

Temperature effects of sputtering of Langmuir–Blodgett multilayers

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) and atomic force microscopy are used to characterize a wedge-shaped crater eroded by a 40-keV C_{60}^+ cluster ion beam on an organic thin film of 402 nm of barium arachidate multilayers prepared by using the Langmuir–Blodgett technique. Sample cooling at 90 K was used to help reduce chemical damage, to improve depth resolution and to maintain constant erosion rate during depth profiling. The film was characterized at 90, 135, 165, 205, 265 and 300 K. It is shown that sample cooling to 205 K or lower helps to inhibit erosion rate decay, whereas at 300 and 265 K, the erosion rate continues to drop after 250 nm of erosion, reaching approximately half of the initial value after removal of the entire film. Depth profiles are acquired from the SIMS images of the eroded wedge crater. The results suggest that sample cooling only slightly improves the altered layer thickness but eliminates the decrease in erosion rate observed at temperatures higher than 265 K. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Molecular depth profiling using secondary ion mass spectrometry (SIMS) and cluster ion beams has been shown to be applicable to a wide range of organic and biological materials.^[1–8] Molecular and fragment distribution information as a function of depth has been successfully obtained for many systems and combined with imaging to yield three-dimensional information.^[2,9–11] During these depth profiling studies, some systems are seen to be dominated by chemical damage buildup. It would be valuable to understand what factors contribute to the success or failure of these experiments.^[8,12,13]

One of the most important parameters that improve the overall quality of the depth profile is the temperature of the sample. Cooling not only allows the secondary ion intensity to remain constant with fluence but also decreases broadening at interfaces.^[8,14–17] To investigate and understand the temperature effects in depth profiling experiments, wedge–crater beveling of a delta layer organic sample as a tool to acquire fundamental information of molecular depth profiling with C_{60} -SIMS has been developed.^[18] One advantage of wedge–crater beveling is that factors involved in depth profiling, including the interface width, topography formation and sputtering yield can be obtained from a single crater measurement.

In this work, we examine temperature effects by wedge–crater beveling of an organic thin film of barium arachidate (AA). The film is produced using a Langmuir–Blodgett (LB) trough. In wedge beveling experiments, the SIMS results are acquired by imaging the eroded wedge crater surface. Atomic force microscopy (AFM) measurements are performed on the same area. Because of the unique information provided by the wedge crater with AFM, we show that erosion rate variations as a function of depth can be obtained. By lowering the sample temperature, erosion rate decay is dramatically reduced. When experiments are performed at temperatures lower than 205 K, there is no

further reduction of the erosion rate decay. The results also suggest that temperature has little effect on interface width after careful depth calibration, indicating that sample cooling does not reduce bombardment-induced interlayer mixing. In general, we suggest that the improvement in the quality of the depth profile at reduced temperature results from the inhibition of erosion rate decay.

Experimental

An LB film of AA was prepared as described elsewhere.^[19] Briefly, a single crystal (100) silicon wafer was used as the substrate after cleaning with UV/ozone for 10 min and rinsing with high purity water several times to achieve hydrophilicity of the Si/SiO₂ surface. Langmuir–Blodgett films of AA were prepared by using a Kibron μ Trough S-LB (Helsinki, Finland). Monolayers of AA were compressed at the air–water interface. The monolayer was transferred onto the Si substrate via vertical deposition. Each AA monolayer is approximately 2.7 nm in thickness, and this multilayer AA film is calculated to be approximately 400 nm in thickness. This thickness value is also consistent with AFM measurements.

Depth profiling was performed in a time-of-flight secondary ion mass spectrometry (TOF-SIMS) instrument equipped with a C_{60} cluster ion source (IOG 40–60; Ionoptika; Southampton, UK),

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directed at a 40° angle relative to the surface normal. The performance of the C_{60}^+ ion source^[3] and the details of this instrumentation have been described elsewhere.^[20] The specifics of the wedge sputtering scheme have been described elsewhere.^[18] Briefly, the surface is subjected to erosion via the 40-keV C_{60}^+ ion beam. In dc mode (erosion mode), the ion beam delivers a primary ion current of approximately 80 pA into a spot size of approximately 8 μm . In data acquisition mode, the ion beam is digitally scanned across a $460 \times 600\text{-}\mu\text{m}$ field of view using a 256×256 pixel raster. The total sputtering time is divided into frames with a beam dwell time of no less than 20 μs on each pixel. To erode a wedge-shaped crater, a linearly increasing ion fluence is applied, which yields zero fluence on one side of the crater and a maximum fluence on the other side. For this purpose, the raster area is varied from frame to frame by sequentially skipping lines in the y direction.

The TOF-SIMS instrument used in these experiments can achieve sample cooling by forcing liquid-nitrogen-cooled nitrogen gas through the sample stage, resulting in the lowest possible sample temperature of 90 K. To achieve temperature values between 90 and 300 K, the cooled nitrogen gas is variably heated by a temperature-controlled copper coiled tube that is attached to the cooling line of the stage entry port. By balancing the heating power, a ± 5 K stable temperature may be obtained within a waiting time of approximately 1 h before the experiment. Wedge craters were characterized by a KLA-Tencor Nanopics 2100 atomic force microscope (AFM).

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 this information from topographical line scans along the wedge (y) direction of the eroded crater has been described previously.^[18]

Briefly, the wedge crater receives a linearly increasing ion fluence along the y direction, and the ion fluence at each data point can be calculated for from the known applied total fluence. Coupled with the AFM measured depths, the average erosion rate from initial surface can be obtained. In a wedge crater, an advantage of having depth information for all fluence

allows the calculation of erosion rate as the function of fluence instead of an average erosion rate. To eliminate the microscopic fluctuations in erosion rates due to surface roughness, the variation in rate as a function of eroded depth is calculated as the average derivative from sets of 40 data points, showing only a macroscopic change in a defined area. The resulting value is plotted at the depth corresponding to the center of each interval, as shown in Fig. 1.

These data show that the initial erosion rate is $160\text{ nm}^3/\text{impact}$ and decreases to $130\text{--}140\text{ nm}^3/\text{impact}$ at the steady state. For experiments at 90, 135, 165 and 205 K, the erosion rate remains fairly constant with no further observed decrease. The fluctuations are mostly likely due to the AFM measurement calibration protocol and slight changes in the C_{60}^+ ion beam current.

For experiments at 265 and 300 K, the erosion rate continues to decay throughout the removal of the 400-nm AA film, reaching approximately 50% of the initial surface value after the film is removed. At 300 K, a severe decay is measured. This finding is in a good agreement with the conventional depth profiles of LB films.^[8] Interestingly, the erosion rate decay at 265 and 300 K accelerates after 200 nm of erosion. A similar observation is observed for the Irganox 3114/1010 delta layers system where the erosion rate drops quickly at approximately 150 nm depth.^[15] We can only speculate that the ion bombardment damage builds to some critical level before major changes are observed. This effect clearly needs to be studied in more detail.

Another unique property of the eroded wedge surface is that it transforms the vertical chemical distribution into lateral information. Therefore, depth profiles can be extracted from SIMS images of the wedge surface. Line scans taken from the SIMS images of the eroded wedge craters allow profiles of signals as a function of ion fluence to be obtained. Information on topography as a function of ion fluence and the depth for each point in the SIMS profiles can be interpolated from the AFM results. Therefore, depth profiles based on an accurate depth scale can be acquired. In this study, the interface width of (AA)-Si is used to compare the depth resolution as a function of temperature. Three line scans are taken from SIMS results of each eroded crater. The interface width was calculated from the 16% to 84% of the maximum Si intensity. The resulting width in micrometers can be converted into vertical width of nanometers by simply measuring the crater length and depth. The average width of three line scans is plotted in the black dots shown in Fig. 2. Because the sputtering yield of Si is significantly smaller than AA, the

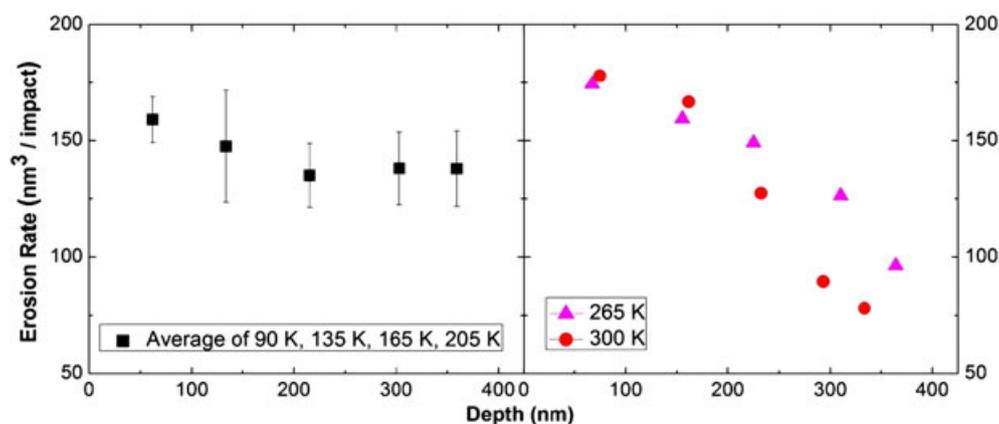


Figure 1. Erosion rate as a function of eroded depth during bombardment of a 400-nm AA film. Left panel: erosion rate determined by averaging data acquired between 90 and 205 K; right panel: erosion rate obtained at 265 K (magenta triangle) and 300 K (red circle). All six wedge craters were created by a 40-keV C_{60}^+ ion beam impinging at 40° with respect to the surface normal.

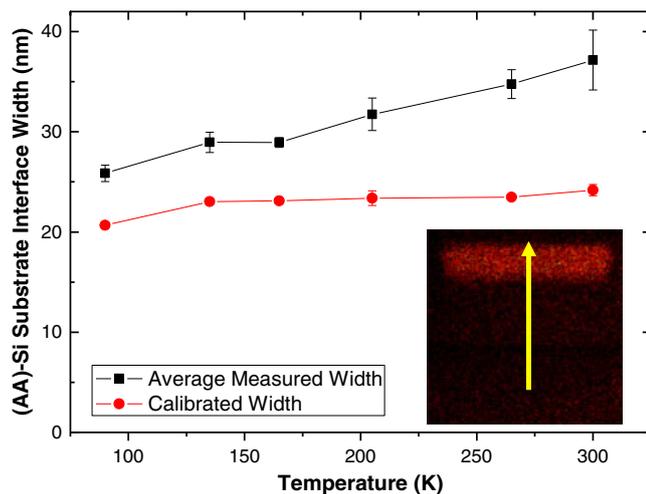


Figure 2. Width of the Si–AA interface as the function of temperature. Data in the black curve are obtained from the three line scans along the y direction. The red curve shows the calibrated interface width from the two strategies described in the text with the error bars showing the agreement between the two strategies. The picture insert shows a Si signal at the Si–AA interface. The line scan is used to calculate the interface width.

measured organic–inorganic interface width cannot accurately represent the actual depth resolution. Two methods were used to calibrate the actual interface. The first method is to locate the depth value difference of the 16% to 84% maximum Si intensity in the AFM. This measurement yields a direct height difference of interface width from AFM measurements. This obtained width is valuable because it does not use SIMS information but is a direct reading. However, microscopic surface roughness will have a small influence on the results.

The second method accounts for the difference of erosion rate between the AA film and the Si. Corrections need to be made by considering the change of erosion rate observed on the Si intensity increases from 16% to 84% of its maximum value. The interface width can be obtained from the calibrated erosion rate as described elsewhere.^[3] The resulting widths from both methods are in good agreement as seen in Fig. 2.

The calibrated interface width is improved only by approximately 2 nm by lowering the sample temperature from 300 to 90 K. This improvement is consistent with that observed from the Irganox delta layer wedge beveling experiments where most improvement in depth resolution of the full width at half maximum was achieved by lowering the temperature to less than 150 K for wedge beveling. These findings suggest sample cooling helps to reduce topography development and erosion rate decay.

Conclusion

We demonstrate that the temperature effects on a Langmuir–Blodgett film can be successfully investigated by wedge–crater beveling. By combining both molecular depth profiling and AFM surface measurements, the effects of temperature on fundamental factors such as erosion rate and interface width are determined. Sample cooling to 205 K reduces the erosion rate decay, and no further improvement is observed by cooling to 90 K. The interface width obtained from wedge-beveling shows that temperature has little influence on the depth resolution. Sample cooling improves depth profiles by reducing the topography development and erosion rate decay. In general, we believe that wedge–crater beveling is an important platform for studying several fundamental parameters that affects molecular depth profiling.

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References

- [1] G. Gillen, S. Roberson, *Rapid Comm. Mass Spectrom.* **1998**, *12*, 1303.
- [2] C. M. Mahoney, S. V. Roberson, G. Gillen, *Anal. Chem.* **2004**, *76*, 3199.
- [3] J. Cheng, N. Winograd, *Anal. Chem.* **2005**, *77*, 3651.
- [4] M. S. Wagner, *Anal. Chem.* **2005**, *77*, 911.
- [5] J. S. Fletcher, X. A. Conlan, N. P. Lockyer, J. C. Vickerman, *Appl. Surf. Sci.* **2006**, *252*, 6513.
- [6] G. Gillen, J. Batteas, C. A. Michaels, P. Chi, J. Small, E. Windsor, A. Fahey, J. Verkouteren, K. J. Kim, *Appl. Surf. Sci.* **2006**, *252*, 6521.
- [7] A. G. Shard, P. J. Brewer, F. M. Green, I. S. Gilmore, *Surf. Interface Anal.* **2007**, *39*, 294.
- [8] L. L. Zheng, A. Wucher, N. Winograd, *Anal. Chem.* **2008**, *80*, 7363.
- [9] A. Wucher, J. Cheng, L. Zheng, N. Winograd, *Anal. Bioanal. Chem.* **2009**, *393*, 1835.
- [10] J. S. Fletcher, S. Rabbani, A. Henderson, N. P. Lockyer, J. C. Vickerman, *Rapid Comm. Mass Spectrom.* **2011**, *25*, 925.
- [11] H. Nygren, B. Hagenhoff, P. Malmberg, M. Nilsson, K. Richter, *Microsc. Res. Tech.* **2007**, *70*, 969.
- [12] C. M. Mahoney, A. J. Fahey, G. Gillen, *Anal. Chem.* **2007**, *79*, 828.
- [13] J. Kozole, A. Wucher, N. Winograd, *Anal. Chem.* **2008**, *80*, 5293.
- [14] C. Y. Lu, A. Wucher, N. Winograd, *Anal. Chem.* **2011**, *83*, 351.
- [15] D. Mao, C. Lu, N. Winograd, A. Wucher, *Anal. Chem.* **2011**, *83*, 6410.
- [16] P. Sjoval, D. Rading, S. Ray, L. Yang, A. G. Shard, *J. Phys. Chem. B* **2010**, *114*, 769.
- [17] A. M. Piwowar, J. S. Fletcher, J. Kordys, N. P. Lockyer, N. Winograd, J. C. Vickerman, *Anal. Chem.* **2010**, *82*, 8291.
- [18] D. Mao, A. Wucher, N. Winograd, *Anal. Chem.* **2010**, *82*, 57.
- [19] L. L. Zheng, A. Wucher, N. Winograd, *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 96.
- [20] R. M. Braun, P. Blenkinsopp, S. J. Mullock, C. Corlett, K. F. Willey, J. C. Vickerman, N. Winograd, *Rapid Comm. Mass Spectrom.* **1998**, *12*, 1246.