

# Investigations of molecular depth profiling with dual beam sputtering

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**ABSTRACT:** In this study, the feasibility of molecular depth profiling using dual beam sputtering of biological materials is examined. The model system is a 402-nm Langmuir Blodgett multilayer film consisting of 149 monolayers of barium arachidate (AA). The thin film was initially subjected to pre-bombardment with a 15-keV Au<sup>+</sup> beam. Subsequently, an imaging depth profile experiment was performed on the pre-irradiated sample using a 40-keV C<sub>60</sub><sup>+</sup> beam. An extremely low erosion rate under Au<sup>+</sup> bombardment is found on this model system. In the subsequent C<sub>60</sub><sup>+</sup> depth profiles, surprisingly large molecular ion signals are detected at the gold pre-irradiated surface. These signals then rapidly decay to nearly zero, indicating a damaged sub-surface layer being generated by the Au<sup>+</sup> pre-bombardment. The thickness of the damaged layer is found to increase with increasing gold ion fluence and saturate at about 100 nm at  $6 \times 10^{14}$  Au<sup>+</sup>/cm<sup>2</sup>. This altered layer thickness is significantly larger than the value of ~50 nm obtained on a trehalose film pre-bombarded with a Ga<sup>+</sup> source. The results also show that the damage caused by the Au<sup>+</sup> beam can be removed by C<sub>60</sub><sup>+</sup> sputtering and that the molecular information is restored after damage removal. Copyright © 2012 John Wiley & Sons, Ltd.

**Keywords:** Dual beam sputtering; FIB-SIMS; Molecular depth profiling; Altered layer; Damage removal

## Introduction

Molecular depth profiling has become a powerful method for organic and biological material characterization with the development of cluster ion beams, particularly C<sub>60</sub> ions. Sputtering by C<sub>60</sub><sup>+</sup> also can be used to recover the molecular ion information from a sample damaged by prior atomic projectile bombardment. Previous studies have shown that the molecular ion signal from histamine molecules embedded in an ice matrix exponentially decreases with Ga<sup>+</sup> bombardment, while sputtering with a high fluence of 20-keV C<sub>60</sub><sup>+</sup> can quickly restore the molecular ion signal.<sup>[1]</sup> Similar results have been confirmed on trehalose films doped with peptides.<sup>[2]</sup> These experimental results suggest that molecular depth profiling may be performed in a dual beam arrangement, using, for instance, a cluster ion beam like C<sub>60</sub><sup>+</sup> or Ar<sub>n</sub><sup>+</sup> for sputtering and a liquid metal ion source for high-resolution imaging data acquisition.<sup>[3,4]</sup> In an alternative approach, it has recently been suggested to employ a focused ion beam (FIB) to erode a three-dimensional object and analyze the resulting cross sections (i.e. the crater wall parallel to the eroding ion beam) with mass spectral imaging as a method to acquire molecular 3D information.<sup>[5]</sup> Such an approach requires a second ion beam for data analysis, which forms an angle with the FIB cutting beam and can therefore serve as the analysis probe. For molecular imaging, it would be necessary to use a cluster beam for that purpose in order to remove the lateral damage produced by the FIB cut and restore the molecular integrity at the cross-section surface.

In this work, we used a Langmuir Blodgett (LB) multilayer thin film as a well-established model system to investigate the feasibility of such a dual beam FIB cross-sectioning approach on biological materials. More specifically, a 402-nm LB film of barium arachidate (AA) was first subjected to high-fluence bombardment with an Au<sup>+</sup> beam, followed by a depth profile experiment with a 40-keV C<sub>60</sub><sup>+</sup> beam rastered over the Au<sup>+</sup> pre-bombarded region. The results reported below show that the FIB cross-sectioning experiment was ineffective on this sample, since an extremely low erosion rate

by the Au<sup>+</sup> beam is found on the LB film. From the analysis of the subsequent C<sub>60</sub><sup>+</sup> depth profile, we show that gold pre-bombardment generates an altered sub-surface layer of about 100-nm thickness, where the molecular integrity of the sample is completely destroyed. Consistent with previous studies, we find that the C<sub>60</sub><sup>+</sup> ion bombardment is able to remove this damaged layer, thereby restoring the molecular information in the mass spectra. By varying the fluence of the gold pre-bombardment, it is possible to investigate the evolution dynamics of the altered layer.

## Experimental

The preparation of the LB films has been described in detail elsewhere.<sup>[6]</sup> A single crystal (100) silicon wafer was used as the substrate for all LB films after being cleaned with ozone for 10 min and rinsed with high purity water several times to ensure hydrophilicity of the Si/SiO<sub>2</sub> surface. The LB monolayer films of AA were prepared on a Kibron μTrough S-LB (Helsinki, Finland). 149 layers of AA monolayer were sequentially deposited on the Si substrate, resulting in a 402-nm thin film.

Sputter depth profiling was performed in a TOF-SIMS instrument equipped with a fullerene cluster ion source (Ionoptika IOG 40–60) and a gold ion source (Ionoptika IOG 25), directed at the same surface area under polar angles of 40° and 45° relative to the surface normal and an azimuthal angle of 135° between both beams.

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Details of this instrumentation have been described elsewhere.<sup>[7]</sup> Depth profile experiments were performed at 100 K. Au<sup>+</sup> ion bombardment was performed using a continuous, focused 15-keV Au<sup>+</sup> beam raster scanned across a surface area of 180 μm × 265 μm. For imaging depth profiling after the gold pre-bombardment, a 40-keV C<sub>60</sub><sup>+</sup> ion beam was operated in continuous mode to erode through the film at an area of 380 μm × 480 μm including the gold pre-bombarded region. Between erosion cycles, static SIMS images with 256 × 256 pixels were acquired from the same area using the pulsed C<sub>60</sub><sup>+</sup> beam at an ion fluence of 10<sup>10</sup> C<sub>60</sub><sup>+</sup>/cm<sup>2</sup>. The pixel size of 1.5 × 1.9 μm was small compared to the C<sub>60</sub><sup>+</sup> beam diameter (~10 μm), ensuring a homogenous erosion profile across the sputter crater. TOF mass spectra were retrospectively extracted from any area of interest inside the sputtered region using the image data.

Film thickness and topography of the sputtered craters were characterized by atomic force microscopy (AFM) using a specialized device optimized for wide scanning area (KLA-Tencor Nanopics 2100).

## Results and Discussion

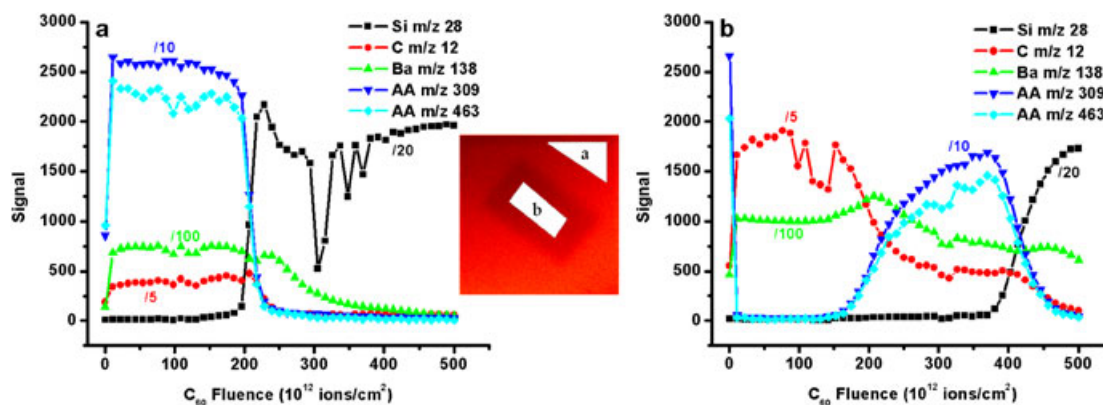
The erosion rate and sputter yield of Au<sup>+</sup> projectiles on the LB multilayer were examined by etching the 402-nm AA film using a focused beam of 15-keV Au<sup>+</sup> with various ion fluences. The beam was rastered over four different areas of 180 μm × 265 μm with an Au<sup>+</sup> fluence of 3 × 10<sup>14</sup> ions/cm<sup>2</sup>, 6 × 10<sup>14</sup> ions/cm<sup>2</sup>, 1.2 × 10<sup>15</sup> ions/cm<sup>2</sup>, and 2.4 × 10<sup>15</sup> ions/cm<sup>2</sup>, respectively. Then, the sample was removed from the vacuum system, and the dimensions of the resulting craters were measured by AFM. Surprisingly, only very shallow craters with depths between 10 and 20 nm were observed in all four cases, regardless of the applied ion fluence.

Based on the result obtained at the largest fluence, the average sputter yield under Au<sup>+</sup> impact on the AA multilayer film would be of the order of 10<sup>-8</sup> molecules/ion, indicating that the AA film erosion is quenched early on during the Au<sup>+</sup> ion bombardment. These findings are in marked contrast to similar studies on spin-coated trehalose films, which have revealed sputter yields of 1.5 and 6 molecule equivalents under 25-keV Au<sup>+</sup> and 15-keV Ga<sup>+</sup> impact, respectively.<sup>[2,8]</sup> The data presented here show that FIB cross sectioning using an atomic ion beam (usually

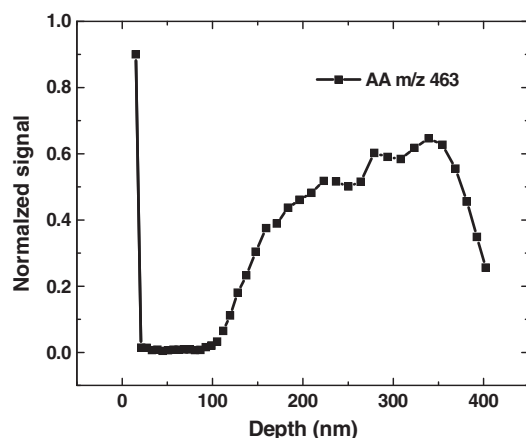
Ga<sup>+</sup>) for site specific milling does not work for the system studied here. The exact reason of the extremely low sputter yield of Au<sup>+</sup> projectiles on the LB film is not clear at the present time. One could speculate that it may be related to the uniquely ordered structure of the LB multilayer. In fact, MD simulation studies have revealed that C<sub>60</sub><sup>+</sup> projectiles can penetrate more than two times deeper into an AA overlayer than into a more densely packed benzene film.<sup>[9]</sup> This could be even more severe for Au<sup>+</sup>, which has been shown to penetrate much deeper into organic material than an iso-energetic C<sub>60</sub> cluster. The open and well-oriented structure of the LB film may therefore allow the Au<sup>+</sup> ions to deposit their kinetic energy at a depth large enough to prevent efficient sputter emission. Using the same argument, one might expect bombardment-induced chemical damage to extend comparatively deep below the sample surface. This hypothesis was examined by the following depth profile experiments with a C<sub>60</sub><sup>+</sup> beam.

Imaging depth profile experiments with C<sub>60</sub><sup>+</sup> were performed over the regions pre-bombarded with Au<sup>+</sup>. The summed total ion image of all SIMS images acquired during the C<sub>60</sub><sup>+</sup> depth profile analysis is shown in Fig. 1. The area pre-bombarded with 6 × 10<sup>14</sup> Au<sup>+</sup>/cm<sup>2</sup> can be easily recognized by the rectangular shadow in the center of the image. Outside the central shadow is the undamaged AA film. By selecting pixels at region **a** indicated in Fig. 1, we can extract mass spectral information from the image data and construct the depth profile of the undamaged AA film (see Fig. 1(a)). The depth profile of the Au<sup>+</sup> pre-bombarded film was obtained in a similar way by extracting the mass spectral information from region **b** (see Fig. 1(b)). Signals at m/z 463 and m/z 309 represent the molecular ion of AA with and without barium attached, respectively. In order to allow a quantitative comparison, the signals shown in the figures are normalized to the number of pixels in the respective region of interest.

As expected, the result obtained from region **a** exhibits the typical C<sub>60</sub><sup>+</sup> depth profile of an undisturbed AA film, which has been observed before.<sup>[10]</sup> The erosion rate and sputter yield of the intact AA film can be calculated from this depth profile using the known film thickness and the ion fluence required to remove the entire film and reach the silicon substrate. The data extracted from region **b** illustrate the depth profile of the Au<sup>+</sup> pre-bombarded film. It starts with a high molecular ion signal, which has about the same level as the undisturbed film. Comparison of the mass spectra measured at the beginning of the depth profile with those obtained from the unbombarded surface reveals a



**Figure 1.** Total ion image summed over all sequential SIMS images taken during a 3D C<sub>60</sub><sup>+</sup> profile of an AA film pre-bombarded with 6 × 10<sup>14</sup> Au<sup>+</sup> ions/cm<sup>2</sup>. The diagrams show depth profiles extracted from the data in undamaged (a) and pre-bombarded (b) regions as indicated.



**Figure 2.** Calibrated depth profile of the molecular ion signal measured for a  $C_{60}^+$ -depth profile of an AA film pre-bombarded with  $6 \times 10^{14}$   $Au^+$ /cm<sup>2</sup>.

striking similarity, indicating that the gold projectiles did not completely fragment the molecules at the topmost surface. Apparently, the  $Au^+$  projectiles must penetrate the surface and deposit their energy at sufficient depth below the surface to leave the topmost layer intact. Upon starting the  $C_{60}^+$  erosion, the molecular signals rapidly decrease to practically zero, while unspecific fragment ions such as  $C^+$  and  $Ba^+$  rise significantly above the levels detected during erosion of the undisturbed region. Hence, a sub-surface layer has been damaged by  $Au^+$  bombardment, resulting in extensive fragmentation of AA molecules. As more  $C_{60}^+$  fluence is applied, the intensities of  $C^+$  and  $Ba^+$  decrease, while the signals of  $m/z$  463 and  $m/z$  309 increase again until they reach a similar level as in the undamaged AA film. This finding demonstrates that – in agreement with earlier studies on trehalose films – the  $C_{60}^+$  beam is able to remove the damage produced by the  $Au^+$  pre-bombardment and recover the molecular ion information from the underlying intact AA layers.

Using the procedures described in detail elsewhere,<sup>[2]</sup> we use a linear interpolation of the erosion rate between the completely damaged AA film and the undamaged AA film based on the measured signals to calculate the momentary erosion rate at any point of the depth profile in region **b**. With the depth scale calculated from this momentary erosion rate, the resulting profile obtained in the pre-bombarded region is plotted in Fig. 2. It reveals unique information about the thickness of the sub-surface layer influenced by  $Au^+$  bombardment. An altered layer thickness of about 100 nm is determined from the depth profile in Fig. 2. Analysis shows that the damaged layer gradually builds up with increasing gold fluence and appears to saturate at a value of several  $10^{14}$  ions/cm<sup>2</sup>, showing the profile depicted in the figure. The resulting steady-state altered layer thickness is surprisingly large, but not physically unreasonable. Using the same technique as applied here, a value of ~50 nm was

measured on a trehalose film bombarded by 15-keV  $Ga^+$ .<sup>[2]</sup> The large altered layer thickness determined here corroborates the speculation that the gold projectiles deposit their energy deep into the LB overlayer, leading to long-range damage along with inefficient surface sputtering.

## Conclusion

In summary, it appears that the FIB cross-sectioning method for depth profiling would not be appropriate for the LB films studied here. Bombardment of a 402-nm film consisting of 149 monolayers of barium-arachidate with  $Au^+$  projectiles shows extremely low sputter efficiency and results in significant sub-surface chemical damage. Interestingly, the molecular ion signals detected under static  $C_{60}^+$  bombardment of the heavily gold pre-irradiated surface are of the same magnitude or even higher than those measured on a fresh, undisturbed sample, indicating that gold pre-bombardment does not completely destroy molecules located directly at the surface and might even enhance their ionization probability. The molecular ion signals then decrease very rapidly with increasing  $C_{60}^+$  fluence, indicating that the  $Au^+$  pre-bombardment generates an altered sub-surface layer where the molecular integrity of the sample is essentially destroyed. Sputtering with a  $C_{60}^+$  beam is an effective way to remove that damaged layer and recover the molecular ion information from the undisturbed sample volume underneath. Combining the mass spectral data with topographical information, we find a steady-state altered layer thickness of about 100 nm under high-fluence conditions. This very large damage depth is interpreted in terms of the open, well-ordered structure of the LB film.

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