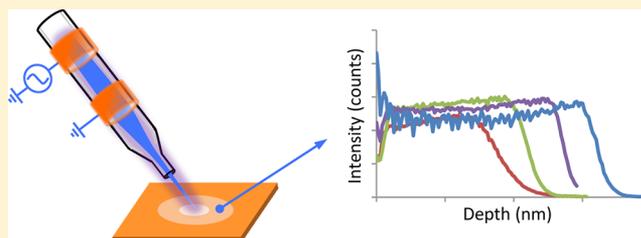


Ambient Low Temperature Plasma Etching of Polymer Films for Secondary Ion Mass Spectrometry Molecular Depth Profiling

Shin Muramoto,* Matthew E. Staymates, Tim M. Brewer, and Greg Gillen

National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

ABSTRACT: The feasibility of a low temperature plasma (LTP) probe as a way to prepare polymer bevel cross sections for secondary ion mass spectrometry (SIMS) applications was investigated. Poly(lactic acid) and poly(methyl methacrylate) films were etched using He LTP, and the resulting crater walls were depth profiled using time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine changes in chemistry over the depth of the film. ToF-SIMS results showed that while exposure to even 1 s of plasma resulted in integration of atmospheric nitrogen and contaminants to the newly exposed surface, the actual chemical modification to the polymer backbone was found to be chemistry-dependent. For PLA, sample modification was confined to the top 15 nm of the PLA surface regardless of plasma exposure dose, while measurable change was not seen for PMMA. The confinement of chemical modification to 15 nm or less of the top surface suggests that LTP can be used as a simple method to prepare cross sections or bevels of polymer thin films for subsequent analysis by surface-sensitive molecular depth profiling techniques such as SIMS, X-ray photoelectron spectroscopy (XPS), and other spatially resolved mass spectrometric techniques.



Low temperature plasma (LTP) probes use a relatively high flow rate (<0.5 L/min) discharge gas to produce a submillimeter diameter visual plasma plume that terminates in a fine point.^{1,2} The surface of the sample is in direct contact with the active part of the plasma, resulting in surface interactions not only with metastable discharge gas atoms (usually helium or argon), but also with energetic ions and radicals. The interaction leads to ionization and physical removal of the sample molecules around the plasma point, resulting in the formation of a beveled crater. The material removal aspect of the technique is particularly intriguing as it opens doors to a fast and easy atmospheric pressure sample preparation tool for removal of contaminants, or removal of overlayers for the preparation of a beveled crater edge. This approach can be a precursor to subsequent analysis by surface-sensitive techniques such as Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectroscopy (XPS) for contaminant-free analysis. In addition, the beveled crater edge can be analyzed using the above-mentioned techniques to resolve buried structures and layers in compositional depth profiling.^{3–5} Bevel crater sectioning using LTP may provide an alternative to other sputter-sectioning methods such as focused ion beams (FIB) and cluster beams.^{6–8}

The high lateral magnification provided by bevel craters gives it the ability to resolve buried features that are below the depth resolution capabilities of conventional sputter depth profiling methods such as cluster SIMS. In sputter depth profiling, the repeated bombardment of energetic ions in the direction of analysis creates unnecessary artifacts such as chemical damage accumulation, mixing effects, and topography generation that contribute to degraded depth resolution.⁹ Bevel production inherently minimizes the creation of such artifacts, making

accurate determination of interface widths possible. Moreover, a single bevel can be analyzed using multiple complementary techniques, the results of which can then be compared with each other without having to worry about the inhomogeneity of the sample.

One caveat with the plasma etching technique, however, is that the interaction of electrons, ions, and radicals may result in chemical modification to the sample. This may convolute the surface analysis data obtained and lead to false conclusions, or it may render the data completely useless. The accumulation of subsurface chemical modification is a problem that needs to be minimized or eliminated for LTP sample preparation to be successful. Molecular depth profiling techniques such as SIMS suffer from this problem, as repeated bombardment of primary ions into the same analysis area eventually leads to bond breaking and atomic mixing, making them unsuitable for depth profiling of thick organic and biological systems.¹⁰

In this article, we investigate the use of LTP probe as a potential sample preparation technique for molecular SIMS applications. This proof of concept study evaluates the performance of sample surface etching in ambient pressure by examining the extent of chemical modification created by the exposure of plasma on two types of thin polymer films. After plasma exposure, the films were depth profiled using time-of-flight secondary ion mass spectrometry (ToF-SIMS) to look at chemical changes along the depth of the polymer film. Specifically, the initial transient region, steady state region, and the interface regions of the depth profiles were compared

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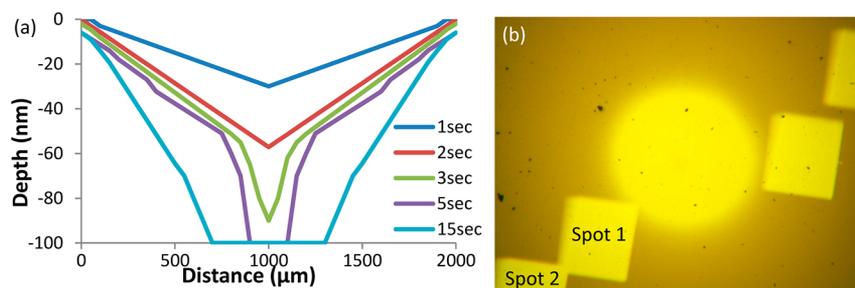


Figure 1. Profilmeter line scan showing the cross-section of a plasma-etched PMMA film (a), and an optical image of the crater from above (b) showing the $500\ \mu\text{m} \times 500\ \mu\text{m}$ ToF-SIMS depth profiled craters along the 15 s etched crater wall.

against those of the control samples to evaluate any changes in chemistry. ToF-SIMS represents an optimal method for assessing chemical modification because it is one of few techniques capable of producing depth profiles with high molecular sensitivity and depth resolution approaching the nanometer level.¹¹

EXPERIMENTAL SECTION

Pellets of isotactic poly(methyl methacrylate) with an average molecular weight of 42 000 Da (Polymer Source, Inc., Montreal, Quebec) and poly(L-lactic acid) with an average molecular weight of 100 000 Da (Polysciences, Inc., Warrington, PA) were dissolved at 20 mg of polymer/g of solvent in toluene and methylene chloride, respectively. (Certain commercial equipment, instruments, or materials are identified in this report 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.) The polymer suspension was then spin-cast at 2000 rpm onto 1 cm \times 1 cm silicon wafers (Silicon Inc., Boise, ID) that had been solvent-cleaned by sequential ultrasonication in methylene chloride, acetone, and methanol.

The LTP probe was made from a glass tube (2 mm inner diameter) that was modified to have a sharp tip with a small opening (roughly $300\ \mu\text{m}$ inner diameter). Two thin copper sheets distanced 3 cm from each other were wrapped around the glass tube to act as outer electrodes, with the wall of the glass tube acting as a dielectric barrier. The upstream copper sheet served as the high voltage (HV) electrode, while the lower stream tape served as ground. An alternating high voltage of 3 kV at a frequency of approximately 2.5 kHz was applied to the HV electrode. The discharge alternating current voltage was provided by a PVM500 plasma driver (Information Unlimited, Amherst, NH). Helium was used as a discharge gas at a flow rate of 500 mL/min. The plasma probe was oriented at an angle of 45° . The polymer samples were placed 1–2 mm away from the tip, and exposed to LTP for durations of 1, 2, 3, 5, and 15 s. Changes in chemistry were investigated using ToF-SIMS in both static analysis and dual-beam depth profiling modes.

ToF-SIMS experiments were performed using an ION-TOF IV (IONTOF GmbH, Münster, Germany) equipped with a 25 kV Bi_n^+ analysis source and a 8 kV SF_5^+ sputter source, both oriented at an incident angle of 45° to the surface normal. Dual-beam depth profiling was performed in the “noninterlaced” mode where analysis and sputtering take place in different ToF cycles. Bi_3^+ in the high-current bunched mode was rastered within a $150\ \mu\text{m} \times 150\ \mu\text{m}$ area, with the sputter beam directed

into a $500\ \mu\text{m} \times 500\ \mu\text{m}$ area. The ion dose densities per cycle were 1×10^{10} ions/cm² for analysis and 1.5×10^{12} ions/cm² for sputtering. The ratio of the analysis beam density to the sputter beam density was kept below 0.01 to ensure minimal chemical damage was being accumulated by the primary analysis beam.¹²

The thickness of the polymer film was measured by scratching the film with a clean razor blade and then using the Asylum MFP-3D AFM (Santa Barbara, CA) to measure the step height. A scan width of $50\ \mu\text{m}$ ensured that the flat part of the film was measured. The ToF-SIMS sputter time was converted to a depth scale by using 50% of the maximum silicon substrate intensity as the film–substrate interface, and assuming constant etch rate throughout the film. For plasma-exposed samples, the depths were calculated assuming a constant sputter rate. A Tencor Alpha-Step 200 (Manassas, VA) was used to obtain a line scan across the plasma-etched crater, and used to create a cross-sectional map.

Multivariate analysis (MVA) was performed using principal component analysis (PCA) provided by a script written in-house for MATLAB (MathWorks, Inc., Natick, MA).^{13,14} A data set containing all peaks between m/z 12 to m/z 300 was used. The peaks in each spectrum were normalized to the sum of total intensity to correct for variations in the total secondary ion yields along each point in the depth profile. The data were mean-centered before processing.

RESULTS AND DISCUSSION

Chemical modification caused by plasma-etching can be evaluated using ToF-SIMS depth profiling, but this requires the sample to be relatively thin ($<500\ \text{nm}$) and be a type II polymer.¹⁵ Thick films tend to show a gradual accumulation of chemical damage from repeated beam-induced bond-breaking and atomic mixing,^{10,16} and type I polymer films cannot be depth profiled because they cross-link under ion irradiation. For these reasons, and despite fast etching rates by LTP (100 nm of PMMA film was completely consumed in tens of seconds), very thin PMMA and PLA films with thicknesses of 100 and 160 nm, respectively, were used. These two systems have been studied extensively in our group for depth profiling applications,^{15–19} and will serve as model systems for establishing the methodology of evaluating chemical damage using ToF-SIMS. As a preliminary study, only the results of these two systems are reported.

A 160 nm PLA film was exposed to LTP for 15 s, after which a $500\ \mu\text{m}$ circular crater bottom was observed with the silicon substrate completely exposed. A crater wall region about $2000\ \mu\text{m}$ in diameter surrounding the crater bottom was readily apparent, indicating a region with residual polymer material. Three spots along this crater wall nearest to farthest from the

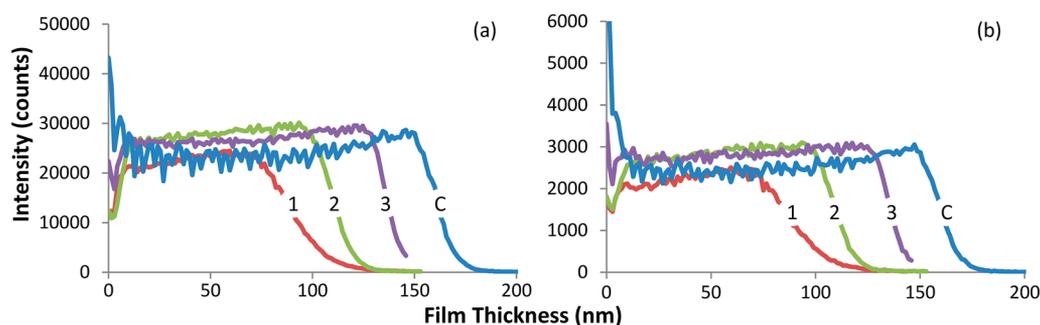


Figure 2. Depth profiles of characteristic PLA fragments (a) $C_3H_3O^+$ (m/z 55) and (b) $C_7H_{11}O_2^+$ (m/z 127). The profiles were obtained at spot (1) closest to the crater bottom, spot (2) 500 μm away, spot (3) another 500 μm away, and (C) control. The intensities were normalized by matching the intensities of the silicon substrate signal.

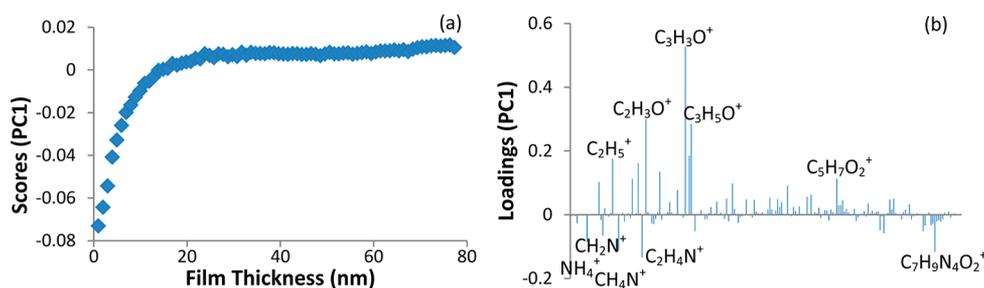


Figure 3. PCA scores plot (a) and loadings plot (b) showing the first principal component which captured 77.2% of the variance.

crater bottom, which represents most to least amount of plasma exposure, respectively, were depth profiled. The cross-section in Figure 1 shows the beveled edge of the crater onto which ToF-SIMS depth profiling was performed (part a), with the location of spots 1 and 2 labeled on the optical image (part b). The nonlinear etch rate presented in Figure 1a is most likely the result of not being able to scan across the center of the etched crater using the profilometer as 1 and 2 s etched craters were difficult to see. The crater wall resulting from the exposure of 15 s of plasma had a bevel angle of roughly 0.007° , and 0.014° for the wall closer to the center of the crater. Thus, SIMS depth profiling on spot 1 with a higher bevel angle would be expected to show a much reduced depth resolution compared to spots 2 and 3. Similar results were reported by Auger electron spectroscopy profiling of beveled craters.^{4,20}

Figure 2 shows the intensities of characteristic PLA fragments (monomer at m/z 55 and dimer at m/z 127) as a function of sputter time for the three spots, including a control for comparison. Films exposed to plasma initially show an increase in intensity which suggests that chemical modification has taken place at the surface, whereas the control shows a decline in intensity typical of polymer depth profiling.^{17,21} The film seems to be affected to a depth of about 10 nm, as the intensities quickly recover to its steady state values of around 25 000 counts and 2500 counts for m/z 55 and m/z 127 fragments, respectively. Near the end of the depth profile, the intensities at spots 2 and 3 fall off very similarly with the control with depth resolutions of roughly 12 ± 2 nm for m/z 55 and 14 ± 2 nm for m/z 127 (defined as the depth interval over which the signal intensity varies from 16% to 84% or vice versa when a sharp interface is crossed),²² a reasonable number given the interface width of 9.3 nm for m/z 55 measured previously for flat PLA films.^{23,24} The degraded depth resolution for spot 1 is most likely due to the uneven crater bottom created by the higher bevel angle. There is a possibility that chemical

modification may be taking place at the film–substrate interface since the plasma can penetrate through the film to the grounded silicon substrate. However, the unaffected depth resolutions for spots 2 and 3 suggest that chemical modification is confined only to about 10 nm of the sample surface. Other characteristic PLA fragments (m/z 56 and m/z 99) showed the same trend (data not shown). No major polymer fragments were seen in the negative ion polarity.

A multivariate analysis method principal component analysis (PCA) was applied to the PLA depth profile data set for spot 2 and presented in Figure 3. The scores plot in part a shows that the topmost surface of the film corresponds with the greatest extent of chemical modification, with successive polymer layers showing a lesser extent of modification until after the first 15 nm of the film, where the chemistry of the polymer seems to be no longer affected by the plasma as indicated by a constant chemical composition. Interpretation of the loading peaks in Figure 3b suggests chemical modification is related to a decrease in intensity of the polymer fragments and an increase in intensities of nitrogen containing fragments. Exposure to plasma seems to break the polymer and liberate monomer and dimer fragments, while incorporating atmospheric nitrogen and contaminants onto the surface. PCA was discontinued after 80 nm of depth profile data because the presence of silicon and its oxides started to convolute the data (matrix effects). The PCA plot of the control sample was also performed, but no conclusive results were obtained since the large signal decay in the initial region of the depth profile overwhelmed any small changes in film chemistry.

It is speculated that the type of chemistry present at the surface will provide some insight into the mechanisms of material deposition and desorption by LTP. The deposition of nitrogen and atmospheric contaminants is presumed to occur after exposure to plasma, where the unstable ions and radicals at the surface trigger the incorporation of contaminants. The

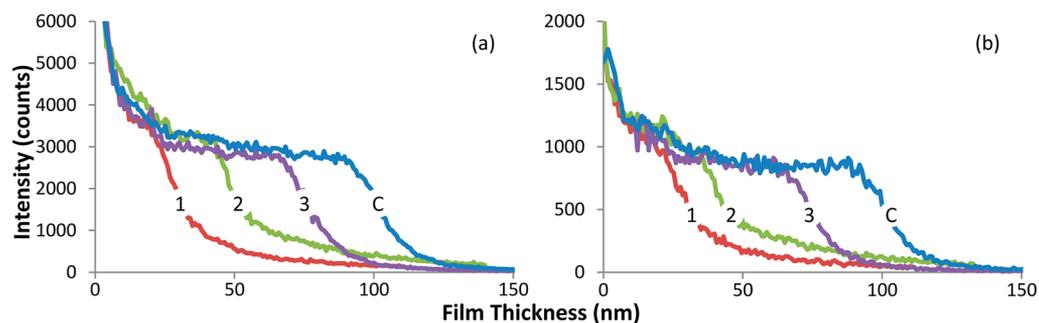


Figure 4. Depth profiles of characteristic PMMA fragments (a) $C_4H_5O^+$ (m/z 59) and (b) $C_6H_{11}O_2^+$ (m/z 115). The profiles were obtained at spot (1) closest to the crater bottom, spot (2) 500 μm away, spot (3) another 500 μm away, and (C) control. The intensities were normalized by matching the intensities of the silicon substrate signal.

desorption of the polymer fragments, on the other hand, may be the result of a two step process. First, metastable helium ions and electrons in the plasma lead to bond breaking of PLA at the ether-oxygen bond of the ester group. This is supported by the loss of intensity of PLA monomers and dimers in both PCA and depth profile results. Then, the momentum of the helium gas is transferred to the neutral and ionized fragments of PLA, leading to desorption. This is supported by the change in the etching rate seen as a function of the flow rate of the discharge gas (data not shown). The exact desorption mechanism in ambient conditions has yet to be elucidated.

Additional insight into the desorption mechanism is suggested by the depth profiles of PMMA (Figure 4). Contrary to the breakdown of polymer chemistry for PLA, the depth profiles of PMMA showed that chemistry was unaffected throughout the depth profile. All spots along the crater wall (spot locations are the same for PLA and PMMA) showed the same signal decay in the transient region as the control. In addition, similar steady-state intensities of around 3000 counts and 1000 counts were observed (m/z 59 and m/z 115, respectively), with depth resolutions of roughly 22 ± 3 nm for both fragments. The literature value for the depth resolution using SF_5^+ primary ion sputtering of flat PMMA films on silicon was 60.7 nm (m/z 59);^{23,24} however, spin-casting conditions, thickness of the substrate oxide, and SIMS sputtering conditions can greatly affect this value. The depth profile of another major PMMA fragment $C_5H_9O^+$ at m/z 85 showed the same trend (data not shown). Contrary to PLA, principal component analysis of the PMMA depth profile data did not show any significant chemical modifications to the polymer backbone.

Regarding contaminants, it was also found that 1 s of plasma exposure was enough to remove a thin film of PDMS present on the PMMA surface, with minimal sample modification to the underlying polymer film other than a small incorporation of atmospheric nitrogen. This suggests that LTP can be used as an easy and effective way to rapidly preclean the sample at atmospheric pressure with minimal modification to the surface chemistry. LTP offers a fast and easy way to prepare bevel craters for compositional depth profiling by surface-sensitive techniques such as AES, XPS, and SIMS, as it can produce a bevel crater with minimal subsurface chemical modification. The low energy and mass of the discharge gas contributes very little to atomic mixing within the sample, and the root-mean-square roughness of the etched polymer pre- and post- (15 s) LTP exposure were both roughly 1.1 nm, suggesting that no significant topography generation occurred for short exposure times.

CONCLUSIONS

This study investigated the feasibility of using an LTP probe to etch polymer films for SIMS molecular depth profiling without chemical modification. ToF-SIMS depth profiles of PMMA films exposed to plasma showed negligible changes in chemistry, while PLA films showed that modification did occur to the top 15 nm of the sample surface. These results show that plasma etching is a viable technique for preparing bevel samples for subsequent analysis by surface sensitive techniques. For the films tested, it became evident that ester groups of PLA are more susceptible to bond breaking than vinyl groups of PMMA, suggesting that chemical modification by LTP is sample-dependent. Also, short exposure to plasma was found to be effective in removing organic contaminants from the sample surface.

Current work in our laboratory is aimed at increasing the number of samples examined, with the goal of trying to elucidate the mechanism of the desorption process. A database of compounds that show successful and unsuccessful results can be used to identify properties that determine the success or the failure of plasma etching for certain samples. Also, an atmospheric pressure quadrupole mass spectrometer has been interfaced with the LTP probe with the intention of using it as a sputter/ionization source for ambient molecular depth profiling, and experiments are underway to create a depth profile of multilayer films. This would allow for measurements of performance characteristics that can then be compared with traditional ultra-high-vacuum depth profiling methods to evaluate the effectiveness of ambient depth profiling. Measurements of performance such as depth resolutions or damage cross sections will aid the development of better designed systems for ambient depth profiling.

AUTHOR INFORMATION

Corresponding Author

*Phone: 1-301-975-5997. Fax: 1-301-417-1321. E-mail: shinichiro.muramoto@nist.gov.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Harper, J. D.; Charipar, N. A.; Mulligan, C. C.; Zhang, X.; Cooks, R. G.; Ouyang, Z. *Anal. Chem.* **2008**, *80* (23), 9097–9104.
- (2) Garcia-Reyes, J. F.; Harper, J. D.; Salazar, G. A.; Charipar, N. A.; Ouyang, Z.; Cooks, R. G. *Anal. Chem.* **2010**, *83* (3), 1084–1092.
- (3) Bishop, H. E.; Greenwood, S. J. *Surf. Interface Anal.* **1990**, *16* (1–12), 70–76.
- (4) Skinner, D. K. *Surf. Interface Anal.* **1989**, *14* (9), 567–571.
- (5) Bisaro, R.; Laurencin, G.; Friederich, A.; Razeghi, M. *Appl. Phys. Lett.* **1982**, *40* (11), 978–980.
- (6) Gillen, G.; Wight, S.; Chi, P.; Fahey, A.; Verkouteren, J.; Windsor, E.; Fenner, D. B. *AIP Conf. Proc.* **2003**, *683* (1), 710–714.
- (7) Mao, D.; Wucher, A.; Winograd, N. *Anal. Chem.* **2009**, *82* (1), 57–60.
- (8) Melngailis, J. *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.—Process., Meas., Phenom.* **1987**, *5* (2), 469–495.
- (9) Green, F. M.; Shard, A. G.; Gilmore, I. S.; Seah, M. P. *Anal. Chem.* **2008**, *81* (1), 75–79.
- (10) Fisher, G. L.; Dickinson, M.; Bryan, S. R.; Moulder, J. *Appl. Surf. Sci.* **2008**, *255* (4), 819–823.
- (11) Wucher, A.; Cheng, J.; Winograd, N. *Anal. Chem.* **2007**, *79* (15), 5529–5539.
- (12) Brison, J.; Muramoto, S.; Castner, D. G. *J. Phys. Chem. C* **2010**, *114* (12), 5565–5573.
- (13) Muramoto, S.; Graham, D. J.; Wagner, M. S.; Lee, T. G.; Moon, D. W.; Castner, D. G. *J. Phys. Chem. C* **2011**, *115* (49), 24247–24255.
- (14) Wagner, M. S.; Castner, D. G. *Langmuir* **2001**, *17* (15), 4649–4660.
- (15) Mahoney, C. M. *Mass Spectrom. Rev.* **2010**, *29* (2), 247–293.
- (16) Mahoney, C. M.; Kushmerick, J. G.; Steffens, K. L. *J. Phys. Chem. C* **2010**, *114* (34), 14510–14519.
- (17) Gillen, G.; Fahey, A.; Wagner, M.; Mahoney, C. *Appl. Surf. Sci.* **2006**, *252* (19), 6537–6541.
- (18) Mahoney, C. M.; Roberson, S. V.; Gillen, G. *Anal. Chem.* **2004**, *76* (11), 3199–3207.
- (19) Mahoney, C. M.; Roberson, S.; Gillen, G. *Appl. Surf. Sci.* **2004**, *231–232* (0), 174–178.
- (20) Procop, M.; Klein, A.; Rechenberg, I.; Krüger, D. *Fresenius' J. Anal. Chem.* **1997**, *358* (1), 358–360.
- (21) Gillen, G.; Roberson, S. *Rapid Commun. Mass Spectrom.* **1998**, *12* (19), 1303–1312.
- (22) ASTM E-42. *Standard Terminology Relating to Surface Analysis E73-91c*; Philadelphia, 1992.
- (23) Mahoney, C. M.; Fahey, A. J.; Gillen, G. *Anal. Chem.* **2007**, *79* (3), 828–836.
- (24) Mahoney, C. M.; Fahey, A. J.; Gillen, G.; Xu, C.; Batteas, J. D. *Appl. Surf. Sci.* **2006**, *252* (19), 6502–6505.