongly visible at about the same depth where surface roughness starts to build up and the erosion rate starts to decrease. It is conceivable that these relocation mechanisms contribute to the image broadening reflected by the fitting parameter $B$ in the previous section, but further experiments are clearly needed to clarify this point.

3.4 Conclusions

We demonstrate that an organic delta layer system (Irganox delta layers) can be successfully characterized by combining wedge molecular depth profiling and AFM. Fundamental parameter associated with molecular depth profiling including surface roughness, erosion rate and depth resolution can be easily determined as a function of the primary ion dose. Depth resolution can be measured directly from the converted actual depth scale depth profile and is comparable to regular depth profiling. Preliminary evidence is also presented that suggests that there may be a large amount of material motion in the lateral plane that would not be observed under normal conditions. In
general, we show that the wedge crater strategy can provide an important investigative tool for unraveling the complexities of molecular depth profiling.

3.5 Acknowledgement

Financial support from the National Institute of Health under Grant No. 2R01 EB002016-18, the National Science Foundation under Grant No. CHE-0908226, and the Department of Energy Grant No. DE-FG02-06ER15803 is acknowledged. The authors are grateful to Alex Shard for providing the delta-layer sample.

3.6 References


Chapter 4

Investigations of Temperature Effects by Wedge-Crater Beveling

This chapter has been reproduced and adapted with permission from D. Mao, etc. from Analytical Chemistry (2011). This paper was submitted for Analytical Chemistry and has been expanded for further clarification in this chapter.

4.1 Introduction

Molecular depth profiling of organic and biological materials using secondary ion mass spectrometry (SIMS) and cluster ion beams has developed in the last decade into feasible experiments within the SIMS community. Molecular and fragment distribution information as a function of depth has been successfully obtained for various materials, a technique which is known as depth profiling. The potential of depth profiling through a material has been demonstrated as a promising application for three dimensional reconstructions. During these depth profiling investigations some experiments were not successful under normal operating experimental conditions. Hence, several approaches have been proposed, developed, and incorporated in depth profiling experiments that increase the likelihood of a successful outcome where the depth profile previously was not successful. The most promising approaches include using a larger
cluster ion source, such as argon clusters,\textsuperscript{21,22} sputtering at glancing angles,\textsuperscript{13,23} cooling of the sample with liquid nitrogen\textsuperscript{9,13,24} and rotation of the sample stage.\textsuperscript{24,25}

Unfortunately, the approaches that have been proposed do not all necessarily prove to be successful either independently or in conjunction with another approach. For instance, the rotation of the sample during a depth profile improves only the quality of a two-dimensional but not a three-dimensional depth profile. Reason being is the complexity of rotating a sample demands the uniformity to be well defined for three-dimensional images obtained in a depth profile, an aspect not achievable for biological systems given there are non-uniform complex chemical distributions. On the other hand, sputtering at a glancing angle is believed to minimize interlayer mixing induced by bombardment as it significantly reduces the trailing edge of the depth profiling peaks.\textsuperscript{13} The use of giant argon cluster ion beams has been shown to minimize the mixing of materials and improve the quality of organic depth profiling.\textsuperscript{26} However, because of the size of the argon cluster, the bottom of the eroded sample is not flat. Also, it has been recently observed experimentally at room temperature conditions that the erosion rate is reduced after a certain ion dose by Vickerman \textit{et al.}\textsuperscript{27}

One of the most promising approaches that improved the overall quality of depth profiling experiments has been tied to the temperature of the sample. Sample cooling has been widely used for biological applications of SIMS since the sample integrity is maintained as well as preservation of cellular information in a hydrated frozen state prevents the collapse of cells in a high vacuum environment.\textsuperscript{28-30} One interesting finding in frozen state cellular SIMS experiments is that the molecular ion signal is enhanced
with the presence of a water ice matrix. This modality of sample analysis has been suggested to be beneficial and a potential standard for SIMS depth profiling experiments. In recent developments of depth profiling experiments carried out at cryogenic temperatures, cooling the sample has proven to have a great impact on a depth profile. For example, cooling the sample not only reduces damage accumulation but also maintains the secondary ion intensity. It improves the interface widths, and also helps to achieve a constant erosion rate. Sample cooling has also been widely investigated for other organic systems including poly (methyl methacrylate) (PMMA), Langmuir-Blodgett multilayered thin films, and Irganox multilayered thin films. Aside from the benefits of cooling organic and biological samples the effects of temperature in a depth profiling experiment remain to be investigated and developed when combined with other promising experimental conditions.

A comprehensive understanding of the temperature effects on molecular depth profiling remain a mystery and demanded to be necessary for further developing the applications of cryogenic experiments. Whether the temperature effects act gradually or dramatically remain unknown. Unfortunately, very few experimental results have been published with limited information due to the technical difficulty in stage cooling experiments, the precise control of temperature, reproducible surface topography measurements and erosion rate. Most recent comparisons between room temperature and liquid nitrogen temperature have been focused on the depth resolution factors involved in depth profiling. It takes tremendous effort to obtain surface
topography and erosion rate even for a single temperature with the conventional depth profile experiment.

To investigate and understand the temperature effects in depth profiling experiments, a supplemental strategy has been proposed. Recently, wedge-crater beveling of delta layer organic samples used as a tool to acquire fundamental information of molecular depth profiling with C$_{60}$-SIMS has been developed in our lab. 32,33 One advantage of wedge-crater beveling is that all factors regarding depth profiling including interface widths, topography and sputtering yield at every point in the depth profile can be obtained from a single crater measurement. With the help of wedge-crater beveling, a detailed investigation of temperature effects can be achieved in a manageable amount of time, delivering a tremendous amount of surface topography information.

In this work, we examine temperature effects in considerable detail by a combination of conventional sputter depth profiling and wedge-crater beveling. An organic multilayered system of Irganox 1010/3114 was used as the sample system for this investigation. This sample has been widely studied and the results from this work can be directly compared to those previously published. 10,24-26 The goal is to acquire and characterize depth profiles of the buried Irganox 3114 delta layers as a function of sample temperatures, ranging from liquid nitrogen (90 K) to room temperature (300 K). The results of conventional depth profiles are compared to those obtained with the wedge-shaped crater beveling technique using a focused 40-keV C$_{60}^+$ ion beam for sample erosion and SIMS data acquisition. Depth profile data is complemented with AFM measurements of the eroded crater, which in combination with the wedge beveling
technique provide extremely valuable additional information regarding the dynamics of erosion rate and surface roughness during the profile. Depth profiles are acquired in the imaging mode, either as a series of mass spectral images separated by homogenous erosion cycles for conventional depth profiling or by acquisition of one single image of the wedge-shaped sputter crater. The results show that erosion rate decay and surface roughening are linked and start to occur abruptly at a certain eroded depth. Both effects are prominent at sample temperatures of 250 K and above, where they keep growing in magnitude with increasing sputtered depth, but can be effectively suppressed if the sample temperature is lowered below 250 K. The results also reveal a degradation of the secondary ion yield which appears to be much more pronounced than the erosion rate decay and is even observed when the erosion rate is maintained throughout the depth profile.

4.2 Experimental Section

An organic delta layer system was constructed by National Physical Lab (NPL) in UK using two different materials, Irganox 1010 and Irganox 3114. Thin marker layers of Irganox 3114 (~ 0.9 nm) were deposited between thick layers of Irganox 1010 (~ 47.1 nm or ~ 94.3 nm), resulting in a delta layer structure which is ideally suited to investigate the depth resolution of the technique in a similar way as has been routinely done in inorganic depth profiling. The film thicknesses of each layer from surface to substrate are listed in Table 4-1.
Depth profiling was performed in a TOF-SIMS instrument equipped with a fullerene cluster ion source (IOG 40-60, Ionoptika; Southampton, U.K.), directed at a 40° angle relative to the surface normal. The performance of C\textsubscript{60} ion source\textsuperscript{2} and details of this instrumentation have been described elsewhere.\textsuperscript{34} For conventional depth profiling experiments, the 40-keV C\textsubscript{60}\textsuperscript{+} ion beam was operated alternatively between data acquisition and material sputtering cycles. A continuous ("dc") beam of measured current of ~ 80 pA into a spot size of ~10 \(\mu\)m was used to erode an area of 190 \(\mu\)m \(	imes\) 250 \(\mu\)m area of the film with removal of 4 ~ 5 nm of material per interval. For the conventional depth profiling, a stable primary ion beam current is crucial because AFM data can be measured only from the completely eroded crater. Current measurements were taken before and after erosion of each crater to ensure the stability of ion beam. The wedge sputter depth profiling scheme has been described in a previous publication.\textsuperscript{33} Briefly, the surface is subjected to one or two erosion cycles with the 40-keV C\textsubscript{60}\textsuperscript{+} ion beam operated in dc mode and digitally scanned across a 460 \(\mu\)m \(	imes\) 600 \(\mu\)m field of view.

<table>
<thead>
<tr>
<th>Layer*</th>
<th>Type</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Irganox 1010</td>
<td>47.1 nm</td>
</tr>
<tr>
<td>2</td>
<td>Irganox 3114</td>
<td>0.9 nm</td>
</tr>
<tr>
<td>3</td>
<td>Irganox 1010</td>
<td>47.1 nm</td>
</tr>
<tr>
<td>4</td>
<td>Irganox 3114</td>
<td>0.9 nm</td>
</tr>
<tr>
<td>5</td>
<td>Irganox 1010</td>
<td>94.3 nm</td>
</tr>
<tr>
<td>6</td>
<td>Irganox 3114</td>
<td>0.9 nm</td>
</tr>
<tr>
<td>7</td>
<td>Irganox 1010</td>
<td>94.2 nm</td>
</tr>
<tr>
<td>8</td>
<td>Irganox 3114</td>
<td>0.9 nm</td>
</tr>
<tr>
<td>9</td>
<td>Irganox 1010</td>
<td>94.2 nm</td>
</tr>
</tbody>
</table>

Structure of the Irganox 1010/3114 delta layer sample manufactured by NPL. Four Irganox 3114 delta layers of 0.9 nm are embedded into an Irganox 1010 matrix film approximately 380 nm) deposited on a silicon substrate covered with silicon dioxide.
using a 256 x 256 pixel raster. The total scanning time of each cycle was divided into frames with a beam dwell time of about 20 μs on each pixel. In order to erode a wedge-shaped crater, a linearly increasing ion fluence was applied which varied between zero on one side of the crater and maximum on the other side. For that purpose, the raster area was varied from frame to frame by sequentially skipping more and more lines in the y-direction, beginning with the line closest to the ion source. The TOF-SIMS instrument used in these experiments has the capability of sample cooling by blowing liquid-nitrogen-cooled nitrogen gas through the sample stage as shown in Figure 4-1. Because the stage is pulsed to high voltage potential during the SIMS analysis, a direct measurement of the sample temperature is not possible during data acquisition. Temperature readings were collected using a thermocouple wired to the stage before and after each experiment. A constant flow of nitrogen gas is first established through a copper tube imbedded into liquid nitrogen. Under normal operating conditions, the N₂ gas was at least partly condensed into a liquid nitrogen flow through the sample stage, resulting in a stable stage temperature of ~ 90 K. In order to stabilize the temperature at higher values between 90 and 300 K, a heater was wrapped around the copper tube and operated at a fixed electrical power using a variable autotransformer. By balancing the N₂ line gas flow and the heating power, a stable stage temperature was obtained within a waiting time of approximately one hour which then remained constant within ± 5 K for the duration of the entire experiment. The stabilized temperature and settings are shown in Table 4-2.
For conventional imaging depth profiling, negative SIMS images were taken from the center area of about 115 µm × 150 µm within the erosion area (190 µm × 250 µm) between subsequent erosion cycles. For wedge-crater beveling depth profiling, SIMS images of the eroded wedge-shaped crater were taken from an analysis field of view of
520 µm × 675 µm when the largest erosion depth reached ~150 nm and ~400 nm, respectively.

Figure 4-2: The optical images of a wedge crater from an Irganox delta layered sample. Top panel (a): wedge crater with the deepest side at 150 nm. Lower panel (b): wedge crater with the deepest side at 400 nm.
The optical images of wedge craters at these two depths are shown in Figure 4-2. In the latter case, the entire film was removed at the deep side of the eroded crater. SIMS images were acquired using the pulsed C$_{60}^+$ beam (pulse width 50 ns) digitally rastered across a pattern of $256 \times 256$ pixels. AFM characterization of the eroded craters was performed using a KLA-Tencor Nanopics 2100 wide area atomic force microscope (AFM). For the analysis of the wedge-shaped craters, the AFM images were taken at 800 µm × 800 µm field of view in order to enclose the entire crater into one image. The data were taken in contact mode, but it was checked that images taken in damping (tapping) mode delivered the same information. Extreme care was taken to process the AFM results, minimizing the instrumentation artifacts of the topography information on the wedge surface.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>N$_2$ Flow (psi)</th>
<th>Variable Autotransformer (V)</th>
<th>Temperature Reading Before Start (K)</th>
<th>Temperature Reading After End (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>298</td>
<td>298</td>
</tr>
<tr>
<td>250</td>
<td>15</td>
<td>64</td>
<td>254</td>
<td>244</td>
</tr>
<tr>
<td>210</td>
<td>15</td>
<td>50</td>
<td>208</td>
<td>212</td>
</tr>
<tr>
<td>160</td>
<td>15</td>
<td>46</td>
<td>159</td>
<td>164</td>
</tr>
<tr>
<td>130</td>
<td>15</td>
<td>36</td>
<td>137</td>
<td>130</td>
</tr>
<tr>
<td>90</td>
<td>15</td>
<td>0</td>
<td>89</td>
<td>89</td>
</tr>
</tbody>
</table>

Required nitrogen gas flow and variable autotransformer voltage settings to achieve certain temperatures. Temperatures reading before and after the experiments are shown in last two columns.

AFM characterization of the eroded craters was performed using a KLA-Tencor Nanopics 2100 wide area atomic force microscope (AFM). For the analysis of the wedge-shaped craters, the AFM images were taken at 800 µm × 800 µm field of view in order to
enclose the entire crater into one image. The data were taken in contact mode, but it was checked that images taken in damping (tapping) mode delivered the same information. Extreme care was taken to process the AFM results, minimizing the instrumentation artifacts of the topography information on the wedge surface.

4.3 Results and Discussion

In previous work, we have shown that by combining topographical information from AFM with SIMS molecular information in a beveled crater, direct information about surface roughness, erosion rate and depth resolution can be obtained from a single measurement. The detailed protocol to extract that information from topographical line scans along the wedge (y-) direction of the eroded crater has been described previously. Briefly, the process utilizes the fact that there is a linear relationship between the y-coordinate along the line scan and ion fluence. The erosion rate can therefore be directly calculated from the average slope of the (smoothed) wedge crater surface and evaluated as a function of depth from one single crater profile. Microscopic fluctuations of the surface height, on the other hand, reflect the surface roughness, which can be obtained by subtracting the original AFM line scan from the smoothed data. At the same time, the depth resolution can be obtained by determining the lateral width of the SIMS signal characteristic for the Irganox 3114 delta layer when plotted along the same line scan across the SIMS image of the crater bottom. The resulting full width at half maximum (fwhm) can be converted into depth resolution after calibration of the depth scale using the AFM data.
In our previous work, we compared experiments where the depth profile analysis was performed at 300 K and 90 K and found a significant improvement at low temperature. The purpose of this work is to investigate the cause of that effect further by varying the sample temperature between these two extremes. Figure 4-3 shows conventional sputter depth profiles measured at four different sample temperatures 90K, 250 K, 150 K and 90 K with $C_{60}^+$ at 40° incident angle. The Irganox 1010 matrix signal ($C_3H_5O_2^-$ m/z 59) is normalized to surface intensity. And Irganox 3114 delta layer signal ($C_{33}H_{46}N_3O_5^-$ m/z 564, CNO$^-$ m/z 42) is normalized to maximum intensity of the entire depth profile.

In our previous work, we compared experiments where the depth profile analysis was performed at 300 K and 90 K and found a significant improvement at low temperature. The purpose of this work is to investigate the cause of that effect further by varying the sample temperature between these two extremes. Figure 4-3 shows conventional sputter depth profiles measured at four different sample temperatures 90K, 250 K, 150 K and 90 K with $C_{60}^+$ at 40° incident angle. The Irganox 1010 matrix signal ($C_3H_5O_2^-$ m/z 59) is normalized to surface intensity. And Irganox 3114 delta layer signal ($C_{33}H_{46}N_3O_5^-$ m/z 564, CNO$^-$ m/z 42) is normalized to maximum intensity of the entire depth profile.
150K, 250K and 300K. The signal of the largest Irganox 3114 specific fragment \((C_{33}H_{46}N_3O_5^-)\) and a relatively small fragment \((\text{CNO}^- \text{ at m/z 42})\) are plotted vs. the \(C_{60}^+\) ion fluence along with that of an Irganox 1010 specific fragment \((C_2H_3O_2^-)\) at m/z 59 for reference. In accordance with previously published data, several observations are evident from the figure:

i. the secondary ion signals representing the Irganox 3114 delta layers track each other.

ii. the signals representing both the Irganox 1010 matrix and the Irganox 3114 delta layers decrease with increasing eroded depth.

iii. the apparent width of the delta layer peaks (fwhm) increases with increasing eroded depth.

Effects ii) and iii) are most pronounced if the depth profile is performed at 300 K, where they agree with similar findings published earlier. They have been attributed to a degradation of the depth resolution which was assumed to be entirely caused by an increased surface roughness being built up under the eroding ion bombardment. It is interesting that there is no depth resolution difference for the 1st delta layer is observed under all four temperatures. This issue will be investigated in more detail below. Moreover, it has been proposed to estimate the average erosion rate between subsequent delta layers using their known depths in combination with the fluence interval between the respective signal maxima in the depth profile. Figure 4-3 shows data obtained using this strategy, using the depth values of 48, 96, 192 and 288 nm for the 1st, 2nd, 3rd and
4th delta layer as given by the manufacturer. The data indicates a decrease of the average erosion rate with increasing eroded depth, which is most pronounced at the highest temperature and appears to be practically absent at temperatures below 150 K.

Figure 4-4: Depth profiles of Irganox 1010/3114 multilayers sample at 300 K (top panel) and 90 K (lower panel) with 40-keV $C_{60}^+$ at 40$^\circ$ incident angle. Each Irganox 1010 matrix signal is normalized to surface intensity.
It appears straightforward to assume that the degradation of the measured secondary ion signal, the depth resolution and the erosion rate are connected and caused by chemical damage of the molecular film building up and accumulating under prolonged ion bombardment. To investigate this notion further, one can trace the SIMS signals of the molecular ion and characteristic fragments of the Irganox 1010 matrix as shown in Figure 4-4. In order to illustrate the trends, the data have been plotted only for the highest and lowest sample temperature studied here. It is immediately evident that the two cases are largely different. At the beginning of the depth profile, all signals exhibit a relatively rapid decay during the fluence interval up to $1 \times 10^{13}$ ions/cm$^2$. This behavior is well known and indicates the onset of ion beam induced fragmentation as described by the erosion dynamics model. The magnitude of the decay is most pronounced for the molecular ion and decreases with decreasing fragment size, indicating a larger damage cross section for the molecular ion. At 90 K, all signals reach a steady state after this initial decay, indicating a stable balance between ion beam induced damage/fragmentation and sputter removal, the latter being characterized by a stable sputter yield or erosion rate. At 300 K, on the other hand, all signals continue to decay with increasing fluence, yet at a slower rate, which is largest for the molecular ion and decreases with decreasing fragment size. One additional observation in Figure 1 in is that when there is no signal decays there is no difference between big and small fragment, indicates this difference is related with sample damage and only occurs after a certain erosion depth. As shown previously, this "quasi steady state" behavior is indicative of a decreasing sputter yield, a notion which is in principal accordance with the data in Figure 4-5.
To investigate these points in more detail and complement the information presented in Figure 4-3, additional depth profiles were obtained using the wedge-shaped crater beveling technique at six different temperature points including 90 K, 130 K, 160 K, 210 K, 250 K and 300 K. The wedge methodology was used because it allows directly extracting information on erosion rates and surface roughness in addition to the depth profiling data. The results obtained as the function of temperature will be discussed in the following sections.

Figure 4-5: Calculated erosion rate from conventional depth profiles by dividing ion fluence from known volume between each layer.
4.3.1 Surface Roughening Effects

For the surface roughness evaluation, the microscopic height fluctuations from the AFM data measured on the wedge-shaped erosion crater can be visually compared. To eliminate the macroscopic depth variations, the AFM topography scan is first smoothed by a 36-point Savitzky-Golay algorithm. The resulting curve represents the average height of the surface as a function of a linearly increasing ion fluence, the latter being represented by the length coordinate along the AFM line scan of the crater bottom. By subtracting this curve from the original AFM data, the microscopic height fluctuations representing the surface roughness can be obtained. The results of AFM line scans and the further calculated height fluctuations are shown in Figure 4-6.

The height fluctuations can be categorized into three groups that are related to the sample temperature. At low temperature (upper panel of Figure 4-6), the height fluctuations remain constantly low during the removal of the entire film and are estimated to be around ±2.5 nm for the maximum peaks, with only minimal differences between 90 K and 130 K. At intermediate temperatures (middle panel of Figure 4-6), the height fluctuations continue to remain constant throughout the entire wedge surface with no obvious increase as a function of ion fluence. However, the resulting curves fluctuate more intense than at 90K, with peak maxima around ±5 nm at 160 K and some even larger at 210 K. These results show that the surface roughening induced by ion bombardment is worse but stable, and the overall surface roughening is still minimal.
Figure 4-6: AFM topography scan along the wedge shaped craters eroded into a 380-nm thick Irganox 1010 film doped with four Irganox 3114 delta layers by a 40-keV \( C_{60}^+ \) ion beam impinging at 40° with respect to the surface normal at 90 K, 130 K, 160 K, 210 K, 250 K and 300 K temperature. The blue curves represent the roughness fluctuations around the average crater profile calculated by subtracting the original data from the smoothed AFM scan data (black curves).
The third group consists of the profiles measured at 250 K and 300 K (lower panels of Figure 4-6). In both cases, the height fluctuations start low at the initial surface and begin to increase at some point during the erosion process. The interesting observation is the relatively sudden onset of the roughening effect at an ion fluence corresponding to a total eroded depth of roughly 200 nm. After this threshold, the surface roughness continues to build up until the entire film has been eroded. The maximum height fluctuations can be as large as ±10 nm and will therefore clearly influence the measured depth resolution. The data presented in Figure 2 nicely illustrate how the dynamics of the roughening process can be observed easily with a wedge shaped crater.

For a more quantitative assessment, the root mean square (rms) roughness value $R_q$ is determined from the AFM data and compared for different sample temperatures. As described in detail elsewhere, the momentary value of $R_q$ value at a specific point $(i)$ in the line scan $a$ is calculated as a running statistical average taken over 40 data points around $(i)$ according to

$$R_q(i) = \sqrt{\frac{1}{2N} \sum_{k=i-2}^{i+2} [\Delta h(k)]^2}$$

using $N = 20$.

The $R_q$ value determined this way was averaged over intervals of 5 points ($i-2$ to $i+2$) and plotted as a function of eroded depth at point $(i)$ in Figure 4-7. The error bars reflect the standard deviation of $R_q$ within the respective 5-point interval. At all investigated temperatures, the roughness starts low at the beginning of the depth profile
(i.e., the original surface) where $R_q$ values are less than 2 nm. The roughness remains at this level during the entire crater erosion at both 90 K and 130 K, with a little more fluctuation at 130 K. At 160 K and 210 K, the roughness increases at an eroded depth around 200 nm but then stops increasing when reaching an $R_q$ of about 2.5 nm. A stronger fluctuation is observed when temperature increases, which suggests a bigger average surface roughening.

A fundamentally different behavior is observed at even larger sample temperatures. As seen in the lower panel of Figure 3, at 250 K and 300 K the roughness starts to rapidly increase at ~200 nm and then keeps increasing with eroded depth until the entire Irganox film is removed and the silicon substrate is reached, resulting in $R_q$ larger than 4 nm at this point. The overall increase of roughness throughout the depth profile is much greater when compared to lower sample temperatures. It is noticed that even at 300 K, the roughness build up is less than 5 nm, which is much smaller than the depth resolution degradation which suggests the degradation is not entirely due the surface roughening.

Overall, the surface topography data presented here show that lowering the sample temperature during ion bombardment inhibits the ion beam induced buildup of roughness on the sample surface. It should be noted at this point that topography information as presented in Figure 4, would be extremely difficult to attain without the wedge beveling strategy. In a conventional depth profile, multiple craters must be eroded to multiple depths for subsequent AFM analysis for each single temperature, thereby greatly prolonging the data acquisition time. Moreover, each individual crater must
naturally be eroded at a different lateral position, making the experiment sensitive to possible lateral inhomogeneities of the deposited molecular film.

Figure 4-7: RMS roughness ($R_q$ value, see text) as a function of eroded depth during sputtering of the Irganox 1010/3114 delta layer film with a 40-keV $C_{60}^+$ ion beam impinging under 40° with respect to the surface normal. The data were obtained at six different sample temperatures during ion bombardment at Top panel: 90 K (black), 130 K (orange), 160 K (magenta) and 210 K (olive); Lower panel: 250 K (blue) and 300 K (red).
4.3.2 Erosion Rate Decays Effects

The dynamics of the erosion rate as a function of the eroded depth can best be investigated using the wedge crater strategy. Since the surface receives a linearly increasing ion fluence along one direction of the raster area, line scans of the resulting surface topography along that direction directly reveals the fluence-depth relation. The erosion rate - defined as the eroded depth interval per unit ion fluence - is given by the derivative of that relation. It has the physical dimension of a volume and can be interpreted as the sputter yield volume, i.e., the average volume of sample removed per C$_{60}^+$ projectile ion impact. In conventional depth profiling, only the average erosion rate can be calculated from a single crater and many different craters would have to be eroded in order to obtain information about dynamic changes of this quantity. In a wedge crater, the advantage of having depth information at all ion fluences allows the determination of the erosion rate as a function of eroded depth, which is calculated in form of a running numerical derivative of the smoothed topographical AFM data as described previously$^{33}$.

To eliminate residual microscopic fluctuations due to surface roughness, and since we are only interested in macroscopic changes, the resulting erosion rate values were averaged over sets of 40 neighbored data points of the AFM line scan and plotted in Figure 5 at the depth corresponding to the center of each set. Again, the results will be discussed in two groups.
Figure 4-8: Erosion rate as a function of eroded depth during bombardment of the Irganox 1010 / 3114 delta layer film at; Top panel: 90 K (black), 130 K (orange), 160 K (magenta) and 210 K (olive); Lower panel: 250 K (blue) and 300 K (red). All six wedge craters were created by a 40-keV \( C_{60}^+ \) ion beam impinging at 40° with respect to the surface normal.
The first group consists of the experiments at 90 K, 130 K, 160 K and 210 K as shown in the top panel of Figure 4-8. It is seen that for these temperatures the erosion rate remains fairly constant during the removal of the entire 380 nm film. Only small fluctuations of ±10% of the data points are observed, which is likely to be induced by the surface roughness calibration and ion beam current fluctuations. The sputter yield volume ranges from 200 nm$^3$/impact to 275 nm$^3$/impact for a 40-keV C$_{60}^+$ ion beam, in agreement with previously reported values.$^{10,33}$

The second group consists of the experiments performed at 250 K and 300 K. These data are plotted in the lower panel of Figure 4-8. At 250 K the erosion rate decays to around 70% of the initial value and starts to fluctuate, while at 300 K it continues to decay throughout the erosion of the rest of the organic film, decaying to about 60% of the original surface value. The last data point at 350 nm depth is only 30% of the original surface value, a finding which might be related to the fact that at this temperature the interface between the Irganox film and the Silicon substrate appears significantly broadened. Therefore, the data plotted at 350 nm (which was averaged over the depth interval 340-360 nm) depth might already be influenced by the strong sputter yield reduction at this interface which is caused by the low silicon sputter yield.

Interestingly, the decay of the erosion rate at 250 K and 300 K begins quite abruptly at ~ 150 nm depth and appears to be earlier than the buildup of surface roughness. At this point, we can only speculate about the cause of this effect. Apparently, the erosion rate begins to decay a bit earlier and uneven sputtering across the surface might be developing hills and valleys, resulting in a surface roughening.
It is also interesting to note that the drop of the erosion rate during the first 75 nm appears more pronounced in Figure 4-5. In principle, we consider the wedge data more reliable, so that the average erosion rate between the surface and the first delta layer must be overestimated. In fact, it is a common observation in delta layer depth profiling that the SIMS signal representing the layer is observed too early, i.e., at a lower ion fluence than needed to erode to the actual depth of the layer. Such an effect can be quantitatively predicted and understood in terms of the statistical nature of the sputtering process. For the system studied here, it would lead to an overestimation of the average erosion rate to the first delta layer. Since the shift remains the same for all following layers, the fluence interval between the deeper layers then correctly reflects the actual distance between those layers, rendering the remaining data in Figure 4-8 correct.

4.4 Conclusion

We demonstrate that the temperature effects on a Irganox organic delta layer system can be successfully investigated by conventional depth profiling and wedge-crater beveling. By combing both modalities of molecular depth profiling, the effect of temperature on fundamental factors such as surface roughness, erosion rate, and depth resolution were determined. From a close look of conventional depth profiles at four different temperatures, it was demonstrated that sample cooling does not improve the depth profile until damage is sustained over 100 nm of eroded depth. It is evident the reduction of the sample temperature below 150 K indicates a quenching of this damage occurs within the 400 nm Irganox organic system. Conventional depth profiling also
resulted in the signal decay of high mass fragments to be pronounce and not necessarily correlated to a decreasing in sputter yield. Depth profiling of the same Irganox organic delta layer system by wedge-beveling shows there is no observable increase in surface roughening but decays in erosion rate occur within the first 100 nm of eroded depth. The lack of erosion decay within the first 100 nm of erosion corroborates the notion that there is no buildup of damage in a conventional depth profile. In this modality, it was demonstrated the majority of surface roughening and erosion rate decays at deep erosion are inhibited with an initial 100 K temperature decrease from 300 K. Also, the early occurrence of the decay in erosion rate when compared to the buildup of roughness is quite possibly the dominant factor in the increased surface roughness. In general, we have shown the temperature effects on fundamental factors involve molecular depth profiling for Irganox 3114/1010 multilayer sample and wedge-crater beveling is an important tool to study these factors

4.5 Acknowledgement

Financial support from the National Institute of Health under Grant No. 2R01 EB002016-18, the National Science Foundation under Grant No. CHE-0908226, and the Department of Energy Grant No. DE-FG02-06ER15803 is acknowledged. The authors are grateful to Alex Shard for providing the delta-layer sample.
4.6 Reference

(1) Mahoney, C. M.; Roberson, S. V.; Gillen, G. *Analytical Chemistry* 2004, 76, 3199.


Chapter 5

Temperature Effects of Sputtering of Langmuir-Blodgett Multilayers

This chapter has been reproduced and adapted with permission from D. Mao, etc. from Surface and Interface Analysis. This paper was submitted and has been expanded for further clarification in this chapter.

5.1 Introduction

Molecular depth profiling of organic and biological materials using secondary ion mass spectrometry (SIMS) and cluster ion beams has developed in the last decade into feasible experiments around the SIMS community. Molecular and fragment distribution information as a function of depth has been successfully obtained for various materials, a technique which is known as depth profiling and reconstructions of three dimensional chemical images. During these depth profiling investigations some experiments were not successful under normal operating experimental conditions and factors has been studied to affects the outcomes.

One of the most promising approaches that improved the overall quality of depth profiling experiments has been tied to the temperature of the sample. In recent developments of depth profiling experiments carried out at cryogenic temperatures, cooling the sample has proven to have the great impact on a depth profile. Sample
cooling not only maintains the secondary ion intensity and constant erosion rate, but also improves the interface widths.\textsuperscript{9,14,15}

To investigate and understand the temperature effects in depth profiling experiments, a wedge-crater beveling of delta layer organic samples as a tool to acquire fundamental information of molecular depth profiling with C\textsubscript{60}-SIMS has been developed in our lab.\textsuperscript{16} One advantage of wedge-crater beveling is that factors involve in depth profiling including interface widths and sputtering yield, etc. in the depth profile can be obtained from a single crater measurement.

In this work, we examine temperature effects by wedge-crater beveling on an organic thin film of 402 nm Langmuir Blodgett (LB) multilayers consisting of barium arachidate (AA). In wedge beveling experiments, the SIMS results were acquired from eroded wedge crater surface and AFM measurements were performed on the same area. Because of the unique information provided by the wedge crater AFM, we show that erosion rate variations as a function of real depth can be obtained. By lowering the sample temperature, erosion rate decay is dramatically reduced. When experiments were performed below 205 K, there is no further improvement on the erosion rate decay. Results also suggest temperature has little effect on interface width. In general, we suggest that majority improvement of LB film depth profile outcomes benefits from the inhibition of erosion rate decay by sample cooling.
5.2 Experimental Section

A Langmuir-Blodgett film of barium arachidate (AA) was prepared as described elsewhere.\textsuperscript{17} Briefly, a single crystal (100) silicon wafer was used as the substrate after cleaned with ozone for 10 minutes and rinsed with purity water several to achieve hydrophilicity of the Si/SiO$_2$ surface. LB films of AA were prepared by Kibron µTrough S-LB (Helsinki, Finland). Monolayers of AA were compressed at the air-water interface. Then the monolayer was transferred onto Si substrate via vertical deposition. Each (AA) monolayer is $\sim$2.7 nm in thickness and this 149-layer of (AA) film is measured around 402 nm in thickness.

Depth profiling was performed in a TOF-SIMS instrument equipped with a fullerene cluster ion source (IOG 40-60, Ionoptika; Southampton, U.K.), directed at a 40° angle relative to the surface normal. The performance of C$_{60}$ ion source\textsuperscript{3} and details of this instrumentation have been described elsewhere.\textsuperscript{18} The wedge sputtering scheme has been described in a previous publication.\textsuperscript{16} Briefly, the surface is subjected to be eroded with the 40-keV C$_{60}^+$ ion beam with a primary ion current of $\sim$ 80 pA into a spot size of $\sim$10 $\mu$m was operated in dc mode and digitally scanned across a 460 $\mu$m $\times$ 600 $\mu$m field of view using a 256 x 256 pixel raster. The total sputtering time was divided into frames with a beam dwell time of no less than 20 $\mu$s on each pixel. In order to erode a wedge-shaped crater, a linearly increasing ion fluence was applied which gives zero fluence on one side of the crater and maximum on the other side. For that purpose, the raster area was varied from frame to frame by sequentially skipping more and more lines in the $\gamma$-direction.
The TOF-SIMS instrument used in these experiments has the capability of sample cooling by blowing liquid-nitrogen-cooled nitrogen gas through the sample stage, resulting sample temperature of 90 K. In order to achieve the temperature at higher values between 90 and 300 K, a heater was wrapped around the copper tube and operated at a fixed electrical power using a variable autotransformer. By balancing the heating power, a stable temperature was obtained within a waiting time of approximately one hour with a stable temperature within ± 5 K for the duration of the entire experiment.

Wedge craters were characterized by a KLA-Tencor Nanopics 2100 atomic force microscope (AFM).

### 5.3 Results and Discussion

In previous work, we have shown that by combining topographical information from AFM with SIMS molecular information in a beveled crater, direct information about erosion rate and depth resolution can be obtained from a single measurement. The detailed protocol to extract that information from topographical line scans along the wedge (y-) direction of the eroded crater has been described previously.16

Briefly, the wedge crater receives a linearly increasing ion fluence along the y direction in wedge craters. The ion fluence can be calculated for each data point along y direction from known applied total fluence. Coupling with the measured depth value from AFM, the average erosion rate from initial surface can be obtained. In wedge crater, an advantage of having depth information for all ion fluence allows the calculation of
running erosion rate instead of average erosion rate. To eliminate the microscope fluctuations of erosion rates due to surface roughness, erosion rate variation as a function of eroded depth is calculated as the average of the derivative was calculated for sets of 40 data points, showing only macroscopic change in a defined area. The resulting value was plotted at the depth corresponding to the center of each interval. The resulting plot of erosion rate for six different temperatures is shown in Figure 5-1.

Figure 5-1: Erosion rate as a function of eroded depth during bombardment of the Langmuir-Blodgett film (AA). Left panel: Average erosion rate of 90 K, 140 K, 165 K and 205 K results; Right panel: erosion rate obtained at 265 K (magenta triangle) and 300 K (red circle). All six wedge craters were created by a 40-keV C$_{60}^+$ ion beam impinging at 40° with respect to the surface normal.

It is shown that for all temperatures the erosion rate starts around 160 nm$^3$/impact and settles around 130~140 nm$^3$/impact after reaching the steady stage. From then for experiments at 90 K, 135 K, 165 K and 205 K, the erosion rate remains fairly constant with no further dropping. Fluctuations are observed, which is likely to be induced by the AFM measurement calibration and ion beam current fluctuations.
For experiments at 265 K and 300 K, the erosion rate continues to decay throughout the entire removal of 402 nm LB film, reaching about 50% of the initial surface value at the end. And 300 K depth profiling experiment experienced worse decay than 265 K. This finding is in a good agreement with the conventional depth profiles of LB films.\textsuperscript{9} Interestingly, the erosion rate decay at 265 K and 300 K accelerates after 200 nm erosion. A similar situation was observed for Irganox 3114/1010 delta layers system where the erosion rate drops quickly at \( \sim 150 \text{ nm} \).\textsuperscript{15} We can only speculate that the ion bombardment damage needs to be built up to a level to influence the outcomes and it is differed by the sample system. Both temperature effects in macroscopic view and erosion rate variation at a single temperature in microscopic view suggest instead of a gentle gradual change, the effects start at a certain level.

Another unique property of eroded wedge surface is that it transforms the vertical chemical distributions into lateral information. Therefore, depth profiles can be extracted from the SIMS images of wedge surface. The detail protocol was described in previous publication.\textsuperscript{15} Briefly, line scans are taken from the SIMS results of erode wedge craters. The profiles of signals as a function of ion fluence can be obtained. AFM measurement provides the topography information as a function of ion fluence and the depth value for each point in SIMS profiles can be interpolated from AFM results. Therefore depth profiles based on real depth scale can be acquired. In this study, interface width of (AA)-Si is used to compare the depth resolution as the function of temperature. Three line scans are taken from SIMS results of each erode craters. The interface width was calculated from 16% to 84% of the maximum Si intensity. The resulting width of \( \mu \text{m} \) can
be simply converted into vertical width of nm by simply measuring crater length and crater depth. The average widths of 3 line scans with errors were plotted in black dots of Figure 5-2. Because the erosion rate decays were observed for deeper depth profiling in these experiments, ion fluence based on calculation of interface width does not accurately represent the actual depth resolution. Calibration is needed to evaluate the interface width. Two methods were used to calibrate the actual interface. First way is to locate the depth value difference of 16% to 84% of the maximum Si intensity in AFM. This gives a direct interface width reading from AFM measurements. However, microscopic surface roughness will have small influence on the results.

Another method is to use the erosion rate of AA film and Si substrate obtained at the end of experiment to calculate the running erosion rate from 16% to 84% of the maximum Si intensity. Then interface width can be obtained from the calibrated erosion rate. The resulting widths from both calibrations are in good agreement and the calibrated width is plotted in red dots of Figure 5-2.

The calibrated interface width was improved slightly by ~2 nm by lowering the sample temperature from 300 K to 90 K. This is the same observation in Irganox delta layer wedge beveling experiments where majority improvement of fwhm was achieved by lowering the temperature to below 150 K. These findings suggest sample cooling help to reduce topography development and erosion rate decays without little change to the alter layer thickness.
5.4 Conclusion

We demonstrate that the temperature effects on a Langmuir-Blodgett film system can be successfully investigated by wedge-crater beveling. By combining both molecular depth profiling and AFM surface measurement, the effect of temperature on fundamental
factors as erosion rate and interface width were determined. From a close look of wedge-beveling results at fix different temperatures, it was demonstrated that temperature effects does not behave gradually between 90 K and 300 K. Sample cooling to 205 K reduces erosion rate decays and no further improvement was observed by cooling to 90 K. It suggests that the reduction of the sample temperature below 205 K indicates a quenching of this damage occurs within the 402 nm LB film system. Interface width obtained from wedge-beveling shows temperature has little influence on the depth resolution. Sample cooling improves depth profiles by reducing the topography development and erosion rate decays. In general, we have shown the temperature effects on fundamental factors involve molecular depth profiling for LB film sample and wedge-crater beveling is an important tool to study these factors.

5.5 Acknowledgement

Financial support from the National Institute of Health under Grant No. 2R01 EB002016-18, the National Science Foundation under Grant No. CHE-0908226, and the Department of Energy Grant No. DE-FG02-06ER15803 is acknowledged. Thanks to NPL VAMAS project A3(f) for invitation to this research and supplying the delta-layer sample.
5.6 Reference

(1) Mahoney, C. M.; Roberson, S. V.; Gillen, G. *Analytical Chemistry* 2004, 76, 3199.


Chapter 6

Conclusions and Future Directions

6.1 Conclusions

The development and commercialization of cluster ion sources expanded the area of interest in Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) community. With reduced chemical damage and enhanced sputter yield of various ion beams, such as $\text{SF}_5^+$, $\text{C}_{60}^+$, Argon gas cluster ion beam (GCIB) etc., organic and biological materials can be characterized by SIMS instruments. Since then, ToF-SIMS has been serving as a powerful surface chemical imager. With the recent breakthrough of molecular depth profiling, chemical information buried under sample surface is accessible by eroding through the materials with cluster ion beams. Therefore, SIMS community is currently in transition of moving towards three dimensional (3-D) chemical images of organic and biological samples, the ultimate goal of ToF-SIMS applications.

However, molecular depth profiling process is very complicated and far from full understood. There are many factors that involve in depth profiling process and affect the quality of outcomes. Research of these factors including experimental temperatures, primary ion beam impact angle, ion beam energy, sample rotation, etc. becomes an emerging topic in the SIMS community. Conventional depth profiling operates by alternatively switching between pulsed beam data acquisition and DC beam material erosions. One eroded crater only delivers the surface topography and depth information
for the end point of the process as there is no in-situ detection of surface topography. Lacking of continues AFM information limits the understanding of surface topography developments, sputter yield decay, etc. The depth scale used for conventional depth profiling is not accurately calibrated and information like depth resolution degradation is still under extensive investigations.

This objective of thesis is focused on developing wedge-crater beveling depth profiling as a useful tool to overcome the difficulties faced by conventional depth profiling. A well constructed delta layer samples system consists of Irganox 1010 and 3114 was used in these investigations. These samples deliver reproducible results and are very stable in normal environment. Conventional depth profiling was performed on this samples and lack of surface topography information limits the understanding of molecular depth profiling process.

Wedge-crater beveling protocol was created and applied on the same sample system. The successful combination of wedge-crate beveling SIMS spectra and AFM crater topography measurements deliver unique and valuable information of microscopic surface topography developments, macroscopic erosion rate variations and even relationship between two factors. Wedge-crater beveling also provides the benefits of shortening the experiment time and therefore it receives a more stable primary ion current during the erosion.

Further application of wedge-crater beveling on temperature effects during depth profiling sputtering reaffirms the advantages of this technique. Before wedge-crater beveling was developed, there is only full comparison between room temperature and liquid nitrogen temperature results. It is observed that sample cooling helps to reduce
surface roughening and maintain constant erosion rate. For the first time, information with these effects developments as the function of temperatures was revealed. With the initial 100 K temperature decrease from 300 K, most surface roughening and erosion rate decay were inhibited. However, for delta layer locates at the depth with no surface roughness and erosion rate decay, improvement on depth resolution does not appear until the temperature falls below 150 K, suggesting continuous reduced ion beam mixing or chemical mixing with the decrease of temperature. This powerful application on temperature effects shows the multi-role of wedge-crater beveling, producing unique information unseen in conventional depth profiling as well as helping the depth scale calibration.

### 6.2 Future Direction

During the investigations, secondary ion intensity, especially molecular ion intensity observed is determined not strong enough for trace of materials inside biological samples. This is a principal drawback of ToF-SIMS because it uses short pulses of primary ion beam. And distinguishing fragments also takes tremendous efforts without MS-MS capability on traditional ToF-SIMS.

In order to overcome the low transmission efficiency of SIMS and provide MS-MS capability, research efforts have been devoted to renovation and enhancement of SIMS instruments. Recently, a quadrupole orthogonal ToF mass spectrometer (Q-ToF) equipped with a C$_{60}$ ion source in place of the laser source has been built in our lab. A similar instrumentation concept has been applied on the newly developed J105 3-D
Chemical Imager by Ionoptika.\textsuperscript{18-21} In both instruments, the primary cluster ion beams are operated in DC mode, with continuous ion beams sputtering at the sample surface. This generates rapid data acquisition and the achieved lateral resolution is also improved without the pulsed beams. Take J105 3-D Chemical Imager as an example; unlike time of light mass analysis in traditional ToF-SIMS, the primary is not pulsed. Instead the secondary ion is collected in the shaped-field buncher with a nonlinear reflectron, which can be used to select ion for analysis, providing MS-MS capability. It takes 85 µs to fill the buncher with secondary ions and then the buncher fires by suddenly applying an accelerating field, creating a time focus at the entry of TOF analyzer.\textsuperscript{19} This configuration allows the inclusion of a collision cell and an intermediate time-of-flight selection gate. So, the analyzer can operate in MS-MS mode as well as normal time-of-flight mode. This revolutionary new instrument delivers higher throughput with reduced analysis time because of the continuous sputtering ion beams which allow depth profiling images series to be generated on a practical time scale. This is certainly a potential breakthrough of moving towards 3-D chemical images of biological samples. One current drawback on these newly developed instruments is that there is still no accurate in-situ surface topography measurement technique out there. In such circumstance, wedge-crater beveling can be applied on these new instrumentations to help understand the factors development involved in 3-D depth profiling.

New ion sources design also helps to enhance the quality of depth profiles. Studies from a recently introduced argon giant cluster ion beams (GCIBs) have shown promising results in characterizations of organic and biological materials.\textsuperscript{22-28} Improvements on lots of aspects including reduced surface roughening, reduced erosion
rate decay and ultra high depth resolution have been observed.\textsuperscript{23,24}

Together, new instruments, new ion sources and new depth profiling strategy can
enhance the performance of molecular depth profiles and achieve the ultimate goal of 3-
D mass spectral imaging analysis of single cells.

6.3 Reference


(3) Mahoney, C. M.; Roberson, S. V.; Gillen, G. \textit{Analytical Chemistry} \textbf{2004}, \textit{76}, 3199.


VITA

Dan Mao

Dan Mao was born in Wuxi, Jiangsu Province, P.R.China to Yunian Mao and Huiying Zhang. He attended Shanghai Jiao Tong University in Shanghai in 2000 and earned a bachelor degree in Applied Chemistry in 2004. In August of 2005, he began his graduate study in Chemistry at the Pennsylvania State University where he joined the research group of Evan Pugh Professor Nicholas Winograd. He studied in the area of analytical chemistry and received his Doctor of Philosophy in December 2011.