Published in final edited form as:

Anal Chem. 2011 January 1; 83(1): 351–358. doi:10.1021/ac102525v.

Molecular Depth Profiling of Buried Lipid Bilayers Using C₆₀-SIMS

Caiyan Lu¹, Andreas Wucher², and Nicholas Winograd^{*,1}

¹Department of Chemistry, Pennsylvania State University, 104 Chemistry Building, University Park, Pennsylvania 16802 USA

²Faculty of Physics, University Duisburg-Essen, 47048 Duisburg, Germany

Abstract

An organic delta layer system made of alternating Langmuir Blodgett multilayers of barium arachidate (AA) and barium dimyristoyl phosphatide (DMPA) was constructed to elucidate the factors that control depth resolution in molecular depth profile experiments. More specifically, one or several bilayers of DMPA (4.4 nm) were embedded in relatively thick (51 to 105 nm) multilayer stacks of AA, resulting in a well-defined delta-layer model system closely resembling a biological membrane. 3-D imaging ToF-SIMS depth profile analysis was performed on this system using a focused buckminsterfullerene (C₆₀) cluster ion beam. The delta layer depth response function measured in these experiments exhibits similar features as those determined in inorganic depth profiling, namely an asymmetric shape with quasi-exponential leading and trailing edges and a central Gaussian peak. The effects of sample temperature, primary ion kinetic energy and incident angle on the depth resolution were investigated. While the information depth of the acquired SIMS spectra was found to be temperature independent, the depth resolution was found to be significantly improved at low temperature. Ion induced mixing is proposed to be largely responsible for the broadening, rather than topography, as determined by AFM, therefore depth resolution can be optimized using lower kinetic energy, glancing angle and liquid nitrogen temperature.

Keywords

molecular depth profiling; SIMS; delta layer; buckminsterfullerene (C₆₀)

INTRODUCTION

Cluster ion beams have begun to play a leading role in organic materials characterization by means of secondary ion mass spectrometry (SIMS) due to the enhanced sputter yield, larger secondary ion yield and lower chemical damage produced by these projectiles. Since cluster ions are able to remove the material without destroying its chemical integrity, molecular depth profiling has been successfully performed on various materials.^{1–8} Successive 2-D SIMS molecular images can be obtained after sample erosion to different depths by cluster beams, thereby allowing 3-D mapping of specific molecules. This method is feasible for biological samples and is providing valuable 3-D chemical information in biological tissues and single cells.^{9–11}

Construction of 3-D molecular ion images requires that some basic issues be sorted out. Fundamental studies are focused on the ion-solid interaction and the physical properties of the sputtering process. Various experimental conditions have been shown to influence these processes and affect the molecular depth profiles and 3-D imaging results, like temperature of the bombarded sample as well as incident angle and energy of the impinging projectiles. Constant molecular secondary ion signals were observed during depth profiles of spin coated trehalose² and biodegradable polymer films¹² at room temperature, while there are also other samples where the steady-state can only be reached at low temperature.^{7, 13, 14} Depth profiles on cholesterol thin films reveal that the incident angle of projectiles changes the energy deposition characteristics and has a significant influence on depth profiles.⁸ The kinetic energy of the primary ion beam controls the energy deposition as well. Analysis of the available experimental data has shown that the success of a molecular depth profile experiment is largely determined by a competition between bombardment induced chemical damage on one hand and sputter removal of (damaged or undamaged) material on the other hand. In short, molecule specific secondary ion signals can be maintained and followed during ion erosion if the sputtering process removes most of the material damaged by the ion impact. Comparison between different cluster ions has shown that this "cleanup" mechanism appears to be most efficient for buckminsterfullerene (C₆₀) projectiles.^{15–17}

Depth resolution is a key factor to evaluate molecular depth profiling and 3-D imaging. This property can in principle be evaluated from the observed interface width of secondary ion signal characteristics for successive sample layers, or from the signal response to a so-called "delta layer" of negligible width. So far, various depth resolution values measured in different ways have been reported, which range from 3 nm to 30 nm.^{2, 14, 18, 19} Probably the best method to characterize the depth resolution is the analysis of a delta layer, i.e., a layer of negligible width embedded in a similar matrix material. Measuring the signal response while profiling across such a layer then directly delivers the depth response function of the method, a concept which has been routinely used in SIMS depth profiling of inorganic material for many years.^{20–21} In order to provide a similar standard for molecular depth profiling, it is therefore highly desirable to design molecular delta layer samples as well. The first successful attempt in this direction was made at NPL (National Physical Laboratory, Middlesex, U.K.), where a delta layer system was designed by alternative vapor deposition of Irganox 1010 (the matrix material) and Irganox 3114 (the delta layer) onto a silicon substrate. This sample has been recently utilized as a standard system in an interlaboratory study on molecular depth profiling, and the results have provided much insight into the factors determining the observed depth resolution. One of the key results of this study has been the observation that both the sputter yield and depth resolution decay with ion fluence. More specifically, atomic force microscopy (AFM) data suggest that surface topography developing during C₆₀ ion beam erosion is the main cause of the degradation of depth resolution.¹⁹ It was also demonstrated that sample cooling^{14, 22} or sample rotation²² during ion erosion can be effective in reducing these effects and improving the quality of organic depth profiling.

High lateral resolution of SIMS makes 3-D imaging of single cells an appealing application of this technique. Molecular dynamics (MD) simulation of the sputtering of different materials indicates that the molecular structure has a critical influence on the sputtering process.²³ Therefore, it is necessary to investigate the factors affecting achievable depth resolution on different biological materials. Langmuir Blodgett (LB) monolayers made of lipids and fatty acids have been widely studied as cell membrane models and appear to be quite suitable for SIMS analysis.^{24–28} Multilayer LB films have well-defined structures and sharp interfaces between layers and have been employed to study the fundamentals of molecular depth profiling.^{7, 14, 29} In this work, we synthesized a 4.4 nm bilayer of barium dimyristoyl phosphatidate (DMPA) embedded in relatively thick (51–105 nm) multilayer

stacks of barium arachidate (AA) on a bare silicon wafer to create a delta-layer model system for the characterization of this type of material as well. As outlined above, such systems are well-suited to investigate the depth profiling characteristics of organic films. The measured depth response function is analyzed in terms of quasi-exponential leading and trailing edges connected by a central Gaussian function as suggested by Dowsett.²⁰ In order to determine the influence of ion bombardment induced topography formation on the measured depth resolution, the surface roughness is studied both at the original film and after sputter erosion down to different depths. Comparison of the surface rms roughness data with the measured depth response function shows that for this system, surface topography development is of minor importance, while ion induced mixing at the organic-organic interface is the dominating factor determining the apparent depth resolution. Cooling the sample to cryogenic temperature during the analysis is shown to reduce the mixing effects and prevent chemical damage accumulation. The influence of beam energy and incident angle was also investigated and the results show consistent with previous studies, that the best depth resolution is obtained with lower beam energy at glancing impact angle. The delta layer made of a DMPA bilayer closely resembles the structure of a biological membrane and will hopefully provide a useful model for 3-D imaging of single cells.

EXPERIMENTAL SECTION

Materials

Arachidic acid, barium chloride (99.999%), copper(II) chloride, potassium hydrogen carbonate (99.7%) and all solvents were purchased from Sigma-Aldrich (Allentown, PA). The DMPA was purchased from Avanti Polar Lipids (Alabaster, AL). All chemicals were used without any further purification. Water used in preparation of LB films was obtained from a Nanopure Diamond Life Science Ultrapure Water System (Barnstead International, Dubuque, IA) and had a resistivity of at least 18.2 MΩ·cm.

LB film preparations

Single crystal (100) silicon wafers were used as the substrate. The Si substrates were cleaned by ozone for 10 min and then rinsed with high purity water several times to ensure hydrophilicity of the Si/SiO₂ surface. A Kibron μTrough S-LB (Helsinki, Finland) was used for isotherm acquisition and multilayer LB film preparation. Details of the LB film preparation have been described elsewhere.⁷ The applied subphase was 70 mL aqueous solution of 10⁻⁴ M BaCl₂, 10⁻³ M KHCO₃ and 10⁻⁷ M CuCl₂. BaCl₂ was added to the solution to form salt with arachidic acid and DMPA at pH 7 which was controlled by addition of KHCO₃. The presence of CuCl₂ helped to enhance film stability after construction of a large number of layers. Monolayers of AA and DMPA at the air-water interface were aged for 30 min and compressed at a constant rate of 7 Å²/molecule/min. The monolayer was transferred onto the Si substrate by vertical deposition at the rate of 10 mm/min when the surface pressure was kept constant at 33 mN/m. Approximately 10 min was allotted between successive film deposition cycles for substrate drying. Three types of delta layer samples were prepared. One has a single bilayer of DMPA (4.4 nm) deposited between 51 and 54 nm AA stacks. The second one has two sets of DMPA bilayers (4.4 nm) separately embedded in 305 nm AA stacks. The third one has two blocks of DMPA with different thickness (8.8 nm of 4 DMPA monolayers and 4.4 nm of 2 DMPA monolayers) separated by ~100 nm AA stacks.

Instrumentation

The depth profile experiments were performed on a ToF-SIMS instrument, which has been described previously.⁷ The sample stage can be cooled to 100 K, so depth profile experiments can be run at liquid nitrogen temperature. A 40-keV C₆₀ source (IOG 40-60,

Ionoptika; Southampton, U.K.) is mounted to the instrument at an angle of 40° with respect to the surface normal. The kinetic energy of the singly charged C_{60}^+ primary ion beam could be varied between 20 and 40 keV. Under typical conditions, the beam current is 150~200 pA and the beam size is 7~10 μm . The incident angle could be altered to 71° using a customized wedge-shaped sample block. The mass spectrometer was operated in a delayed extraction mode with 50 ns delay time between the primary ion pulse and the secondary ion extraction pulse. Charge compensation was found to be unnecessary during positive ion SIMS mode due to a charge balance between primary and secondary ion currents. For depth profiling, the C_{60}^+ ion beam was operated in DC mode to erode through the film at an area of $\Delta x \cdot \Delta y$ with $\Delta y = \Delta x / \cos\theta$ and Δx ranging from 300 to 500 μm (θ is the impact angle of the primary beam relative to the surface normal). Between erosion cycles, SIMS images were acquired from the same area using the pulsed C_{60}^+ projectile beam with a total ion fluence below 10^{11} cm^{-2} . A digital raster scheme with 256×256 pixels was employed during both the erosion and data acquisition cycles, which corresponds to a pixel step size (1–2 μm) well below the beam width. The ToF mass spectra were retrospectively extracted from various pixel areas of the image data in order to investigate crater edge effects and determine the optimum gating area as described elsewhere.³⁰ No edge effects were observed at the central area of 192×192 pixels inside the sputtered region, therefore mass spectra from these areas were used for depth profile analysis. For the depth profile experiments at a 71° incident angle, the extraction electrical field was distorted because the sample was mounted on a wedge-shaped sample block during data acquisition, resulting in lower secondary ion extraction efficiency. Therefore, when the primary ion beam is rastered over a larger area, only the secondary ions emitted from the central stripe area can be detected. This influence doesn't affect the ion intensity we used for depth profile analysis since the analysis area is within the stripe region.

AFM and Ellipsometry measurement

An AFM (Nanopics 2100, KLA-Tencor, San Jose, CA) was used to characterize the film thickness, the eroded crater depth and the surface roughness. Film thickness and crater depth were measured in contact mode, while surface roughness data were acquired within a $10 \mu\text{m} \times 10 \mu\text{m}$ area in tapping mode. Since the AFM data were measured after the depth profile experiment was completed and the sample was taken out of the vacuum system, surface relaxation after ion bombardment is possible. In order to examine this influence, topography images were taken within 15 min, 30 min, 1 hour and a day sequentially after the depth profile analysis and no significant difference in topography was found during this timescale after sputtering. The thickness of the LB monolayer was determined by a single wavelength (632.8nm, 1-mm spot size, 70° angle of incidence) Stokes ellipsometer (Gaertner Scientific Corp., Skokie, IL; mode LSE).

RESULTS AND DISCUSSION

Previous work has shown that LB delta layers represent a good model system to study the depth resolution of molecular depth profiling and 3-D imaging experiments of biological materials.³¹ The objective of this work is to evaluate factors that determine the depth resolution and investigate the role of various experimental parameters controlling the sputter process. The molecule specific signals at m/z 355, 371 and 525 are found to be representative peaks of DMPA. The AA film is characterized by a molecule specific signal at m/z 463. The intensities of DMPA were corrected by the method used previously³¹ to deduce the signals contributed by AA. All three measured signals from DMPA exhibit a similar shape. Hence, only signals at m/z 355 are shown here for simplicity.

Effects of sample temperature

The signal response, i.e., the m/z 355 signal as a function of eroded depth, arising from a single DMPA delta layer is shown in Figure 1. The depth scale was calibrated using the strategy employed previously.³¹ In order to elucidate the temperature effect, data obtained at 100 K and 300 K are compared. Both traces exhibit the typical shape observed in depth profiling of delta dopant structures in semiconductors. Clearly, the depth profile at 100 K exhibits a much narrower peak than that at 300 K. The depth resolution was determined by the full width half maximum (FWHM) of the response function as suggested for inorganic depth profiling.³² As listed in Table 1, by performing the experiments at 100 K, the depth resolution was significantly improved to 20.7 nm compared to the value of 29.7 nm previously reported at 300 K using 40-keV C_{60}^+ projectiles at a 40° incident angle.³¹

To quantitatively analyze the profile, Dowsett's empirical function^{20, 31} was applied to describe the measured signal response as

$$R(z') = N \left[(1 - \text{erf}(\xi_1)) \exp\left(\frac{z'}{\lambda_g} + \frac{\sigma^2}{2\lambda_g^2}\right) + (1 + \text{erf}(\xi_2)) \exp\left(\frac{z'}{\lambda_d} - \frac{\sigma^2}{2\lambda_d^2}\right) \right] \quad (1)$$

with $\xi_1 = \frac{1}{\sqrt{2}} \left(\frac{z'}{\sigma} + \frac{\sigma}{\lambda_g} \right)$ and $\xi_2 = \frac{1}{\sqrt{2}} \left(\frac{z'}{\sigma} - \frac{\sigma}{\lambda_d} \right)$. This function contains three fitting parameters, namely a leading edge growth length (λ_g), a trailing edge decay length (λ_d) and the standard deviation (σ) of a central Gaussian connecting the exponential rise and decay functions. The fitting results obtained from the single delta layer sample are listed in Table 1. It is interesting to notice that, although the half width is smaller at low temperature, the exponentially leading edge exhibits the same slope at 100 K as at 300 K, which is depicted by the same value of $\lambda_g = 4.9$ nm at both temperatures. As discussed by Dowsett et al.,²⁰ the leading edge slope reflects influences of the escape depth of the detected sputtered particles in combination with secondary effects resulting in the release of analyte species through the surface such as segregation. Since these effects should certainly be temperature dependent, our results suggest that λ_g is mainly determined by the information depth of the (static) SIMS spectra, which itself must be largely temperature independent. Considering the monolayer thickness of the LB films used here to be 2.2 to 2.7 nm, the measured information depth is within the range of 1–2 monolayers, similar to what is found in inorganic depth profiling.³³

The temperature has more significant effects on the trailing edge slope and the central Gaussian width. At 100 K, we obtain $\lambda_d = 8.9$ nm and $\sigma = 5.9$ nm, both smaller than the respective values of 16.3 nm and 7.7 nm observed at 300 K, making the 300 K profile more asymmetric than the low temperature profile. From the large data base available for inorganic depth profiling, it is known that the asymmetric peak broadening is mainly caused by bombardment induced interlayer mixing.³² Apparently the largest influence is observed here for the trailing edge, which has been connected with the combined effects of collisional mixing and bombardment enhanced diffusion of analyte species into the underlying matrix.^{20,34} Due to the strong temperature dependence, we believe the latter to significantly contribute to the measured decay length for the system studied here. These diffusion-like mixing effects appear to be strongly reduced at low temperature, thereby greatly improving the observed depth resolution.

A sample with two identical delta layers at different depths was used to evaluate the damage accumulation and depth resolution degradation induced by ion beam erosion. The total thickness of this sample is 314 nm with two 4.4 nm DMPA bilayers located at 103 nm and

209 nm depth, respectively. Depth profiles obtained at 300 K and 100 K with 40-keV C_{60}^+ projectiles at a 40° incident angle are shown in Figure 2. In both profiles, there is an initial rise of the AA matrix signal at m/z 463, which has been shown to be associated with the removal of surface contamination.¹⁴ At 300 K, the AA signal never reaches a steady-state and exhibits a continuous decay until the film is completely removed. A similar decay is found for the DMPA signals as well. For example, both the peak height and the integrated peak intensity of the signal at m/z 355 dropped by 35% at the second delta layer compared to the first delta layer. In addition to the secondary ion signal decay, the sputter yield is found to decrease with increasing primary ion fluence. With the known thickness of the AA matrix and the C_{60}^+ fluence needed to reach the respective DMPA signal maxima, we are able to calculate the average sputter yield on each AA block. The average sputter yield is 260 molecule equivalents/ C_{60} on the top AA block, while 206 molecule equivalents/ C_{60} is measured as the average sputter yield on the second one, decreased by ~20%. Both findings indicate accumulation of chemical damage during ion beam sputtering. The depth resolution measured on the two delta layers is 33.4 nm and 36.4 nm, respectively.

In contrast, the depth profile measured at 100 K shows an AA matrix signal which reaches a steady-state and stays quite constant through the removal of the film except two dips at the position of the DMPA delta layers. At the same time, the signal from the DMPA layers is well maintained and the same peak heights and integral peak intensities are observed for both delta layers. In addition, the primary ion fluence used to remove the same amount of AA matrix at a different depth appears to be the same during the erosion of the entire film. Hence, at 100 K, the sputter yield does not decrease with C_{60}^+ ion fluence. Moreover, the depth resolution measured for the two delta layers is 21.6 nm and 21.3 nm, which agrees with the value obtained on the single delta layer sample under the same experimental conditions. These findings show that low temperature can effectively reduce the damage accumulation and eliminate its influence on the shape of depth profiling. At present, it is not clear why this is so. The mechanisms behind ion bombardment induced chemical damage, its accumulation under repeated impact onto the same surface area and its influence on the sputter yield of an organic material are still largely unknown. An energetic C_{60} impact constitutes an immense local disturbance which almost instantaneously pushes the material far out of equilibrium. At this stage, the macroscopic sample temperature is most likely irrelevant. During the time *between* subsequent impacts, however, the material will undergo complex relaxation chemistry, which can spread into previously undamaged volume and lead to further damage there. For the well ordered LB films investigated here, one could, for instance, imagine cross-linking between neighbored molecules to effectively enhance the surface binding energy and reduce the sputter yield. Our data indicate that this chemical "afterglow" of an ion impact can be greatly reduced by lowering the sample temperature.

Another LB multilayer film was constructed to check whether the observed depth resolution is affected by the thickness of the delta layer. This sample has two DMPA thin layers embedded in three thick AA films. The first DMPA layer is located at a depth of 100 nm and contains two DMPA bilayers (8.8 nm), while the second one is composed of one DMPA bilayer (4.4 nm) and is located at a depth of 200 nm below the surface. Using 40-keV C_{60}^+ projectiles with a 40° incident angle at 100 K, both DMPA layers gave about the same FWHM, 22.2 nm and 23.6 nm (Figure 3), similar to the results acquired on all other delta layers with a single bilayer. It is evident that the FWHM is not affected by the layer thickness and therefore accurately represents the delta depth response function. On the other hand, the layer thickness does change the ion intensity. Since the 8.8 nm layer contains twice as many molecules, the integrated peak intensities and the peak height are both doubled in the depth profile as expected.

Surface roughness

There are two theories which describe the depth resolution function of a sputter depth profile, such as Dowsett's function and the so-called MRI model.^{20, 32, 35} In the MRI model, the achievable depth resolution is limited by mixing length (M), surface roughness (R) and information depth (I).³² Studies on an Irganox delta layer sample have shown that the depth resolution is purely determined by surface roughness.¹⁹ In order to examine this issue for the system studied here, AFM was used to measure the surface roughness and its change after ion beam erosion to different depths at room temperature. As shown in Figure 4(a), the original surface roughness of a freshly prepared 314 nm LB film is represented by an rms value of 3.7 nm. After etching to the first delta layer at the depth of 103 nm, the surface roughness is measured to be 4.2 nm. At the depth of 209 nm, the rms value obtained from the AFM image is 4.9 nm. Unlike the dramatic surface roughening observed for the Irganox system, the ion beam induced surface topography is obviously quite small for the LB sample and cannot serve as an explanation for the observed degradation of the depth resolution. An overlay of the sample surface height distribution extracted from the AFM data and the DMPA SIMS profile is shown in Figure 4(b–c). It is clear that the measured depth response function is much broader than the height distribution profile, a finding which is in pronounced contrast with the data obtained from the Irganox film, where a complete match of both distributions was found. In particular, the standard deviation (σ) of the central Gaussian determined from the LB delta layer signal is more than two times larger than the standard deviation of the surface height distribution (i.e., the rms roughness value). Therefore, other factors must affect the depth resolution. In Dowsett's function, σ is interpreted as a convolution of delta layer peak broadening due to intrinsic layer thickness, ion beam induced surface roughening and interlayer mixing. As mentioned before, the asymmetric shape of the SIMS profiles indicates that mixing is playing an important role in the peak broadening. In any case, bombardment induced surface microtopography may in part be responsible for the relatively small peak width increase between the first and second delta layer in Figure 2, but is probably not the dominating factor determining the depth resolution observed for the LB system studied here. Instead, the depth resolution is mainly affected by ion beam induced mixing at the organic-organic interfaces.

Projectile kinetic energy and incident angle

Previous studies on alternating LB films illustrated that better depth resolution (i.e., smaller interface width) can be achieved by lowering the primary ion beam energy.¹⁴ Using the LB delta layer we are able to directly measure the kinetic energy effects on the depth resolution. The depth profiles using 20- and 40-keV C_{60}^+ for both sputter erosion and data acquisition are shown in Figure 5 and the depth resolution measured by the FWHM of the DMPA signal response is listed in Table 1. At a 40° incident angle, the depth resolution improves from 20.7 nm to 16.0 nm using a 20-keV C_{60}^+ beam. Using a glancing impact angle of the sputtering ion beam is another way to improve the depth resolution.⁸ For 40-keV C_{60}^+ at a 71° impact angle, we obtained a depth resolution of 15.5 nm (see Figure 5). Molecular dynamics (MD) simulation has shown that the energy deposition is related to the incident angle of the projectiles.³⁶ Increasing incident angle results in a smaller altered layer thickness since the incident energy is deposited closer to the solid surface.⁸ Combining lower beam energy and glancing angle, the FWHM on the LB delta layer was pushed to 12.1 nm with a 20-keV C_{60}^+ beam at a 71° incident angle and the sample cooled to 100 K.

The listing of Dowsett's fitting parameters obtained under various experimental conditions in Table 1 illustrates how the kinetic energy and incident angle change the sputtering process. The kinetic energy has a direct influence on the crater depth produced by a single impact, and therefore the depth from which molecules contribute to a static SIMS spectrum changes as a function of the projectile impact energy. The higher the kinetic energy, the

larger the information depth as the leading edge slope λ_g increases from 3 nm at 20 keV to 4–5 nm at 40 keV. No significant difference was observed for λ_g when the incident angle changed from 40° to 71°, indicating that the information depth is largely independent of the impact angle. The trailing edge decay length λ_d as well as the central Gaussian width σ are affected by both the kinetic energy and incident angle. Since ion beam induced topography was low on this sample, smaller values of λ_d and σ indicate less mixing during the ion beam bombardment at lower energy and glancing angle.

Material dependency

Two delta layer model systems have been established so far, namely the NPL Irganox delta layer and the LB delta layer presented here. As part of an interlaboratory study conducted under the auspices of VAMAS (Versailles Projects on Advanced Materials and Standards) TWA2, surface chemical analysis,³⁷ we analyzed the Irganox delta layer sample on the same instrument and under the same experimental conditions as used in this work. Using a 40-keV C_{60}^+ beam at room temperature with a 40° incident angle, the resulting depth profile is shown in Figure 6(a). The depth resolution (FWHM) extracted for the first three Irganox 3114 delta layers is plotted as a function of depth in Figure 6(b) along with reference data,¹⁹ measured on a similar sample under 30-keV C_{60}^{3+} bombardment. It is seen that the observed depth resolution as well as its dependence on sputtered depth is well reproduced. The FWHM value measured for the first Irganox delta layer (~17 nm) is significantly smaller than that observed for the LB delta layer located at the same depth of 50 nm (29.7 nm). Apparently, the achieved depth resolution is not only dependent upon experimental conditions but also significantly depends upon the type of analyzed material. LB multilayers are composed of long, well-organized linear molecules and have an open and ordered structure. MD simulations of sputtering of LB multilayers by C_{60} have shown that the primary energy of projectile fragments can be channeled by the geometrical structure of the AA overlayer due to the unique structure of LB films.²³ The penetration depth of C_{60} projectiles in LB films is 4 to 5 times larger than that in other materials, like molecular benzene^{38, 39} or polymer samples.^{40, 41} The experimental results are consistent with the MD simulation data, and it is not surprising that the vapor deposited Irganox sample always gives better depth resolution than LB films under otherwise identical conditions.

CONCLUSIONS

We show that an organic delta layer system can successfully be constructed by LB techniques and used to investigate the fundamental aspects of molecular depth profiling. For the system studied here, the measured surface roughness is shown to be smaller than the measured interface width. Under these circumstances the results indicate that this width is controlled mainly by interface mixing induced by the bombardment and not by topography. This observation is especially important since it allows evaluation of the relative degree of ion beam mixing as the incident angle of the primary ion and the temperature of the sample are systematically varied.

The LB lipid bilayer is reminiscent of cellular membranes, although the precise structure is quite different since no membrane proteins are involved. Hence, this model study demonstrates that such structures are in principle identifiable in molecular depth profiling experiments and therefore should provide a useful guide for future 3-D bioimaging experiments. Clearly, cryogenic conditions using 20-keV C_{60}^+ bombardment at glancing angles yield the most reliable information.

Acknowledgments

The authors acknowledge the Lipid MAPS Consortium (GM069338-07) for financial support. Also additional financial support from the National Institutes of Health (2R01 EB002016-17), the National Science Foundation (#CHE-0908226) and the Department of Energy grant no. DE-FG02-06ER15803 is appreciated.

REFERENCES

1. Mahoney CM, Roberson SV, Gillen G. *Anal. Chem.* 2004; 76(11):3199–3207. [PubMed: 15167802]
2. Cheng J, Winograd N. *Anal. Chem.* 2005; 77(11):3651–3659. [PubMed: 15924401]
3. Sostarecz AG, McQuaw CM, Wucher A, Winograd N. *Anal. Chem.* 2004; 76(22):6651–6658. [PubMed: 15538789]
4. Sostarecz AG, Sun S, Szakal C, Wucher A, Winograd N. *Appl. Surf. Sci.* 2004; 231-2:179–182.
5. Wucher A, Sun SX, Szakal C, Winograd N. *Anal. Chem.* 2004; 76(24):7234–7242. [PubMed: 15595864]
6. Wagner MS. *Anal. Chem.* 2005; 77(3):911–922. [PubMed: 15679361]
7. Zheng LL, Wucher A, Winograd N. *J. Am. Soc. Mass Spectrom.* 2008; 19(1):96–102. [PubMed: 18293488]
8. Kozole J, Wucher A, Winograd N. *Anal. Chem.* 2008; 80(14):5293–5301. [PubMed: 18549239]
9. Fletcher JS, Rabbani S, Henderson A, Blenkinsopp P, Thompson SP, Lockyer NP, Vickerman JC. *Anal. Chem.* 2008; 80(23):9058–9064. [PubMed: 19551933]
10. Nygren H, Hagenhoff B, Malmberg P, Nilsson M, Richter K. *Microsc Res Techniq.* 2007; 70(11):969–974.
11. Jones EA, Lockyer NP, Vickerman JC. *Anal. Chem.* 2008; 80(6):2125–2132. [PubMed: 18278949]
12. Mahoney CM, Roberson S, Gillen G. *Appl. Surf. Sci.* 2004; 231-2:174–178.
13. Mahoney CM, Fahey AJ, Gillen G. *Anal. Chem.* 2007; 79(3):828–836.
14. Zheng L, Wucher A, Winograd N. *Anal. Chem.* 2008; 80(19):7363–7371. [PubMed: 18778034]
15. Cheng J, Wucher A, Winograd N. *J. Phys. Chem. B.* 2006; 110(16):8329–8336. [PubMed: 16623517]
16. Cheng J, Kozole J, Hengstebeck R, Winograd N. *J. Am. Soc. Mass Spectrom.* 2007; 18(3):406–412. [PubMed: 17118671]
17. Wucher A, Cheng J, Winograd N. *J. Phys. Chem. C.* 2008; 112(42):16550–16555.
18. Shard AG, Brewer PJ, Green FM, Gilmore IS. *Surf. Interface Anal.* 2007; 39(4):294–298.
19. Shard AG, Green FM, Brewer PJ, Seah MP, Gilmore IS. *J. Phys. Chem. B.* 2008; 112(9):2596–2605. [PubMed: 18254619]
20. Dowsett MG, Rowlands G, Allen PN, Barlow RD. *Surf. Interface Anal.* 1994; 21(5):310–315.
21. Fine J, Navinsek B. *Surf. Interface Anal.* 1995; 23(6):391–392.
22. Sjoval P, Rading D, Ray S, Yang L, Shard AG. *J. Phys. Chem. B.* 2010; 114(2):769–774. [PubMed: 20020719]
23. Paruch R, Rzeznik L, Czerwinski B, Garrison BJ, Winograd N, Postawa Z. *J. Phys. Chem. C.* 2009; 113(14):5641–5648.
24. Sostarecz AG, McQuaw CM, Ewing AG, Winograd N. *J. Am. Chem. Soc.* 2004; 126(43):13882–13883. [PubMed: 15506723]
25. McQuaw CM, Sostarecz AG, Zheng LL, Ewing AG, Winograd N. *Langmuir.* 2005; 21(3):807–813. [PubMed: 15667151]
26. McQuaw CM, Sostarecz AG, Zheng L, Ewing AG, Winograd N. *Appl. Surf. Sci.* 2006; 252(19):6716–6718. [PubMed: 18079999]
27. Zheng L, McQuaw CM, Ewing AG, Winograd N. *J. Am. Chem. Soc.* 2007; 129(51):15730–15731. [PubMed: 18044889]
28. Baker MJ, Zheng L, Winograd N, Lockyer NP, Vickerman JC. *Langmuir.* 2008; 24(20):11803–11810. [PubMed: 18788765]
29. Zheng L, Wucher A, Winograd N. *Appl. Surf. Sci.* 2008; 255(4):816–818. [PubMed: 19551160]

30. Zheng L, Andreas W, Nicholas W. *Surf. Interface Anal.* 2010
31. Lu C, Wucher A, Winograd N. *Surf. Interface Anal.* 2010
32. Hofmann S. *Surf. Interface Anal.* 2000; 30(1):228–236.
33. Eckstein W, Biersack J. *Nucl Instrum Meth B.* 1984; 2(1–3):550–554.
34. Wittmaack K. *J. Appl. Phys.* 1982; 53(7):4817–4820.
35. Rar A, Hofmann S, Yoshihara K, Kajiware K. *Appl. Surf. Sci.* 1999; 144-45:310–314.
36. Ryan KE, Smiley EJ, Winograd N, Garrison BJ. *Appl. Surf. Sci.* 2008; 255(4):844–846.
37. Shard AG, Foster R, Gilmore IS, Lee JLS, Ray S, Yang L. *Surf. Interface Anal.* 2010
38. Smiley EJ, Winograd N, Garrison BJ. *Anal. Chem.* 2007; 79(2):494–499. [PubMed: 17222012]
39. Ryan KE, Garrison BJ. *Anal. Chem.* 2008; 80(17):6666–6670. [PubMed: 18686971]
40. Delcorte A, Garrison BJ. *Nucl Instrum Meth B.* 2007; 255(1):223–228.
41. Delcorte A, Garrison BJ. *J. Phys. Chem. C.* 2007; 111(42):15312–15324.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Table 1

Depth resolution and Dowsett's fitting results of depth profiles of single delta layer sample under various experimental conditions.

Sample Temperature	Kinetic Energy	Incident Angle	FWHM (nm)	λ_g (nm)	λ_d (nm)	σ (nm)
300 K	40 keV	40°	29.7±1.5	4.9±0.1	16.3±1.1	7.7±0.5
100 K	40 keV	40°	20.7±0.8	4.9±0.1	8.9±1.2	5.9±0.1
100 K	40 keV	71°	15.5±0.4	4.5±0.5	7.6±0.7	3.8±0.3
100 K	20 keV	40°	16.0±1.0	3.0±0.2	7.7±0.8	4.4±0.2
100 K	20 keV	71°	12.1±0.9	3.3±0.1	5.6±1.0	3.2±0.1