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Low Temperature Plasma for Compositional Depth Profiling of Crosslinking Organic Multilayers: Comparison with C₆₀ and Giant Argon Gas Cluster Sources

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Introduction

Low temperature plasma (LTP) is a dielectric barrier discharge that generates a low power non-thermal plasma in atmosphere,^[1] and is used for ozone generation,^[2, 3] polymer surface treatments,^[4–6] and biological decontamination.^[7, 8] In a cylindrical configuration, such as a glass capillary, a carrier gas stream (typically helium) forces the plasma to extend beyond the pair of electrodes and out of the capillary to make a plasma jet. In addition to a thermal component, constituents of helium plasma at atmosphere include electrons, metastable helium species, N₂⁺, O₃[−], OH[−], protonated water clusters, radicals, and ultraviolet light.^[1, 9] By directing this jet at a sample surface, organic molecules on the surface can be desorbed through a combination of thermal and chemical etching and form gaseous ions, making this technique a practical desorption and ionization source for ambient mass spectrometry.^[10–18]

The desorption aspect of the technique is particularly intriguing as it provides a fast and easy atmospheric sample preparation method for removal of excess overlayers or contaminants,^[19] leaving minimal residual chemical damage on the etched surface.^[20] The plasma is able to etch through a wide variety of organic materials, including polymers with conjugated bonds and aromatic molecules that would be expected to crosslink under ion irradiation. Due to these features, plasma etching is potentially of relevance for preparing samples for subsequent molecular depth profiling of etched bevels or crater edges,^[21–27] utilizing techniques such as secondary ion mass spectrometry (SIMS) or x-ray photoelectron spectroscopy (XPS). Both of these techniques utilize energetic ion bombardment in vacuum for depth profiling and potentially suffer from artifacts such as chemical damage accumulation,^[28–30] collisional mixing,^[31–33] and topography generation.^[34, 35] The compositional depth profiling of plasma etched crater edges by SIMS seems advantageous since it provides high lateral magnification to resolve buried structures while minimizing the creation of these artifacts, making accurate determination of interface widths possible.

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In the field of organic electronics, devices such as organic light-emitting diodes (OLEDs), transistors, and photovoltaic cells are fabricated using conjugated aromatic molecules that actively transport charge. These organic semiconductors are either discrete small molecules deposited by evaporative processes, or polymers that are deposited through solution processing. Oftentimes, the system is a multilayer composite structure for purposes of charge transport, light emission, and/or light absorption, with each layer having a thickness ranging from 10 nm to a few hundred nanometers. Although the technology has shifted from research and development to production,^[36] there remain questions concerning the stability of the active layers when exposed to high current densities over extended periods of time. Challenges such as interlayer diffusion and interfacial oxidation,^[37–39] which occur in length-scales of a few nanometers requires a molecular depth profiling technique that is capable of nanometer depth resolution. These materials, particularly organometallic chelates such as aluminum hydroxyquinolate (Alq3) used for electron-transport and host emitting material in OLEDs presents a unique challenge for ToFSIMS depth profiling, as the material is prone to crosslink under ion bombardment and the presence of the metal tends to promote deposition of the primary sputter source onto the crater bottom.^[40]

To demonstrate the capability of the low temperature plasma source for crater edge depth profiling, a multilayer system made of aluminum hydroxyquinolate (Alq3) as the matrix, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine or BCP) as a contaminant (delta) layer was prepared. This film was etched using LTP, and the depth resolution of the delta layers determined from ToFSIMS images of the crater edge. Dual-beam depth profiling using C_{60}^{2+} and argon cluster sputter sources were performed for comparison.

Experiment

Sample Preparation

A 10 cm Si(100) substrate purchased from Silicon Valley Microelectronics* (Santa Clara, CA) was diced into 10 mm × 10 mm square pieces using a Kuliche & Soffa 780 dicing saw with a 15 μm diamond impregnated blade (Willow Grove, PA). The diced Si substrates were soaked in 5% hydrofluoric acid (Sigma Aldrich, St. Louis, MO) for 5 min to remove the native oxide layer. The substrates were then rinsed in ultrapure water and dried under a stream of nitrogen. Tris(8-hydroxyquinolato)aluminum (Alq3) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine or BCP), both sublimed grade with over 99 % trace metals basis, were purchased from Sigma Aldrich and used as received. The Edwards Auto 306 Thermal Evaporator with a built-in quartz crystal microbalance (QCM) was operated at 2.0×10^{-6} kPa (2.0×10^{-6} mbar), and used to create a repeating multilayer structure of 30.0 ± 1.1 nm Alq3 and $1.0 \text{ nm} \pm 0.5 \text{ nm}$ BCP (Figure 1). The QCM was calibrated for both Alq3 and BCP in order to measure the deposited mass (and hence film thickness) *in situ*. The calibration was done by measuring the thickness of the deposited films using a profilometer.

Low Temperature Plasma

The LTP probe was constructed in-house from a glass capillary tube (2 mm ID) with a high voltage copper electrode wrapped around the tube and the ground electrode connected to the sample.^[20] The upstream electrode can carry alternating high voltage in the range of 1.0 kV up to 6.0 kV (rms) at a frequency of approximately 20 kHz. Ultrapure helium gas was supplied at 500 mL/min to sustain the discharge. The LTP source was positioned 7 mm above the sample surface, and was directed at an incidence angle of 40° with respect to the sample surface.

Crater Profile and Surface Topography Measurements

The profile of the plasma-etched crater was obtained using a Tencor Alpha-Step 200 profilometer (Manassas, VA) with a 1 mg stylus weight. A 2 mm line scan was used to ensure that a large enough region outside the crater was measured to provide sufficient area for leveling. Roughness of the crater surface was measured from a 15 $\mu\text{m} \times 15 \mu\text{m}$ scan using a Digital Instruments Multimode Atomic Force Microscope (Santa Barbara, CA) operated in intermittent contact mode in air, equipped with a MikroMash™ NSC19 single tip rectangular cantilever with a 80 kHz resonant frequency and 0.6 N/m force constant (NanoAndMore Inc., Lady's Island, SC).

Time-of-Flight Secondary Ion Mass Spectrometry

ToFSIMS depth profile experiments were performed using two different ToFSIMS instruments (IONTOF, Münster, Germany). The first instrument (University of Washington) was equipped with a 25 keV Bi_3^+ liquid metal ion source for analysis and a 20 keV C_{60}^{2+} source for sputtering, both sources striking the sample surface at an angle of 45°. Depth profiling was performed in non-interlaced mode where the analysis and sputtering occurred in different ToF cycles, with a 100 $\mu\text{m} \times 100 \mu\text{m}$ analysis area confined within a 500 $\mu\text{m} \times 500 \mu\text{m}$ sputter area. The ion dose densities were 3.07×10^8 ions/cm² and 1.64×10^{12} ions/cm² per cycle, respectively. The second instrument (IONTOF Germany) was equipped with a 15 keV Bi_3^+ liquid metal ion source for analysis and a 2.5 keV argon gas cluster source ($\text{Ar}_{1000-2500}$) for sputtering, both at an angle of 45°. Depth profiling was performed in non-interlaced mode, with a 200 $\mu\text{m} \times 200 \mu\text{m}$ analysis area confined within a 500 $\mu\text{m} \times 500 \mu\text{m}$ sputter area. The ion dose densities were 4.20×10^8 ions/cm² and 2.74×10^{12} ions/cm² per cycle, respectively. The depth profiles were created in the positive mode by recording the intensity of the m/z 361 $[\text{M}+\text{H}]^+$ ion of BCP, m/z 172 ion of Alq_3 (aluminum bound to just one of the 8-hydroxyquinoline ligands), and m/z 28 ion of elemental Si as a function of sputter ion dose.

Imaging of the plasma-beveled crater was performed at NIST using a TOFSIMS IV instrument equipped with a 25 keV Bi_3^+ liquid metal ion source, operated in high mass resolution mode over an area of 500 $\mu\text{m} \times 500 \mu\text{m}$ with an imaging pixel density of 512 pixels $\times$ 512 pixels. After the sample was exposed to the plasma jet in a fume hood, it was transferred to the TOFSIMS instrument within 5 min.

*Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply

recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Results and Discussion

C₆₀ and argon cluster depth profiles

Alq3 is a molecule with three hydroxyquinoline ligands coordinated around aluminum (Figure 1). The phenyl groups in the ligands are thought to crosslink under ion irradiation, and have been shown to induce a nonlinear sputter rate during depth profiling with a C₆₀ sputter source.^[40] As shown in Figure 2a, the depth profile obtained using the C₆₀ source showed a nonlinear sputter rate, with ion doses of $(1.76 \times 10^{14}, 1.07 \times 10^{15}, \text{ and } 3.14 \times 10^{15})$ ions/cm² required to reach the two buried delta layer interfaces and the silicon wafer, positioned within the film at depths of (31, 62, and 93) nm, respectively (the interface was defined as the depth of the leading edge of the delta at which the signal was 50% of the peak signal intensity). The ion dose required to sputter through 93 nm of Alq3 film was consistent with results in ref ^[40], which was 3.3×10^{15} ions/cm² to sputter away 89 nm of the film. Because the C₆₀ sputter rate was found to be dependent on ion dose, the sputtered yield volume (sputtered volume per sputter ion) was calculated for each of the 30 nm thick layers of Alq3. They were (16.9, 3.4, and 1.5) nm³/ion, respectively, clearly showing the significant decrease in sputter rate as a function of increased C₆₀ dose. For the ion doses investigated, the sputter rate obeyed a power function of the form,

$$y = ax^b \quad (1)$$

where y was the ion dose in 10^{13} ion/cm², x was the sputtered depth in nm, and a and b were constant real numbers determined to be 0.102 and 2.55 through a mathematical fit, respectively. As shown in Figure 2b, the model agreed well with the experimental data, with a correlation coefficient of 0.9998. To convert the raw depth profile to depth, a nonlinear transformation was used to correct for the nonlinear sputter rate. The regression equation was derived by taking the logarithm of Equation 1, which was then used to obtain the modified ion dose shown in Equation 2. This was then rescaled to a sputtered depth in nanometers to reconstruct the depth profile shown in Figure 2c. On the re-scaled plot, the onset of the BCP and silicon interfaces corresponded linearly with the actual interface positions.

$$x' = 10^{\log(x)} = 10^{\frac{1}{b}\log(y) - \frac{1}{b}\log(a)} \quad (2)$$

In this depth profile, a rapid decay of signal was seen in the initial transient region, indicating an accumulation of beam induced damage. Despite a constantly changing sputter rate, the profile experienced a steady state region after the second delta layer (first one is on top of the structure), after more than 50 nm of material was sputtered away. As can be seen in Figure 2c, the intensity of Alq3 was at a minimum when the second delta layer was reached. This steady state region did not continue for long after the third delta layer, as the ion yield of the Alq3 molecule was seen to start falling after roughly 80 nm of the film was

removed. For reasons that are not clear, an increase in Alq3 intensity was observed after the transient region, which correspondingly showed an increase in signal of the third delta layer in relation to the second layer. The peak intensity of the third layer was roughly a factor of two greater than that of the second layer. Since steady state is achieved when the disappearance rate of the molecules and the supply rate induced by surface erosion reach equilibrium,^[41] the intensity of molecules do not generally increase in this region. Therefore, it is thought that the second delta layer generated fewer signals relative to the third layer because the sputter rate was faster through this region.

In comparison, the argon cluster depth profile showed an approximately constant sputter rate. As shown in Figure 2b, the interfaces were reached at ion dose densities of (7.6×10^{13} , 1.6×10^{14} , and 2.5×10^{14}) ions/cm², respectively, sputtering through the entire multilayer system in an order of magnitude lower ion dose than with C₆₀ depth profiling. The calculated sputtered yield volumes were (39.7, 35.8, and 34.7) nm³/ion, respectively, suggesting a slight decrease in sputter rate as a function of sputtered depth. It was possible that there was a transient change in sputter yield that may have occurred at greater depths, but this cannot be determined from the limited data available. More importantly, since the argon cluster source had a sputter yield that was more than twice that of the C₆₀ source during the sputtering of the first Alq3 layer, this indicated that the argon cluster source had the ability to remove a much larger fraction of the damaged volume during dual-beam depth profiling.^[42] This may explain the much higher secondary ion intensities of BCP and Alq3 observed during argon cluster depth profiling. The average normalized secondary ion yields of Alq3 during the steady state region for the C₆₀ and argon cluster depth profiles were $(1.55 \pm 0.35) \times 10^{-4}$ counts/ion and $(1.39 \pm 0.02) \times 10^{-2}$ counts/ion, respectively, showing two orders of magnitude difference in yield and illustrating an advantage of using argon clusters for depth profiling of these samples.

As a side note, it should be mentioned that the kinetic energy differences of the incident Bi₃⁺ analysis beam used for this experiment (25 keV Bi₃⁺ for C₆₀ depth profiling versus 15 keV Bi₃⁺ for argon depth profiling) were not expected to significantly affect the difference in secondary ion yields, as yield enhancements of only up to a factor of two were claimed to have been seen when the energy of a triatomic liquid metal ion source was increased from 15 keV to 25 keV.^[43]

Craters using low temperature plasma

To create craters using the LTP, the Alq3/BCP multilayer system was exposed to the plasma jet at an angle of 40° with respect to the sample surface, taking 120 seconds at 6.0 kV to reach the silicon substrate (etching speed of approximately 0.8 nm/s). Compared to normal incidence, the 40° angle of incidence seemed to create a higher fraction of consistently shaped craters. The AFM-measured roughness at the bottom of the crater where silicon is exposed showed an order of magnitude increase in rms roughness compared to the virgin surface (11.9 nm versus 1.6 nm). However, the surface roughness along the crater edge did not increase with depth (Figure 3), which seemed to suggest that post-plasma analyses along the crater wall using surface sensitive techniques should not experience complications associated with surface topography.

The etching behavior of the LTP was anisotropic, characterized by the radial spread of material desorbed from the point of impact of the plasma jet. The profilometer trace of the crater showed a 600 μm diameter elliptical hole where the substrate was exposed, with roughly a 350 μm long crater edge that extended to the top layer of the film in the direction of the plasma jet, making an angle of 0.00027° with respect to the silicon substrate. Figure 3 shows ToFSIMS images taken along the un-etched surface, the crater edge, and the crater bottom, showing the distribution of the BCP molecular ion, Alq3 fragment ion, and the nitrogen-containing contaminant ion characteristic of plasma deposition. The SIMS images of the BCP molecular ion distribution clearly showed the two rings indicative of the two delta layers buried in the matrix. Similar to the argon cluster depth profile, the ion intensity of the third delta layer was lower than the second, suggesting that the third BCP layer may have been thinner. In addition, it is possible for the third delta layer, which is located deeper in the crater, to have sustained increased plasma-induced chemical damage. Although plasma exposure incurred minimal chemical damage to polymers,^[20] conjugated molecules may be more sensitive to chemical damage such as through photo degradation caused by the transfer of electrons or by exposure to ultraviolet light from the plasma. This may very well be the reason why the first BCP delta layer on top of the multilayer structure was degraded. Instead of a uniform film, small islands of BCP were seen.

Another possibility for the attenuated intensity of the third delta layer could be the presence of a contaminant overlayer. The use of LTP for material removal was almost always associated with the deposition of nitrogen-containing molecules on the surface, which were seen as NH_4^+ , CH_4N^+ , NO_3^- , and $\text{C}_2\text{H}_8\text{N}^+$ ions using SIMS. The formation of these molecules was most likely triggered by the collision of energetic helium metastables with atmospheric nitrogen and oxygen to create radicals,^[1, 44] which then either combine with each other through dissociative recombination to create NO_2^- and NO_3^- , or with atmospheric contaminants to form molecules such as CH_4N^+ and $\text{C}_2\text{H}_8\text{N}^+$.^[14, 45, 46] These molecules then readily adsorb onto the surface. ToFSIMS analysis of a polymer sample directly exposed to LTP showed similar chemical composition at the surface,^[20] confirming that these nitrogen-containing molecules were a byproduct of plasma interaction with air and not a sample contamination. In Figure 3, the $\text{C}_2\text{H}_8\text{N}^+$ molecule was chosen to represent the distribution of nitrogen-containing fragments that were seen in the crater region (including, but not limited to NH_4^+ , CH_4N^+ , and NO_3^-). However, their intensities were not seen to increase upward along the crater edge.

Depth resolutions obtained from the depth profiles

The depth resolution for depth profiles of the buried delta layers was determined using two different methods. First, the depth resolution was measured by fitting a Gaussian distribution and measuring the full width at half maximum (FWHM) of the intensity peaks,^[47] as modelled by Dowsett.^[48] Second, the depth resolutions were measured by calculating the depth over which the signal of the delta layer fell to $1/e$ of the maximum value, referred to as the $1/e$ decay length and calculated using the following equation,

$$\lambda = \frac{(x_1 - x_2)}{\ln(I_{x_2}/I_{x_1})} \quad (3)$$

where x_1 and x_2 are depths in nm, and I_{x1} and I_{x2} are the secondary ion intensities at those depths.^[49] The 84% - 16% method used in organic ToFSIMS depth profiling to calculate the depth resolution was not used in our experiments as this approach is typically applied to samples having compositional depth variations approximating a step function.

Using the FWHM method, the depth resolutions of the second and third delta layers derived from the C₆₀ depth profile with the re-scaled x -axis averaged 5.6 nm and 7.3 nm, respectively. In comparison, the depth resolutions obtained from the argon cluster depth profile were 6.2 nm and 5.8 nm, respectively, which were comparable to the depth resolutions of 6.9 nm and 6.0 nm obtained from the ion images of the plasma-etched craters, respectively (Table 1). The three techniques suggested a slight difference in thickness between the second and third delta layers, with the C₆₀ depth profile indicating a thicker third layer and the latter two techniques indicating a thinner layer. Because of the large variation in sputter rate for the C₆₀ depth profile, the results from the argon depth profile and the plasma craters seemed to be reflective of the actual film thickness due to the lack of sputter rate artifacts.

One disadvantage of assuming a Gaussian distribution is that it cannot accommodate asymmetrical peaks, such as those seen in the argon cluster depth profile. As can be seen in Figure 4b, the trailing edges of the peaks were wider, probably indicating some sort of SIMS artifact. Therefore, calculating the 1/e decay length may be more appropriate for accurately comparing the depth resolutions. The decay lengths of the delta layers were 3.5 nm and 3.4 nm for argon cluster depth profiling, respectively, and 2.0 nm and 1.8 nm for the plasma-etched craters, respectively. The decay lengths of the peak tails in the C₆₀ depth profiles were 1.7 nm and 2.3 nm, respectively. The smaller decay lengths seen in the C₆₀ depth profiles were attributed to the rescaled x -axis and lack of signal. Therefore, decay lengths calculated from the corrected profiles were not considered reliable and were not used for further comparison.

The asymmetrical delta layer peaks in the argon cluster depth profile did not agree with the shape of the delta layer peaks in the Irganox® multilayers shown by Lee et al.,^[50] where the FWHM of the delta peaks became symmetrically broader with depth. Widening of the symmetrical peaks was most likely due to a gradual decrease in sputter yield, but asymmetrical peaks could be a result from a number of effects. In elemental depth profiling the trailing edge of the delta peak can be extended by collisional mixing due to the energetic analysis beam, but this was unlikely in this case since organic molecules are more prone to fragmentation rather than displacement inside a solid matrix. Another possibility was the BCP layer having a significantly lower sputter yield than Alq3, in which case the trailing of the peaks indicated a slowing of the sputter rate. For a pure film of BCP with a thickness of around 30 nm, the sputter yield was determined to be $19.1 \pm 1.9 \text{ nm}^3/\text{ion}$, roughly half that of the Alq3 film. Argon cluster sputtering has shown remarkable success in sputtering away a wide variety of organic films, but it seems that determining interface widths of complex multilayers can be troublesome if the sputter yields vary significantly.

For the plasma-etched crater, the smaller 1/e decay lengths and the symmetrical delta peaks showed that the technique did not experience artifacts seen in argon cluster depth profiling.

This assumed that the crater edge was linear with a constant slope, estimated from the profilometer trace in Figure 3. The rescaling of distance into depth to create the intensity versus rescaled depth plot in Figure 4d requires an accurate slope measurement, since the calculation of depth resolution is heavily dependent on the peak width of the delta layers. This is important to note since plasma etched craters have shown nonlinear crater edges as a result of the non-uniform etching behavior of the plasma jet. This has led to ion images of buried deltas with various line widths due to changing crater angles (Figure S-1, Supplemental Information). The assumption of a straight crater edge in these cases can greatly distort peak widths, which can lead to incorrect calculation of depth resolutions. The non-uniform etching is thought to be due to variations in plasma density of the filamentary jet during etching.

Conclusions

An organic delta layer system containing films of small molecules that crosslink under ion irradiation were used to evaluate the effectiveness of using a helium low temperature plasma for creating craters for compositional crater edge depth profiling with ToFSIMS. The FWHM of the delta peaks and the 1/e decay lengths of their trailing edges were used to compare the quality of the depth profiles. The FWHM measurements showed that both plasma-etched craters and ToFSIMS cluster depth profiles were in close agreement. However, due to large variations in sputter rate and the need to rescale the axis, the depth resolutions derived from the C₆₀ depth profile were not very reliable. In comparison, the 1/e decay lengths for plasma-etched craters and argon cluster depth profiles revealed that argon cluster depth profiling produced wider trailing edges as a result of SIMS depth profiling artifacts. The lack of this artifact in plasma-etched craters seemed to be an advantageous over ToFSIMS depth profiling, however it came with its own set of problems. This included non-uniform etching by the plasma, the degradation of the first delta layer, and deposition of nitrogen-containing fragments onto the surface.

The non-uniform etching aspect of the plasma is currently being addressed, with a motorized linear stage implemented so the plasma jet can raster the surface to create a beveled crater with a constant bevel angle. This way, a more consistent magnification of the buried structures can be realized. The degradation of the first delta layer can be minimized by the application of an aperture between the LTP and the sample. Restricting the dispersion of the plasma is expected to preserve the chemistry of the film outside of the etching area. Finally, although isobaric interferences between plasma-induced contaminants and analyte peaks were not seen for this system, other systems with nitrogen may suffer from this problem. The deposition of nitrogen-containing fragments may be reduced by igniting the plasma inside a chamber backfilled with a noble gas such as Argon or inside a low vacuum. These problems are currently being addressed, and the results will be reported in future communications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Schematic of the BCP/Alq3 alternating multilayer, and chemical structures of BCP (MW 360.45 g/mol) and Alq3 (MW 459.43).

Figure 2.

Depth profile of the Alq3/BCP delta layer obtained using the (a) C₆₀ sputter source as a function of ion dose. (b) Shows the relationship between sputtered depth versus ion dose for both C₆₀ (○) and argon (○) cluster sources, with the inset showing the same plot in a log-log format. Depth profiles of (c) C₆₀ and (d) argon cluster sources as a function of sputtered depth. Ion yield refers to a normalized secondary ion yield, defined as the number of secondary ions generated per incident primary ion.

Figure 3.

ToFSIMS images of BCP $[M+H]^+$ (top row), Alq3 fragment (middle row), and $C_2H_8N^+$ (bottom row) along the crater edge. Each image is $500 \mu m \times 500 \mu m$, and is positioned to correlate with the crater profilometer trace. In the crater profilometer trace, arrows indicate the position of the buried delta layers, and numbers in circles show the position along the crater edge where the rms roughness measurements were made. The LTP jet impacted the surface from the right-hand side at an angle of 40° with respect to the sample surface.

Images of additional secondary ions can be found in Figures S-2 and S-3, Supplementary Information.

Figure 4.

Plots showing the normalized secondary ion yield intensity versus sputtered depth of the buried delta layers obtained using (a) the C₆₀ source and (b) the argon cluster source. The curves were fit assuming a Gaussian distribution. (c) and (d) are line scans produced from the ToFSIMS image of the crater; (c) shows the intensity versus position, and (d) shows the same intensity plot on a re-scaled axis (depth), calculated using the slope of the crater. The curves were fit assuming a Gaussian distribution. The inset shows the direction of scan, and the region of interest from where the intensity was integrated (73 pixels out of 512 pixels in the y-axis were used for intensity integration) for both (c) and (d) figures.

Table 1

The FWHM depth resolution and 1/e decay lengths of the second and third delta layers for the C₆₀ and argon cluster depth profiles, and from an ion image of a plasma etched crater.

		Depth resolution (nm)		
		LTP	C60	Ar
FWHM	2 nd delta	6.9 ± 0.9	5.6 ± 0.8	6.2 ± 0.3
	3 rd delta	6.0 ± 0.8	7.3 ± 0.9	5.8 ± 0.4
1/e decay length	2 nd delta	2.0 ± 0.5	1.7 ± 0.3	3.5 ± 0.2
	3 rd delta	1.8 ± 0.4	2.3 ± 0.3	3.4 ± 0.3