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Strong-field Photoionization of Sputtered Neutral Molecules for Molecular Depth Profiling

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Abstract

Molecular depth profiles of an organic thin film of guanine vapor deposited onto a Ag substrate are obtained using a 40 keV C₆₀ cluster ion beam in conjunction with time-of-flight secondary ion mass spectrometric (ToF-SIMS) detection. Strong-field, femtosecond photoionization of intact guanine molecules is used to probe the neutral component of the profile for direct comparison with the secondary ion component. The ability to simultaneously acquire secondary ions and photoionized neutral molecules reveals new fundamental information about the factors that influence the properties of the depth profile. Results show that there is an increased ionization probability for protonated molecular ions within the first 10 nm due to the generation of free protons within the sample. Moreover, there is a 50% increase in fragment ion signal relative to steady state values 25 nm before reaching the guanine/Ag interface as a result of interfacial chemical damage accumulation. An altered layer thickness of 20 nm is observed as a consequence of ion beam induced chemical mixing. In general, we show that the neutral component of a molecular depth profile using the strong-field photoionization technique can be used to elucidate the effects of variations in ionization probability on the yield of molecular ions as well as to aid in obtaining accurate information about depth dependent chemical composition that cannot be extracted from TOF-SIMS data alone.

Keywords

ToF-SIMS; C₆₀ ion beam; Depth scale calibration; Enhanced ionization probability

1 Introduction

Bombardment of molecular solids with energetic cluster ion beams has been shown to result in erosion of the sample on the nanometer scale while preserving much of the chemical composition information.^{1–10} By combining molecular depth profiling with imaging secondary ion mass spectrometry (SIMS), it now appears feasible to acquire 3-dimensional information from a wide range of materials, including single biological cells.^{1,11–13} Efforts are also aimed toward developing a theory to explain the physics behind molecular depth profiling and to predict whether a successful analysis can be achieved for any specified material.^{9,13,14} Issues such as depth resolution, topography formation, chemical damage accumulation and ionization probability are all of interest in maximizing the information content of this phenomenon.

Depth profiles are typically obtained by monitoring the intensity of various secondary ions desorbed from the sample as a function of the primary ion fluence. The resulting signal is a convolution of the yield of neutral molecules and their ionization probability. Changes of the ionization probability within the matrix can be large, and are known to make quantitative analysis problematic.¹⁵ To avoid this complication, our laboratory has utilized laser photoionization of the sputtered neutral molecules to reduce the influence of matrix ionization effects by decoupling the ionization event from the desorption process.^{16,17} In this configuration, the laser light is directed parallel to and ~500 μm above the sample to efficiently intercept the plume of desorbing molecules. Early experiments, however, were restricted to particularly rigid molecules such as polycyclic aromatic hydrocarbons.^{18–20} The sputtered molecules contain a wide range of internal energies that results in significant photon-induced fragmentation, degrading the quality of the data.^{21–23}

More recently, nearly fragment-free photoionization of sputtered molecules has been demonstrated using high-field, mid-infrared, femtosecond-pulsed laser light as an ionization source.²⁴ The degree of photon-induced fragmentation was observed to remain low for a variety of molecules even when produced by sputtering with a C_{60} cluster ion beam. With this new approach, then, it is possible to monitor the desorbed neutral species during a molecular depth profile, providing a more direct route for elucidation of the important physics associated with interactions of the cluster ion with the sample.

For an idealized depth profile of a uniform molecular thin film, the intensity of the molecular ion should remain constant with fluence from the initial bombardment event until an interface is reached. This behavior would indicate that the primary ion beam leaves no chemical damage to accumulate during erosion. Typically, however, molecular depth profiles are characterized by three regions.^{3,8,9} The first region involves a surface fluctuation followed by a near exponential drop in signal intensity. The second region is characterized by a steady state signal as equilibrium is reached between chemical damage accumulation and removal. For a select population of molecules, there is a continuous decay of signal intensity throughout the depth profile as damage accumulation continues to occur. The third region may be described as the interfacial region and often exhibits strong matrix ionization effects. In many cases, there is beam-induced chemical mixing that has the effect of decreasing the depth resolution of the experiment.^{12,25–30}

Fluctuations in the near surface region of molecular depth profiles have been observed and studied almost from the genesis of cluster ion beam sources. Presently, the cause of these fluctuations is under debate. The most probable explanation is that they originate from a combination of removal of surface impurities, chemical damage buildup, and a change in the ionization probability arising from a change in the character of the chemical matrix. The change in ionization probability has been hypothesized to arise from a buildup of protons in an altered layer near the surface that are produced by fragmentation of hydrogen-containing organic molecules.³¹ Experiments performed on water-ice samples, for example, showed that the m/z 19/18 ratio increased as the fluence of C_{60} primary ions increased.^{32,33} Moreover, for molecules doped into the ice layer, changes in the protonated molecular ion signal paralleled changes in the 19/18 ratio, indicating a connection between proton accumulation and ionization probability.

In this work, we aim to unravel the complexities of molecular depth profiling by directly measuring the yield of neutral molecules in conjunction with the corresponding yield of protonated molecular ions. A thin film of the nucleotide base guanine is vapor-deposited onto a Ag substrate as a model system since it exhibits a strong protonated molecular ion signal, $[\text{M} + \text{H}]^+$, and an equally intense molecular ion signal, M^+ , in the photoionization spectrum. By measuring these quantities as a function of incident projectile ion fluence, one can deduce the

effect of bombardment-induced chemical damage on the ion formation process, which is otherwise not accessible from the detection of secondary ions alone. The results show that the guanine ionization probability increases during the first 10 nm of erosion, and drops to nearly zero at the film/Ag interface, an observation consistent with the proton implantation model discussed above. The value 10 nm is obtained for the near surface region and does not describe the mixing that occurs at the interface between the film and the substrate. Strong fluctuations of the substrate ionization probability are also observed at the film/Ag interface, and are attributed to implantation of atomic carbon and oxygen atoms into the substrate. It is possible that the substrate atoms mix more extensively into the organic layer than the carbon and oxygen atoms penetrate into the silver layer. However, either process can lead to the observed increase in secondary Ag ions at the film/Ag interface. These effects lead to a discrepancy between the erosion rate determined for the secondary ions and the secondary neutral molecules. This observation has important implications in the rendering of 3-dimensional mass spectral images. Finally, we report on the behavior of neutral fragment ions observed in the laser photoionization mass spectra in order to provide direct information about the mechanism associated with chemical damage accumulation. In general, these experiments promise to improve our fundamental understanding of molecular depth profiling with cluster ion beams and to expand the applications of this powerful analytical tool.

2 Experimental Section

2.1 Materials and Film Preparation

Guanine was purchased from Sigma-Aldrich and was used without further purification. A pre-cut 5 mm × 5 mm Si wafer was supplied by Ted Pella Inc. (Redding, CA). This wafer was subsequently coated with approximately 150 nm of silver by vapor deposition. Guanine molecules were then vapor deposited onto the silver coated silicon shards resulting in a thin film of amorphous guanine. Thicknesses, as determined by the atomic force microscope (AFM), typically ranged from 100 nm to 200 nm. A simple masking lithography technique was applied to these films leaving approximately 5% of the silver coated shard bare on each end. The samples were then mounted to a copper sample block using copper tape. Silver paste was used to maintain electrical continuity between the copper block and the silver substrate layer. This sample preparation method has been shown to significantly reduce the charging effects often observed when depth profiling of an amorphous molecular film.³⁴ Characterization of this film is presented below.

2.2 Instrumentation

Details of the ToF-MS instrumentation used for these experiments has been described in detail elsewhere,²³ but will be briefly discussed here. Molecular thin films were analyzed in a ToF-MS equipped with a 40 keV C_{60}^+ ion source (Ionoptika, Ltd.). The C_{60} ion source generates a 50 pA beam measured in direct current mode and was focused to a spot size 5 μ m in diameter. The primary ion pulse was set to a value of 2 μ s ensuring a broad emission velocity interval to be sampled for the desorbed molecules.

The strong-field photoionization source utilized an optical parametric amplifier (OPA) to pump a femtosecond laser. This system consisted of a Ti:Sapphire oscillator (Clark-MXR, Inc.) pumped by a Verdi V5 diode-pumped laser (Coherent, Inc). The final output at 1450 nm consisted of 125 fs pulses at 400 μ J incident at a 1 kHz repetition rate. The laser beam was introduced into the mass spectrometer through a calcium fluoride (CaF_2) window transparent to mid-infrared wavelengths. The laser beam was focused to a diameter of $\sim$ 250 μ m and guided parallel to the surface at a distance of $\sim$ 500 μ m. Additional details concerning the laser apparatus have been reported elsewhere.²⁴

The secondary ion extraction was switched on shortly (~ 20 ns) after the end of the projectile ion pulse. The laser pulse was fired with a 400 ns delay with respect to the ion extraction pulse. This extraction setup leads to a flight time separation of secondary ions and photoionized neutral molecules, since the flight time zero for secondary ions is determined by the extraction pulse, while that of the photoionized neutral molecules is determined by the laser firing time. Although this detection scheme adds complexity to the measured spectra, it is appropriate for the present work since it allows a direct comparison of secondary ion and neutral signals acquired in the same ToF spectrum.

The depth profiling experiments were performed by alternating between sputter erosion and data acquisition cycles. Erosion was performed by digitally rastering the C_{60} beam in direct current mode over an area of $290\text{ }\mu\text{m}$ by $368\text{ }\mu\text{m}$ lateral area for 30 second intervals. A crater depth of 200 nm could be achieved with 40 sputtering cycles, applying a total fluence of 3×10^{14} ions- cm^{-2} . The overall sputter area that can be measured using the photoionizing laser is limited by the laser focal point. At $250\text{ }\mu\text{m}^2$, no spatial effects are observed from the laser profile. During data acquisition, ToF mass spectra were obtained using the C_{60} ion beam in pulsed mode, accumulating a total fluence of 4.4×10^{11} ions- cm^{-2} (summed over all data acquisition cycles) within a field-of-view of approximately $145\text{ }\mu\text{m} \times 184\text{ }\mu\text{m}$ centered in the crater bottom. The AFM field-of-view of $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$ was used to analyze the full area of the sputter crater. The total fluence accumulated over all acquisition cycles is included in the overall total fluence of 3×10^{14} ions- cm^{-2} . No evidence is seen for secondary crater formation as a result of the ion fluence accrued during the data acquisition cycles.

Prior to the depth profile, AFM measurements (Nanopix 2100, TLA Tencor, Inc.) were taken from the guanine thin film revealing a 2 nm root mean squared (RMS) roughness. Similarly, measurements from within the crater after the completion of the depth profiling experiment showed a slight roughening of the sample with a RMS roughness of 2.5 nm. The thickness of the guanine film was determined by AFM using the exposed edge of the Si shard as a reference point. An AFM calibration standard was employed to insure proper cantilever and tip response. The total erosion depth was also determined by AFM in order to determine the amount of Ag removed after the guanine/Ag interface was reached. For the example given here, the guanine film thickness was measured to be 164 nm, and the total crater depth was measured to be 200 nm, indicating removal of 36 nm of Ag.

3 Results and Discussion

The primary goal of this work is to obtain a depth profile of an organic thin film utilizing not only secondary ions, but also the neutral component of the sputtered flux. As shown below, the comparison of these depth profiles yields useful information about the nature of chemical damage accumulation and provides a fundamental understanding of ionization effects occurring primarily at the surface and interface regions.

The SIMS spectrum and the laser IR-photoionization spectrum of the model guanine thin film target taken with 40 keV C_{60}^+ bombardment are shown in Figure 1. The separate ion and neutral components are obtained by acquiring spectra using three different scenarios. First, data is acquired with both the laser and the ion beam operational. Separate spectra are then obtained by blanking the laser to reveal the SIMS-related features, and by blanking the ion beam to reveal any possible laser-induced background signal. A MATLAB script was employed to extract the individual results by creating a matrix for the laser and ion beam, laser only, and ion beam only operational modes. The laser only and ion beam only matrices are then subtracted from the laser and ion beam matrix yielding a mass spectrum free of gas phase photoionized neutral species and secondary ions. The ion beam only mass spectrum is left unmodified and represents the SIMS signals shown in Figure 1a. Note that both mass spectra appear to be free

of any peaks associated with surface contaminants. The intensity of the molecular ion peaks for the SIMS and laser IR-photoionization spectra are dependent upon a variety of experimental factors including, but not limited to laser wavelength, power density and the ion extraction field. Hence it is not possible to determine the ionization probability by directly comparing the intensity in the ion and the neutral channel.

The neutral and ion components of a molecular depth profile of the model guanine thin film are shown in Figure 2a and 2b. These two profiles are obtained simultaneously from the same surface location. The two profiles exhibit significantly different variations in signal intensity for the intact molecular signals at the surface and for the Ag signals at the interface between the organic thin film and the substrate. These differences are quantified as shown in Figure 2c and 2d by plotting the intensity ratio of secondary ions to photoionized neutral species as a function of depth. As outlined above, this quantity is a measure of the change in ionization probability as a function of projectile ion fluence or eroded depth. Note that the ionization probability of desorbed guanine molecules increases by roughly a factor of two during removal of the first few nanometers. On the other hand, the ionization probability of sputtered Ag substrate atoms shown in Figure 2d is found to exhibit a pronounced maximum while traversing through the film-substrate interface. From these observations, we can begin to evaluate and understand changes in ionization efficiency due to changes in the chemical environment throughout the depth profile.

3.1 Surface Matrix Effects

Fluctuations occurring at the original surface, at the beginning of the profile, evolve and are quenched rapidly, resulting in the formation of a steady state after removal of the first 25 nm. In order to probe these effects more accurately, a near surface profile was obtained with smaller erosion steps. A plot of this profile is depicted in Figure 3a, showing the removal of the first 40 nm of the guanine thin film. From this plot it is clear that the protonated molecular secondary ion signal increases at the start of the ion bombardment, eventually peaking at an ion fluence which corresponds to an eroded depth of ~3 nm. The current hypothesis is that the increase in the formation probability of $[M+H]^+$ is attributed to an accumulation of free protons in the near surface region as a consequence of the ion bombardment.

The ion beam induced chemical damage to the guanine molecules, on the other hand, is illustrated by an exponential decay of the neutral, non-protonated molecule signal to about 50% of its initial intensity. In principle, such a decay of the molecular signal into a steady state value is predicted by a simple erosion dynamics model of molecular depth profiling. As can be seen in Figure 3a, the decay is also observed for the guanine secondary ion although the decay is perturbed by the surface ionization changes.

The data presented in Figure 3a provide a critical insight not only into the qualitative behavior of these two competing phenomena, but also provide a quantitative picture of where these variations take place in depth. For example, it is clear from Figure 3a that accumulation of chemical damage continues past the region of proton-enhanced ionization. In fact, the characteristic length scale observed for the decay is 4.5 nm, about twice that observed for the rise which occurs over 2.4 nm as shown in Figure 3b. While the ionization probability is constant after removal of the first 10 nm, a steady state for chemical degradation appears to be reached only after profiling through 25 nm of the guanine film. It is apparent that the neutral component profile is indicative of chemical damage only, while the secondary ion data constitute a convolution of ionization and damage accumulation effects. Moreover, the data indicate that our previous approach to assess chemical damage accumulation from the exponential decay of the secondary ion signal after its maximum appears to be essentially correct.⁹

If the hypothesis about proton enhanced ionization is correct, other protonated secondary ion signals should follow the same trend. Several examples are shown in Figure 4b where the depth profiles are similar, but not identical to, the $[M+H]^+$ ion shown in Figure 4a. Note that only those fragments containing the initial proton accepting site of the guanine molecule should exhibit this behavior. Guanine has two basic sites capable of accepting a proton, although the N-7 site is by far the most basic site under normal pH conditions.³⁵ The three prominent fragments shown in Figure 4b are m/z 125, assigned to $[M+H-HCN]^+$, m/z 97, assigned to $[M+H-HNCOC]^+$ and m/z 28, $[HCN+H]^+$. Each of the fragments are created from $[M+H]^+$. Interestingly enough, there appears to be a dependence of m/z on the amount of observed chemical damage accumulation. Therefore, the occurrence of lower mass species is indicative of increased chemical damage accumulation, whereas the occurrence of higher mass fragments indicates a lesser degree of chemical damage.

3.2 Erosion Dynamics

It is possible to gain semi-quantitative information about the expected behavior of these fragment species by extending the erosion dynamics model for depth profiling that has been extensively developed over the last several years.¹⁴ Parameters such as the molecular sputtering yield, the damage cross-section of the molecule, and the thickness of a surface layer altered by the projectile are included in the model. In addition, the erosion dynamics are intimately linked to the transfer of energy from the primary ion to the surface molecules and thus have a substantial effect on the energy landscape of the ejected molecules. The energetic stability of the ejected molecules is probed in the following discussion on photofragmentation and thus related to the erosion dynamics model.

The model can be extended to examine the behavior of fragment ions during depth profiling. By following a similar procedure as reported earlier, the variation of the concentration c_f of a fragment within the altered layer formed beneath an ion bombarded surface as a function of ion fluence f should vary as:

$$\frac{dc_f}{df} = (\sigma_p \cdot c_p - \sigma_f \cdot c_f) \cdot f \quad (1)$$

where c_p denotes the concentration of the parent molecule, or larger fragment, from which, the fragment is derived, σ_p denotes the corresponding fragment production cross-section and σ_f is the cross-section for further fragmentation. This equation is easily solved to yield:

$$c_f(f) = \sigma_p \cdot \int_0^f c_p(f') \exp(\sigma_f f') df' \quad (2)$$

The fluence dependence of the corresponding fragment signal, which is assumed to be proportional to c_f , is then determined by the fragmentation cross-section σ_f along with the fluence dependent parent concentration c_p . In a fragmentation chain, this leads to a system of coupled differential equations, which must be solved from top to bottom, starting at the largest fragment with the original molecule as its parent. Assuming, for simplicity, that a fragment directly derives from the parent molecule decaying with a disappearance cross-section σ , this leads to an expected signal variation according to:

$$S(f) \propto [1 - \exp(-(\sigma - \sigma_f)f)] \cdot \exp(-\sigma_f f) \quad (3)$$

which is predicted to go through a maximum at an ion fluence of:

$$f_{max} = \frac{1}{\sigma - \sigma_f} \ln \frac{\sigma}{\sigma_f} \quad (4)$$

The predictions of Equation (3) and Equation (4) can be used to assess limiting cases. If further fragmentation is slow compared to the disappearance of the parent molecule, representative of the primary fragmentation channel indicative of dissociation directly from the parent molecule, a complementary behavior of fragment and parent is expected, with the fragment signal rising in correspondence with the parent decay, reaching a steady state that is synchronized with the parent ion. This behavior is illustrated for the m/z 125 fragment ion as shown in Figure 4b. In fact, a cross-section ratio of $\sigma/\sigma_f \approx 55$ is estimated from the maximum ion intensity observed after erosion of ~ 20 nm of the guanine film. If, on the other hand, further fragmentation occurs faster than production, representative of the secondary fragment channel indicative of dissociation from a previously dissociated molecular fragment, the fragment signal will exhibit a fast rise and then essentially track the parent signal. This behavior is illustrated for the fragment ions at m/z 97 and m/z 28, also plotted in Figure 4b. The position of the observed signal maxima can be used to determine ratios $\sigma/\sigma_f \approx 2$ and $\sigma/\sigma_f \approx 0.2$ for the fragment ions at m/z 97 and m/z 28, respectively. Hence, the trend in degree of fragmentation is m/z 28 > m/z 97 > m/z 125.

To further support the proton-ionization hypothesis, we examine the behavior of a fragment ion that is not derived from the protonated molecular ion. This type of fragment should follow the behavior of the neutral guanine molecule since there is no mechanism available to produce guanine positive ions as efficiently as is possible with protons. The behavior of the $[M-OH]^+$ ion, for example, is shown in Figure 4d, exhibiting nearly parallel behavior to that of guanine shown in Figure 4c.

In addition to surface fluctuations, there is a substantial change in ionization probability as the molecular depth profile reaches an interface between two dissimilar species. Here, we aim to determine at what point this change in ionization probability begins, how it influences the calibration of the depth scale and what can be learned about interface width broadening and interfacial chemical mixing. We begin by revisiting the initial comparison between the secondary ion and photoionized neutral depth profiles. There is undoubtedly a substantial increase in ionization probability for sputtered Ag atoms when traversing through the film-substrate interface. Before developing a detailed explanation for this behavior, it is pertinent to characterize how this variation affects the depth scale calibration, the determination of sputter rates for the guanine thin film as well as the Ag substrate and the calculation of the interface width between the organic film and the substrate.

3.4 Depth Profiling Characteristics

Typically, in a SIMS molecular depth profile the depth scale is calibrated by combining the molecular ion signal intensity variation as a function of ion fluence with AFM data taken after the completion of the experiment.^{8,12,36} To acquire an accurate depth scale, the correct sputter rate for each component of the system must be known. The sputter rate is reported in $\text{nm}\cdot\text{s}^{-1}$ and, therefore, if the number of seconds sputtered and the thickness of the material removed is known, the average sputter rate is easily calculated. The AFM data presented in Figure 5d show a representative line scan of the sputter crater. An averaged measurement across the entire sputter crater reveals a total crater depth of 200 nm. As noted earlier, 164 nm of the crater depth arises from guanine and the bottom 36 nm of the crater consists of Ag. Generally, the interface between molecular layer and substrate is considered to be reached when the molecular ion signal intensity has decreased to $\sim 50\%$ of its steady state value.

By following this simple recipe, however, it is immediately apparent that the secondary ion and photoionized neutral profiles yield different sputter rates. For the secondary ion profile, the interface is reached after 480 seconds of total sputter time, resulting in a sputter rate of 0.367 nm-s^{-1} . The photoionized neutral profile, on the other hand, reaches this point after 570 seconds of total sputter time, corresponding to a sputter rate of 0.318 nm-s^{-1} . In addition, the sputter rate of the Ag substrate is observed to be 0.047 nm-s^{-1} for the secondary ions and 0.055 nm-s^{-1} for photoionized Ag. These calculations are based on the observed signal intensities obtained from the mass spectra contained within the depth profile. Any variations in signal, primarily resulting from matrix effects at the surface and interface regions of the profile, will affect the resulting calculation. These data show that ionization effects can have real influences on depth scale calibration as well as determining the correct sputter rates for unknown systems. Without the depth profile of the neutral component for comparison with the secondary ion component, the magnitude of these ionization effects, which in some cases may be large, will remain unknown and uncorrected.

Molecular yield calculations may also be affected by uncertainty in the molecular ion signal intensities. In order to calculate the total sputtering yield (Y_{tot}) of the molecular film using Equation (5), the ion fluence needed to reach the film/substrate interface must be known in order to determine the total number of projectiles (N_p) needed to remove a fixed number of molecules; in this case guanine (N_G). The number of guanine molecules removed

$$Y_{\text{tot}} = \frac{N_G}{N_p} \quad (5)$$

can be calculated by using the AFM data to determine the total crater volume combined with the known molecular density of guanine of $8.77 \text{ molecules-nm}^{-3}$. These values result in 1.54×10^{14} molecules of guanine removed during the depth profile by $1.68 \times 10^{11} \text{ C}_{60}^+$ primary ions or a total sputter yield of 920 guanine equivalents removed per projectile impact. This high value is consistent with previous values reported for C_{60} bombardment of water ice⁶, trehalose,³ and cholesterol films^{8,37}. Using the secondary ion signal intensity for determination of the Y_{tot} value, however, results in a total yield of 1092 guanine molecules per impact. These two numbers are not identical due to the fact that they are derived from signal intensities obtained from the corresponding SIMS and IR-photoionized mass spectra. Any variations in signal intensity will be mirrored in the resulting sputter yield calculation. Although the deviation is small and possibly within the error bar, it is worth noting that experimentally derived sputtering yield values have become increasingly valuable for comparison with molecular dynamic simulations^{38–40} and, therefore, one must be concerned with acquiring these values accurately.

The final characteristic to be defined in a sputter depth profile deals with the determination of an accurate interface width between the guanine thin film and the Ag substrate. Typically, this value is reported by calculating the depth between the guanine signal as it is reduced in intensity from 84% to 16% of its steady state value. In addition, variations of the erosion rate throughout the interface region must be taken into account based upon the percent abundance of each component. Due to the single component nature of the surface region, the weighting correction presented here is not applied to possible fluctuations of the sputter rate in the near surface region. Usually, a simple correction scheme is applied involving a linear interpolation between the erosion rates of the organic overlayer and the substrate.² Both molecular and substrate ion signal variations are employed in Equation 6 to determine the correct weighting factors applied to the interface region,

$$SR = \frac{I_G / I_G^{max}}{I_G / I_G^{max} + I_{Ag} / I_{Ag}^{max}} SR_G + \frac{I_{Ag} / I_{Ag}^{max}}{I_G / I_G^{max} + I_{Ag} / I_{Ag}^{max}} SR_{Ag} \quad (6)$$

where I_G is the signal intensity of guanine molecular ions, I_{Ag} is the signal intensity of silver ions, SR_G is the sputter rate for guanine, and SR_{Ag} is the sputter rate for silver. In the past, this approach has been used to account for signal variations, which often occur between the organic overlayer and the substrate⁹. This interpolation scheme yields interface width values of 39 nm and 51 nm calculated from the photoionized neutral and secondary ion profiles, respectively. Previous data from a myriad of samples show significant variation in the observed interface width values even under similar sputtering conditions.^{8,12,36,41–43} It is our contention, that this variation is directly linked to changes in the ionization probability resulting from changes in the interfacial chemical environments. Although the content of Equation 6 is capable of accounting for much of the variation in the signal intensity, significant changes in ionization probability, as seen here, can only be completely eliminated by obtaining a photoionized neutral depth profile.

3.5 Damage and Mixing at the Film-Substrate Interface

Attempts to understand and quantify chemical damage accumulation and interface mixing at the film/substrate interface from secondary ion information alone have proven to be problematic. With the high field fs IR laser system employed here, it is feasible to monitor the behavior of various neutral fragment ions as their intensity changes in the interfacial region. As shown in Figure 6a the photoionized neutral signals of C and C₃ fragments increase by ~50% over the steady state value ~25 nm before reaching the guanine/Ag interface. Moreover, these signals persists ~6 nm past the point where the guanine film has been removed. Although only the C-containing fragments are shown, their observed behavior is in no way exclusive to these fragments. Other fragment signals, such as CH and C₃H (not shown), follow a similar trend indicating that the increase in fragment signal intensities originates from chemical damage of the organic thin film rather than implantation of ion beam degradation products into the sample. Interestingly, the O signal also increase, but by a much smaller percentage. Hence, the damage accumulation in the organic film is characterized by an increase in the C-containing fragments which subsequently lead to an increase of the Ag substrate secondary ion signal as illustrated in Figure 6b. Increased C-containing fragment signal intensity indicates an increase in chemical mixing occurring at the film/Ag interface, which alters the chemical environment and promotes the ionization of Ag atoms through a strong matrix ionization effect. In this situation, both the ion and the neutral signal help to reveal details about interface mixing.

3.6 The Altered Layer Thickness

There is fundamental interest in determining how much chemical damage is produced by C₆₀⁺ projectile in the sub-surface region of the film. The magnitude of the altered layer thickness is important in assessing the quality of the depth profile, and in determining how far the erosion can continue without catastrophic results. There are two ways of experimentally measuring this parameter. From the photoionized neutral fragment profiles, chemical damage accumulation is seen to begin well before reaching the interface between the guanine film and the Ag substrate. This behavior is likely a result of the mismatch between the high density Ag substrate and the more open structure of the guanine film. It is possible that as the eroding surface approaches the film/substrate interface, energy deposited in the organic material by the C₆₀ ion impact starts to be reflected back into the organic matrix by the relatively hard metal substrate.^{39,44,45} In principle, this effect should be observed when the remaining film thickness equals the thickness of the sub-surface layer altered by the ion bombardment. The data presented in Figure 6, therefore, point at an altered layer thickness of ~20 nm.

An alternative method to determine the altered layer thickness is to analyze the neutral molecule depth profile in terms of the erosion dynamics model.^{13,46} The initial exponential decay of the photoionized-M^o signal yields a calculated decay length of ~5 nm. In combination with the molecular density of the guanine film of 8.8 molecules per nm³, this corresponds to a disappearance cross-section $\sigma \cong 21 \text{ nm}^2$. According to the model, the ratio between the steady state signal S_{ss} and the starting signal S_0 at the beginning of the depth profile is determined by the cleanup efficiency

$$\varepsilon = \frac{Y_{tot}}{nd\sigma_d} \quad (7)$$

i.e., the efficiency for the projectile to remove the fragmentation debris produced by ion induced chemical damage, described by the damage cross-section (σ_d), in the course of the same impact event, by

$$\frac{S_{ss}}{S_0} = \frac{\varepsilon}{\varepsilon + 1} \quad (8)$$

In equation (7), d denotes the altered layer thickness, Y_{tot} the total sputter yield and n the molecule density of the guanine film. The damage cross-section σ_d is related to the disappearance cross-section σ by

$$\sigma_d = \frac{\sigma}{\varepsilon + 1} \quad (9)$$

From the measured value of S_{ss}/S_0 of ~1/3, $\varepsilon \approx 0.5$, and 14 nm^2 . In connection with the measured value of $Y_{tot} = 920 \text{ molecules/impact}$, the model predicts an altered layer thickness of about 15 nm, which appears to be in very good agreement with the depth at which the maxima of the fragmentation profiles are observed.

Regardless of the cause, chemical damage accumulation is evident in the photoionized neutral depth profile. The buildup of chemical damage leads to a significant amount of chemical mixing of small molecular fragments with substrate atoms. This effect naturally increases the apparent interface width between the guanine thin film and the Ag substrate, effectively reducing the overall depth resolution. Here we see how both the secondary ion and photoionized neutral profiles provide complementary information to the depth profiling experiment. The major components observed in the mixing region result from oxygen, carbon and carbon containing fragments present in the photoionized neutral profile along with Ag ions observed in the secondary ion profile. These data illustrate how preferential ionization may lead to substantial matrix effects. It has been shown that the presence of oxygen enhances the ionization probability of Ag atoms.⁴⁷ The interface maximum observed for the Ag secondary ions is therefore produced by the counteracting influences of a rising contribution of Ag in the sputtered flux, multiplied by a rapidly falling ionization probability due to the depletion of oxygen and carbon fragments as the interface is approached. A similar matrix effect for Si secondary ions has also been observed for trehalose films deposited on a Si substrate.³

4 Conclusion

Here we show that molecular secondary ion depth profiles may be distinctly influenced by variations in the ionization probability of sputtered neutral particles. More specifically, we find that the transients observed both at the original surface and at interfaces between different

layers of the sample can be significantly influenced by such effects. Apart from inaccuracies associated with using measured molecular secondary ion signals to represent the true chemical composition, these effects may also have implications for accurate calibration of the depth scale. In this respect, laser photoionization methods enabling the detection of neutral species desorbed from the bombarded surface prove to be of considerable value. It is likely that variations in projectile energy, ion fluence and sample temperature may also yield molecular depth profiles with significant differences between the neutral and ion components.

As a result of these studies, transients of the ionization probability of desorbed parent molecules are reported at the surface of the film and at the interface between the film and the inorganic substrate. While the surface transient appears to be only of the order of a factor of 2, the variation of the molecular ionization probability observed at the film/substrate interface can be as large as an order of magnitude or more. In addition, strong interface matrix effects are observed for the substrate ions. The results show that such effects must be properly accounted for if accurate information about the depth dependent chemical composition is to be extracted from the secondary ion profiles alone.

Comparison of the data presented here with many of our previous molecular depth profiles measured using the secondary ion component alone suggests that the findings of this work are presumably not specific for the particular model system utilized here, but rather reveal general features of molecular sputter depth profiles. The results also show, however, that meaningful data can still be extracted from secondary ion profiles in cases where photoionization data are not available, provided these effects are kept in mind and acknowledged by suitable correction schemes. Changing the depth scale calibration from the first attempts presented by Wagner *et al.*² to more sophisticated interpolation approaches represented by Equation (6) represents an important step towards the determination of accurate interface widths. Correction of the surface transient by extrapolation of the subsequent exponential decay of molecular ion signals represents another example of how the analysis can be improved. As a consequence, it would be an overstatement to posit that the photoionized neutral profile is superior to the secondary ion profile or vice versa. It is the combination of these two techniques that provides the most accurate and complete understanding of depth profiling phenomena.

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Figure 1.

Comparison of (a) the secondary ion mass spectrum and (b) the 1450 nm photoionization mass spectrum of a guanine thin film produced by bombardment with 40 keV C₆₀ primary ions using 1 kHz, 400 mW, 125 fs laser pulses for ionization. The secondary ions are characterized by the protonated guanine molecular ion $[M+H]^+$ and $[M-OH]^+$. The photoionization mass spectrum exhibits the un-protonated guanine photoionized neutral M^+ . The y-axis in counts- nC^{-1} is calculated from the primary ion fluence and the signal intensity.

Figure 2.

Molecular depth profiles of a guanine thin film supported on a Ag coated Si substrate. The signal intensity is monitored as a function of depth for (a) the photoionized M° (black) and Ag° (red) neutral species and (b) the secondary $[M+H]^+$ (black) and Ag^+ (red) ions. The depth scale is related to the 40 keV C_{60} primary ion fluence. The molecules were photoionized using a wavelength of 1450 nm. Ion ratios observed as a function of depth for (c) the $[M+H]^+$ secondary ion signal divided by the M° photoionized neutral signal and (d) for the Ag^+ secondary ion signal divided by the Ag° photoionized neutral signal. The vertical dotted line indicates the interface between the guanine thin film and Ag substrate measured by AFM.

Figure 3.

Molecular depth profiles of the near surface region of a guanine thin film supported on a Ag coated Si substrate. The signal intensity is monitored as a function of depth (a) for the secondary ion $[M+H]^+$ (red) and the photoionized neutral M° (black). The depth scale is related to the 40 keV C_{60} primary ion fluence. The photoionizing wavelength used is 1450 nm. In (b), the ion ratio for the $[M+H]^+$ secondary ion signal over the M° photoionized neutral signal is plotted as a function of depth.

Figure 4.

Molecular depth profiles of the near surface region of a guanine thin film supported on a Ag coated Si substrate. The signal intensity is monitored as a function of depth for (a) the secondary ion $[M+H]^+$, (b) secondary ions $[M+H-HCN]^+$ m/z 125 (black), $[M+H-HNCOC]^+$ m/z 97 (blue), and $[HCN+H]^+$ m/z 28 (red) resulting from the fragmentation of the protonated guanine molecular $[M+H]^+$, (c) the photoionized neutral M° , and (d) a secondary ion fragment $[M-OH]^+$ m/z 134 resulting from the dehydroxylation of the guanine molecular ion. The depth scale is related to the 40 keV C_{60}^+ primary ion fluence and the photoionizing wavelength used is 1450 nm.

Figure 5.

AFM images a guanine thin film supported on a Ag coated Si substrate. Image of the sputter crater at the completion of the depth profile generated by a 40 keV C_{60} ion beam (a) showing a total eroded area of $290\ \mu\text{m} \times 368\ \mu\text{m}$. The depth of the sputter crater is observed by taking a cross-section (d) of (a) denoted by the white line. The depth of the crater is measured at 200 nm. Surface roughness measurements taken at a field-of-view of $25\ \mu\text{m} \times 25\ \mu\text{m}$ of the pristine guanine thin film (b) and from within the sputter crater (c) yield root mean squared (RMS) values of 2.0 nm and 2.5 nm respectively. Intensity scales shown range from black to yellow corresponding to low to high height values.

Figure 6.

Molecular depth profiles of a guanine thin film supported on a Ag coated Si substrate. The signal intensity is monitored as a function of depth (a) for the photoionized neutral fragments C₃ m/z 36 (blue), C (x0.1) m/z 12 (green), and O m/z 16 (black) and (b) for the photoionized neutral signals M⁺ (black), C (x2) (green), and Ag⁺ (red) and the secondary ion signal Ag⁺ (blue). The depth scale is related to the 40 keV C₆₀ primary ion fluence and the photoionizing wavelength used is 1450 nm. The vertical dotted line indicates the interface between the guanine thin film and Ag substrate measured by AFM.