

RESEARCH ARTICLE

Effect of SIMS ionization probability on depth resolution for organic/inorganic interfaces

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Secondary ion mass spectrometry (SIMS) relies on the fact that surface particles ejected from a solid surface are ionized under ion bombardment. By comparing the signal of molecular secondary ions desorbed from an organic film with that of the corresponding sputtered neutral precursor molecules, we investigate the variation of the molecular ionization probability when depth profiling through the film to the substrate interface. As a result, we find notable variations of the ionization probability both at the original surface and in the interface region, leading to a strong distortion of the measured SIMS depth profile. The experiments show that the effect can act in two ways, leading either to an apparent broadening or to an artificial sharpening of the observed film-substrate transition. As a consequence, we conclude that care must be taken when assessing interface location, width, or depth resolution from a molecular SIMS depth profile.

KEYWORDS

depth profiling, femtosecond, guanine, interface, ionization, ionization probability, LPI, organic, post-ionization, SIMS, SNMS, sputtering

1 | INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a powerful tool for chemical imaging due to the submicron spatial resolution and the ability to obtain molecular information with great surface sensitivity.¹⁻³ Molecular imaging of organic compounds has benefitted from increased sensitivity provided by the introduction of new primary ion projectiles such as metal, fullerene, or gas clusters. Moreover, these cluster ion beams allow the erosion of the sample surface without accumulating bombardment-induced chemical damage, which has opened the possibility of molecular sputter depth profiling.^{4,5} These aspects greatly expand the versatility of the technique with respect to 3D imaging applications.

A fundamental problem when characterizing multicomponent materials, however, regards the ionization efficiency of a sputtered molecule, a quantity which is at present largely unknown. Particularly when profiling across interfaces between 2 different components, variations of the chemical composition may be superimposed upon matrix dependent changes of the ionization probability, leading to great uncertainty when trying to quantify the measured SIMS data.^{6,7} It is therefore highly desirable to collect information about possible variations of the ionization probability of a sputtered molecule when profiling through an interface. Unfortunately, experimental data of this kind are scarce. To unravel the ejection and ionization processes of a

sputtered molecule, it is necessary to detect the molecular ion and its neutral precursor under otherwise identical experimental conditions, which requires post-ionization experiments with well characterized ionization efficiency.

A possible strategy to photoionize sputtered molecules without photofragmentation is via strong field photoionization in the near-infrared wavelength range.⁸ This method has been shown to permit the intact ionization of many organic molecules.⁹⁻¹¹ In these experiments, the post-ionization process is decoupled from the emission, so that sputtered neutral molecules are detected with constant efficiency regardless of the momentary surface chemistry.

Comparing the mass resolved signal detected for a molecular secondary ion and its neutral counterpart therefore directly delivers information about the SIMS ionization probability.⁸ We have used this methodology in the past to determine the formation of molecular secondary ions for a few organic molecules sputtered from a homogeneous film.¹²⁻¹⁴ It was found that even when profiling through such a single component material, the ionization probability changes as a function of applied ion fluence due to the chemical surface modification induced by prolonged ion bombardment. Here, we focus on the influence of possible ionization efficiency changes when profiling through an interface between different layers. As exemplary cases, we study the film-substrate interface when depth profiling through a guanine and a trehalose film deposited on a silicon substrate. The

results show that such changes may lead to strong distortions of a SIMS depth profile, a finding which bears significant implications with respect to the assessment of the interface position as well as interface width and depth resolution.

2 | EXPERIMENTAL

The time-of-flight (ToF) SIMS instrument used in these experiments has been described previously.¹⁵ In brief, the instrument consists of a 40 keV C_{60}^+ primary ion source (Ionoptika IOG C60-40, Ionoptika Ltd, Southampton, UK),¹⁶ a temperature controllable sample stage, a reflectron mass spectrometer, and a microchannel plate detector equipped with a high transmission grid above the detector surface, and a calcium fluoride window to introduce a femtosecond laser beam for post-ionization. All experiments were performed with a liquid nitrogen-cooled sample stage, which was held at ground potential during the pulsed ion bombardment. Secondary ions and post-ionized neutral particles are extracted into the ToF mass spectrometer by pulsing the stage to positive potential immediately after the end of the primary ion pulse. A voltage in excess of the extraction potential is applied to the high transmission grid in front of the microchannel plate detector to prevent gain saturation from low mass photoionized fragments by blocking them from reaching the detector. During the acquisition of a ToF spectrum, the grid is pulsed to ground potential to allow only detection of ions above m/z 60. For all experiments, the primary ion pulse width was set to 2000 ns, which was found long enough so that the measured signals did not increase with a further increase of the pulse width, thereby ensuring that the probed number density of sputtered particles is integrated over the entire emission velocity distribution of the sputtered particles.¹⁷

Post-ionization of sputtered neutral particles was performed with a commercially available chirped pulse amplification laser system (Coherent Legend Elite Duo, Santa Clara, California) coupled to an optical parametric amplifier (Light Conversion TOPAS-C-HE, Vilnius, Lithuania), providing 40-fs pulses of 1500-nm radiation at a repetition rate of 1 kHz. The beam is focused with a 150-mm (at 587.6 nm) BK-7 lens positioned outside the analysis chamber to generate a peak intensity of 3×10^{14} W/cm² in the beam waist. The lens is moved in a motor-controlled manner to steer the beam and overlap its waist with the plume of sputtered neutral particles within the sensitive volume of the mass spectrometer.

Guanine films were prepared in situ by low-temperature vapor deposition on 5×5 -mm Si shards (Ted Pella Inc., Redding, California) previously ultrasonicated in hexane, isopropyl alcohol, methanol, and water for 15 minutes per solvent and dried via N_2 stream. The substrates were precooled to the deposition temperature (~ 100 K) at the sample stage, then quickly transferred to a side chamber of the ToF instrument where the guanine films were deposited with the substrate held at low temperature and then transferred to the precooled sample stage for analysis without breaking the vacuum. Depth profiles of guanine were performed with a 20-keV C_{60}^+ primary ion beam operated in alternating analytical and sputter erosion cycles, using fluences of 1×10^{11} ions/cm² and 6×10^{12} ions/cm², respectively. Trehalose films were prepared ex situ by spin-coating a 1M aqueous

solution on the Si shards at ~ 3000 rpm. Depth profiles of trehalose were performed with a 40-keV C_{60}^+ primary ion beam at fluences of 3×10^{10} and 6×10^{12} ions/cm² for the analytical and erosion cycles, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Guanine-silicon interface

The molecule-specific signal of guanine observed in the SIMS spectra is the protonated $[M + H]^+$ molecule at m/z 152. Using laser post-ionization (LPI), one finds the molecular $[M]^+$ ion at m/z 151 which is generated by photoionization of the intact neutral guanine molecule M^0 . The silicon substrate is represented by the Si_4^+ tetramer ion at m/z 112 observed in both the SIMS and the LPI spectra. All 3 signals are plotted as a function of primary ion fluence in Figure 1. The molecular guanine signal shows an exponential decay for both ionized and neutral molecules as the fresh sample surface accumulates ion bombardment induced chemical damage. At a flux of $\sim 2.5 \times 10^{13}$ ions/cm², an equilibrium is reached between the damage created by primary ion bombardment and damage

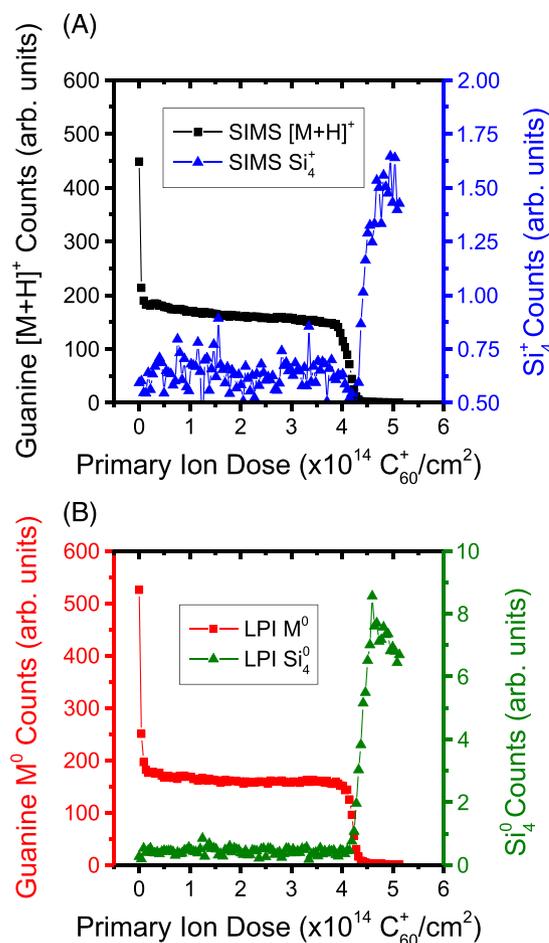


FIGURE 1 A, Secondary ion mass spectrometry (SIMS) and B, laser post-ionization (LPI) signal as a function of primary ion fluence for guanine film deposited on silicon substrate. Both SIMS and LPI signals for guanine are on the left scale and silicon, on the right

removed by the sputtering process, leading to a steady state plateau of the measured signals. The ratio of the LPI signal measured under these conditions to that detected at the beginning of the depth profile provides the cleanup efficiency of the system, or the amount of damage removed per primary ion relative to the total sputter volume, as described elsewhere.¹⁸ For the guanine sample bombarded with 20-keV C_{60}^+ , the cleanup efficiency determined from the LPI depth profile is 0.31, while the same ratio determined from the SIMS depth profile is 0.36. An exponential fit of the initial signal decay performed for the LPI data set produces an altered layer depth of 17 nm and damage cross section of 21 nm^2 , while the same procedure applied to the SIMS data results in values of 12 nm and $\sim 23 \text{ nm}^2$, respectively. After the steady state region, the guanine signal declines while the Si_4^+ cluster ion signal rises, indicating that the interface between the organic film and the silicon substrate has been reached. This transition is shown in Figure 2 for both the LPI and SIMS depth profiles.

To convert the applied ion fluence into eroded depth, the possible variation of the erosion rate across an interface must be accounted for. This is particularly important for an interface between an organic film and an inorganic substrate as investigated here, since it is well known that the sputter yield induced by C_{60} impact onto a molecular film is significantly larger than that of the silicon substrate. The sputter yield volume of the guanine film was determined as $Y_M = 152 \text{ nm}^3$ by eroding a crater into the film and measuring its depth using atomic force microscopy (AFM). The silicon sputter yield under 40-keV C_{60} bombardment,¹⁹ on the other hand, is known to be $Y_{Si} = 2.5 \text{ nm}^3$. It has been argued how the transition between these values should be

handled when eroding across a film-substrate interface. A possible approach to account for the erosion rate variation is by linear interpolation between the values measured for the film and the substrate, respectively, with weighing factors determined from either the molecule or the substrate signals.^{18,20-22} Plots of the interface region using different versions of this nonlinear depth axis calibration are included in the Supporting Information. Here, we revert to the simpler approach by assuming a constant erosion rate until the film is removed, with the latter condition identified as the point where the silicon substrate signal has risen to its maximum value. Note that this oversimplified depth axis calibration will result in inaccurate values for the interface width and underestimation of the actual depth resolution. To improve the depth axis calibration across the interface, the fluence dependent variation of the erosion rate must be determined, for instance by eroding a wedge crater as described in detail elsewhere.²³ The focus of the present work, however, is not set on a quantitative assessment of interface widths and depth resolution but rather to elucidate differences between these quantities as derived from secondary ion and neutral depth profiles, respectively. For that purpose, we feel that the simple linear depth scale calibration as applied here is sufficient and will in the following refer to it as the "apparent depth" scale.

As shown in Figure 2A, the SIMS signals measured for the guanine-silicon interface are plotted as a function of apparent depth. In interpreting the observed signal variation, note that the silicon signal is apparently convoluted with a signal arising from a known fragment of molecular guanine, so that the peak intensity measured at m/z 112 contains contributions from the film as well as the substrate. However, it is reasonable to assume that the guanine fragment signal follows a similar decay at the interface as observed for the molecular ion signal. Its contribution has therefore already fallen to negligible values when the silicon signal starts to rise. The beginning of the plot refers to the steady state region of the depth profile, where the molecular guanine SIMS signal remains constant. The apparent interface width is derived between points with signal levels of 84% and 16%,²⁴⁻²⁶ marked by vertical drop lines in Figure 2, and the location of the interface is identified as the point where the signal level has reached 50% with respect to either the steady-state value for the molecular signal or the signal maximum for the substrate signal. Note that the interface location derived from both plotted signals significantly differs, with the silicon signal rising later than the decay of the molecular signal. This finding indicates the presence of an interlayer between the guanine film and the substrate. A detailed inspection of the mass spectra acquired in this region reveals the occurrence of oxygen containing silicon clusters such as a Si_2O_2 in both the SIMS and the LPI profiles, providing strong indication for a silicon oxide or hydroxide interface layer. The fact that the interlayer is more pronounced than what we usually find is presumably due to the sample preparation technique used here. Since the silicon substrate is precooled at the sample stage, a thin ice layer is formed on its surface before the film is deposited, which becomes buried underneath the deposited film and forms the detected interface layer. In spite of the different interface location, the apparent interface width determined from the guanine and substrate SIMS signals ($\sim 39 \text{ nm}$) is about the same.

As shown in Figure 2B, the LPI signal for the guanine-silicon interface is plotted as a function of apparent depth. The LPI molecule signal

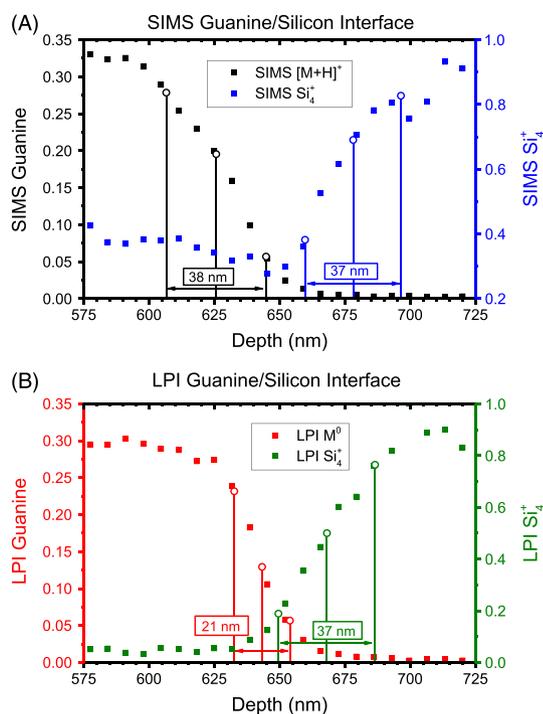


FIGURE 2 A, Molecular secondary ion mass spectrometry (SIMS) $[M + H]^+$ and B, laser post-ionization (LPI) $[M]^0$ signal measured across the guanine-silicon interface as a function of apparent depth. The depth scale has been calculated assuming a constant erosion rate as described in the text. The vertical lines denote the 84%, 50%, and 16% levels of the signal variation observed across the interface

remains at steady-state conditions much longer than the corresponding SIMS signal, ie, until ~ 625 nm as opposed to that of ~ 600 nm for the SIMS signal. The signal then declines sharply, reaching 84% and 16% levels at 633 and 654 nm, respectively, resulting in an apparent interface width of 21 nm. The LPI signal for the silicon tetramer begins to increase around 630 nm, reaches 16% and 84% of its maximum at 650 and 687 nm, respectively, producing an apparent interface width of 37 nm. While this value is similar to that determined from the SIMS profiles, the interface deduced from the LPI guanine signal is significantly sharper.

The difference between the information obtained from corresponding LPI and SIMS depth profiles must be attributed to the change in ionization probability of the sputtered particles when going through the interface. To elucidate the magnitude of this variation, the SIMS/LPI signal ratio for sputtered intact guanine molecules is presented as a function of apparent depth in Figure 3. In addition, the apparent interface position as evaluated from the SIMS and the LPI depth profile is included for reference. It is obvious that the protonation efficiency forming the $[M + H]^+$ secondary ion begins to decline at an apparent depth of ~ 605 nm. The fact that the LPI signal is constant indicates that the sputter yield does not change, unless the changes were coincidentally counterbalanced by a change in the emission velocity and angle distributions of the sputtered molecules. We feel that the latter is highly unlikely and, hence, assume that the erosion rate does not significantly change in that region. This means that the ionization probability is starting to become influenced already about 30 nm before the actual interface is reached, leading to an apparently poorer depth resolution in the SIMS profile. As a consequence, the apparent interface locations determined from the SIMS and LPI depth profiles differ by 18 nm, with the SIMS profile obviously indicating the interface too early. Overall, the ionization efficiency of the sputtered guanine molecules is reduced about threefold upon going through the film-substrate interface. On the other hand, we find the ionization probability of sputtered silicon clusters representing the substrate material (data not shown) to remain constant throughout the interface.

At this point, we can only speculate about the reason for the changes of the ionization efficiency when going through the interface. In principle, the velocity-integrated ionization probability measured

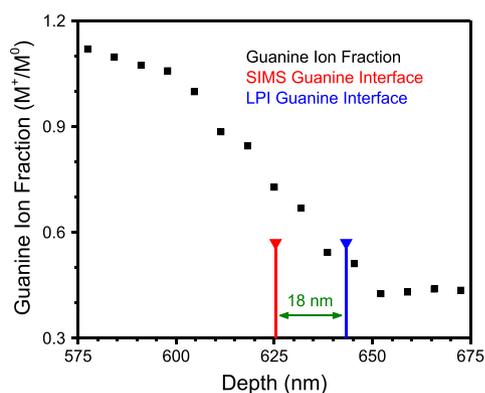


FIGURE 3 Ratio of secondary ion mass spectrometry (SIMS) $[M + H]^+$ signal to laser post-ionization (LPI) M^0 signal for molecular guanine as a function of depth. The vertical drop lines indicate the interface position as derived from the 50% points as described in the text

here can be influenced by variations of the emission velocity distribution.¹² While this dependence has been discussed (and debated) mainly for inorganic materials and ejectees,^{27,28} we feel that it is an unlikely cause for changes in the chemical ionization mechanism responsible for the formation of the quasi-molecular ions studied here. We therefore believe that the effects observed here are due to a change in the chemistry at the interface.

3.2 | Trehalose-silicon interface

In the preceding section, an example was presented where suppression of the ionization efficiency when reaching the interface lead to an apparent broadening of the film-substrate interface width observed with SIMS. However, reaching a chemical interface is also capable of enhancing the ionization probability, as shown here for the case of a trehalose-silicon interface. The structure of trehalose and a characteristic fragment detected in the mass spectra are shown in Figure 4. To obtain a true steady state region, the depth profile must be run at low temperature, as described in the experimental section. Since the trehalose samples were prepared ex situ and had to be cooled after introduction into the vacuum system, a thin layer of adsorbed water ice is created on the sample surface. This ice layer must be removed at the beginning of the depth profile, thereby masking the initial variation of the signals as the steady state is approached. For this reason, the cleanup efficiency cannot be determined from the depth profiles measured here but has been reported for this system many times before.^{18,20}

In both the SIMS and LPI spectra recorded on trehalose, the molecular ion signals at m/z 343 ($[M + H]^+$, SIMS) and 342 (M^0 , LPI) observed under C_{60} bombardment are usually very small. However, a molecule specific fragment at m/z 325 is readily detectable in both spectra, which corresponds to the parent trehalose molecule having lost an OH group. In the following, we therefore investigate the ionization probability of this characteristic molecular fragment. The SIMS and LPI signals obtained at m/z 325 are shown in Figure 5 as a function of apparent depth along with the signals detected for other characteristic fragments at m/z 179, 145, and 131, respectively. The signals representing the silicon substrate are not shown, as they exhibit the same behavior as observed for the guanine/silicon interface. The average interface position as evaluated from the decay of the molecular signal was located at apparent depths of 328 nm for the SIMS and 325 nm for the LPI depth profiles, while the average value of the apparent interface width was 20 nm for the SIMS and 48 nm for the LPI depth profiles.

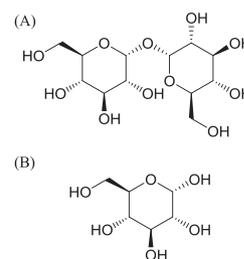


FIGURE 4 A, Structure of the trehalose molecule and B, characteristic fragment F

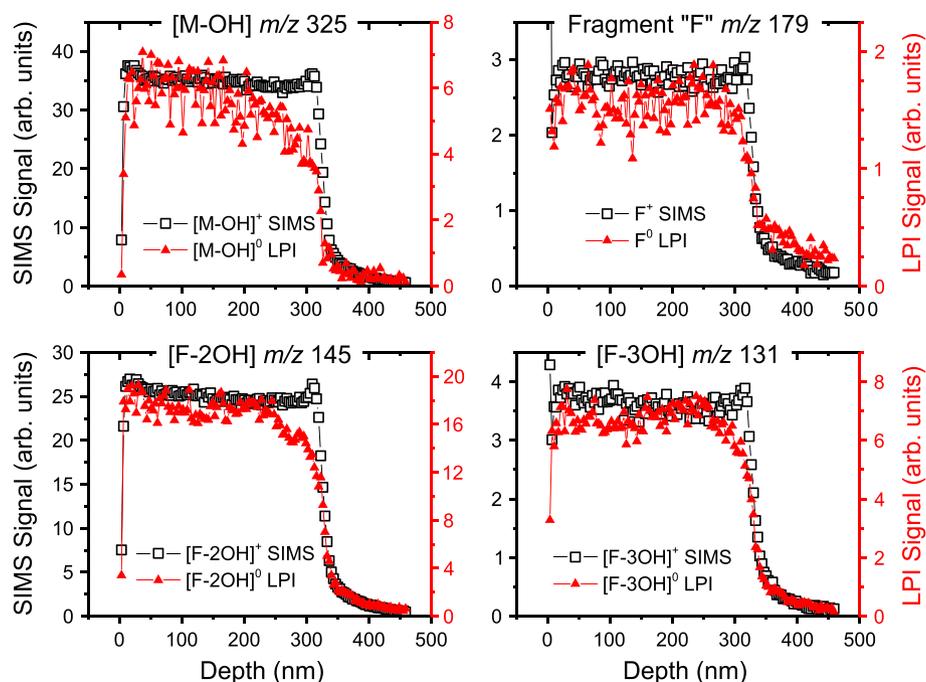


FIGURE 5 Secondary ion mass spectrometry (SIMS) and laser post-ionization (LPI) depth profiles of characteristic fragments of trehalose. The depth scale has been calculated assuming a constant erosion rate and may therefore be inaccurate beyond the film-substrate interface

In this case, the LPI signal in each instance shows a characteristic decline in the signal when approaching the film-substrate interface, while the SIMS signal shows a prolonged steady state with even a slight increase before declining at the interface. From the SIMS/LPI signal ratio plotted in Figure 6, it is obvious that the effective ionization probability of a sputtered trehalose molecule must increase at the interface, with the magnitude of the effect being of the order of a factor 2. About the reason for this increase we can only speculate.

Scrutiny of the mass spectra acquired at different cycles in the depth profile reveals a number of peaks that exhibit pronounced intensity maxima within the interface region. The intensity variation of these peaks is illustrated in Figure 7, which shows a section of the recorded LPI spectra as a function of the depth profile cycle number. It is seen that the signals recorded at m/z 62 and 63 clearly represent the trehalose film. The signal at m/z 68 contains 2 components, one representing an organic fragment of the trehalose film and the other one—detected at slightly lower mass—representing the inorganic Si_2C

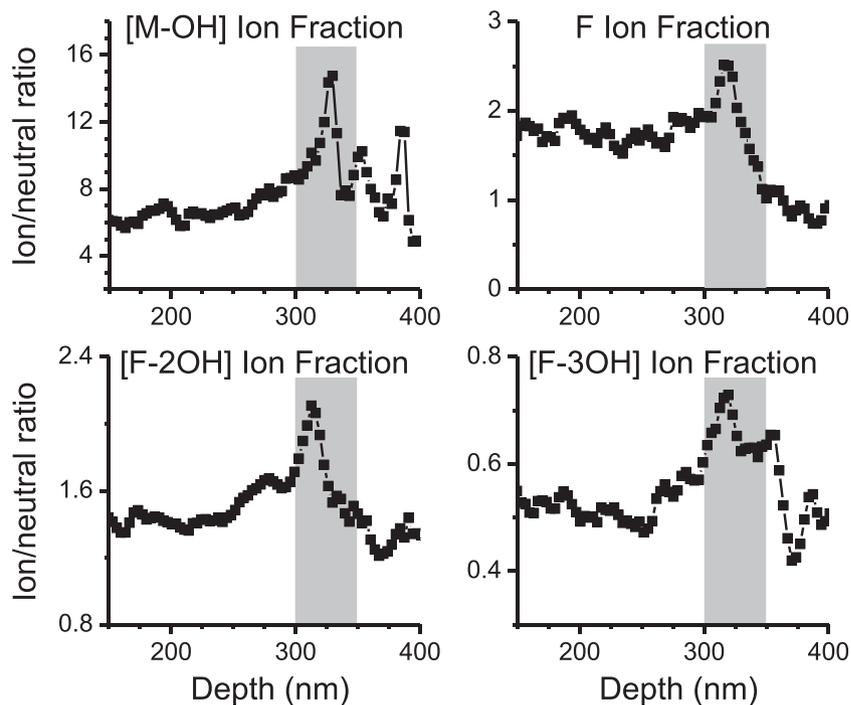


FIGURE 6 Ionization probability of different molecule specific fragment ions of trehalose as function of apparent depth. The grey depths show the average laser post-ionization interface width

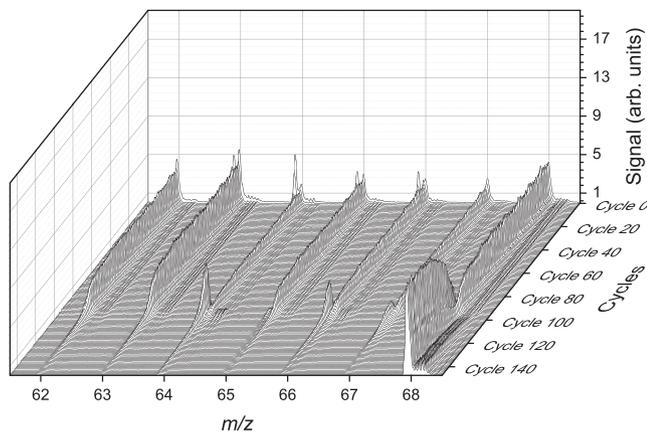


FIGURE 7 Section of laser post-ionization mass spectra recorded as a function of depth profile cycle number. The interface between the trehalose film and the silicon substrate is located around cycle #100

cluster arising from the silicon substrate. The signals recorded at m/z 64 to 67 also show this organic-inorganic mass transition, albeit with a maximum of the inorganic component at the interface. The interface maximum of the m/z 67 signal is observed in the SIMS spectrum as well, as shown in the Supporting Information. Similar interface maxima are also observed at various other masses, all representing inorganic components such as Na as well as a number of $\text{Si}_x\text{O}_y\text{H}_z$ clusters. The occurrence of these signals clearly indicates a modified surface chemistry when profiling through the interface, which may be due to accrued collision-induced damage or a change in the pre-existing chemistry at the interface. This modified chemistry then acts to enhance the formation probability of the $[\text{M-OH}]^+$ ion. In contrast to the guanine molecules, the trehalose fragments experience an enhancement in ionization probability at the film-substrate interface, which, superimposed with the simultaneous reduction of the trehalose surface concentration, results in an apparently sharpened interface width.

4 | CONCLUSIONS

The results presented here indicate that care must be taken when assessing interface widths and depth resolution from molecular SIMS depth profiles. We show 2 exemplary cases where the ionization probability of molecules sputtered from an organic film deposited on an inorganic substrate is found to change notably while profiling through the film-substrate interface. The observed changes reflect a modified surface chemistry when approaching the interface. These changes may in part be induced by a change of the energetics within the collision cascade due to energy reflection at the hard inorganic substrate or by the presence of interface layers between film and substrate. In any case, it is evident that the ionization probability is not only dependent upon the chemical identity of the sputtered molecule but also is affected by the changing chemical environment when profiling through an interface.

It is shown that the effect may act in two ways. If the ionization probability of a molecule representing a particular sample component varies in the same way as its surface concentration, the interface

observed in the SIMS depth profile appears to be broadened, as demonstrated here for a guanine film deposited on silicon. If, on the other hand, the ionization probability exhibits the opposite trend, i.e., increases with decreasing surface concentration (or vice versa), the interface observed in the SIMS depth profile may appear artificially sharpened or even exhibit apparent interface maxima, as exemplified here for the case of a trehalose film deposited on silicon. In both cases, the measured interface location and width are found to significantly deviate from the more realistic values evaluated from an LPI depth profile.

For the guanine system investigated here, we show that the SIMS ionization probability of sputtered intact guanine molecules already becomes influenced at a distance of 30 nm before the actual interface is reached. It is interesting to note that this value is of the same order as the altered layer thickness, albeit by about a factor 2 larger, indicating that chemical modifications induced by an upcoming interface may in principle range even farther than the bombardment induced chemical damage accrued while eroding through a homogenous film. In future experiments, it will be interesting to see if this is a characteristic of the organic-inorganic interfaces studied here or applies for interfaces between different organic layers as well. In the latter case, one would expect significant ion bombardment induced interface mixing to occur, which may then lead to even stronger distortions of a SIMS depth profile in addition to the matrix effects studied here. In any case, it is clear that understanding the complex interplay between ion-induced modification of the surface chemistry and its influence on the ionization probability of a sputtered molecule is paramount to understanding the complexities of SIMS depth profiling through chemical interfaces.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SUPPORTING INFORMATION

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