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Investigating the fundamentals of molecular depth profiling using strong-field photoionization of sputtered neutrals

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Molecular depth profiling of model organic thin films were performed using a 40 keV C_{60}^+ cluster ion source in concert with TOF-SIMS. Strong-field photoionization of intact neutral molecules sputtered by 40 keV C_{60}^+ primary ions was used to analyze changes in the chemical environment of the guanine thin films as a function of ion fluence. Direct comparison of the secondary ion and neutral components of the molecular depth profiles yields valuable information about chemical damage accumulation as well as changes in the molecular ionization probability. An analytical protocol based on the erosion dynamics model is developed and evaluated using guanine and trehalose molecular secondary ion signals with and without comparable laser photoionization data. **Copyright © 2010 John Wiley & Sons, Ltd.**

Keywords: TOF-SIMS; C60 ion beam; enhanced ionization probability

Introduction

Depth profiles are generally acquired by monitoring the intensity of the secondary ion signals of interest as a function of the primary ion fluence. The resulting signal is characterized by a convolution of the yield of neutral molecules and their corresponding ionization probabilities. Surface and interfacial artifacts arising from changes in the ionization probability within the matrix are well known and often make quantitative analysis of various types of samples difficult.[1] One method that has been pursued to reduce or eliminate this complication, identified as laser photoionization of sputtered neutral molecules, successfully decouples the ionization event from the desorption process.[2] Implementation of recently realized strong-field photoionization techniques combined with C_{60} cluster ion beams allows for the real-time monitoring of desorbed neutral species as well as secondary ions during a molecular depth profile.[3]

In order to untangle the complex nature of molecular depth profiles, the data presented here simultaneously measure the yield of neutral molecules by strong-field laser photoionization and the protonated molecular secondary ions from a model organic sample. A vapor-deposited thin film of guanine supported by a Ag substrate was chosen as a model system. Guanine is a fully conjugated, amphophilic small molecule that yields both a strong protonated molecular ion signal, $(M+H)^+$, in the secondary ion mass spectrum, and an equally intense molecular ion signal, M^+, in the laser photoionization mass spectrum. Direct measurement of both these species provides valuable insight into the effects of cluster ion-induced chemical damage on the protonated ion formation process that would otherwise not be accessible from the detection of the secondary ion species alone.

Additionally, a previously described analytical model is used to determine the efficacy of estimating the neutral yield by fitting an exponential decay function to the secondary ion data alone.[4] This model, aimed at quantifying the changes in ionization probability as a function of the near-surface depth, is validated using the guanine secondary ion and neutral molecule depth profiling data, and is subsequently applied to previously acquired depth profiles of spin-coated trehalose films on Si substrates where only secondary ion information is available. This analytical model coupled with a better understanding of the fundamentals of the cluster ion-solid interactions may lead to more effective extraction of chemical information from past and future molecular depth profiling experiments.

Experimental

The experiments were performed using a time-of-flight secondary ion mass spectrometry (TOF-SIMS) instrument described in detail elsewhere.[5] The instrument is equipped with a fullerene ion source delivering a beam of mass-selected C_{60} ions (Ionoptika, Ltd.) and a calcium fluoride (CaF_2) window for integration of 1450 nm, 125 fs, 400 μJ, 1 kHz light generated by the optical parametric amplification of a titanium–sapphire femtosecond pump laser. The design of the instrument allows for precise extraction of both secondary ions and photoionized neutrals making simultaneous detection of both species possible. Depth profiling experiments were performed by alternating between consecutive erosion and data acquisition cycles. The initial film thicknesses and amount of material removed during the depth profiles were measured by atomic force microscopy (AFM; Nanopics 2100, TLA Tencor Inc.).

The vapor-deposited guanine thin films of ~165 nm were prepared on precut 5 × 5 × 0.5 mm Si shards (Ted Pella Inc.) coated

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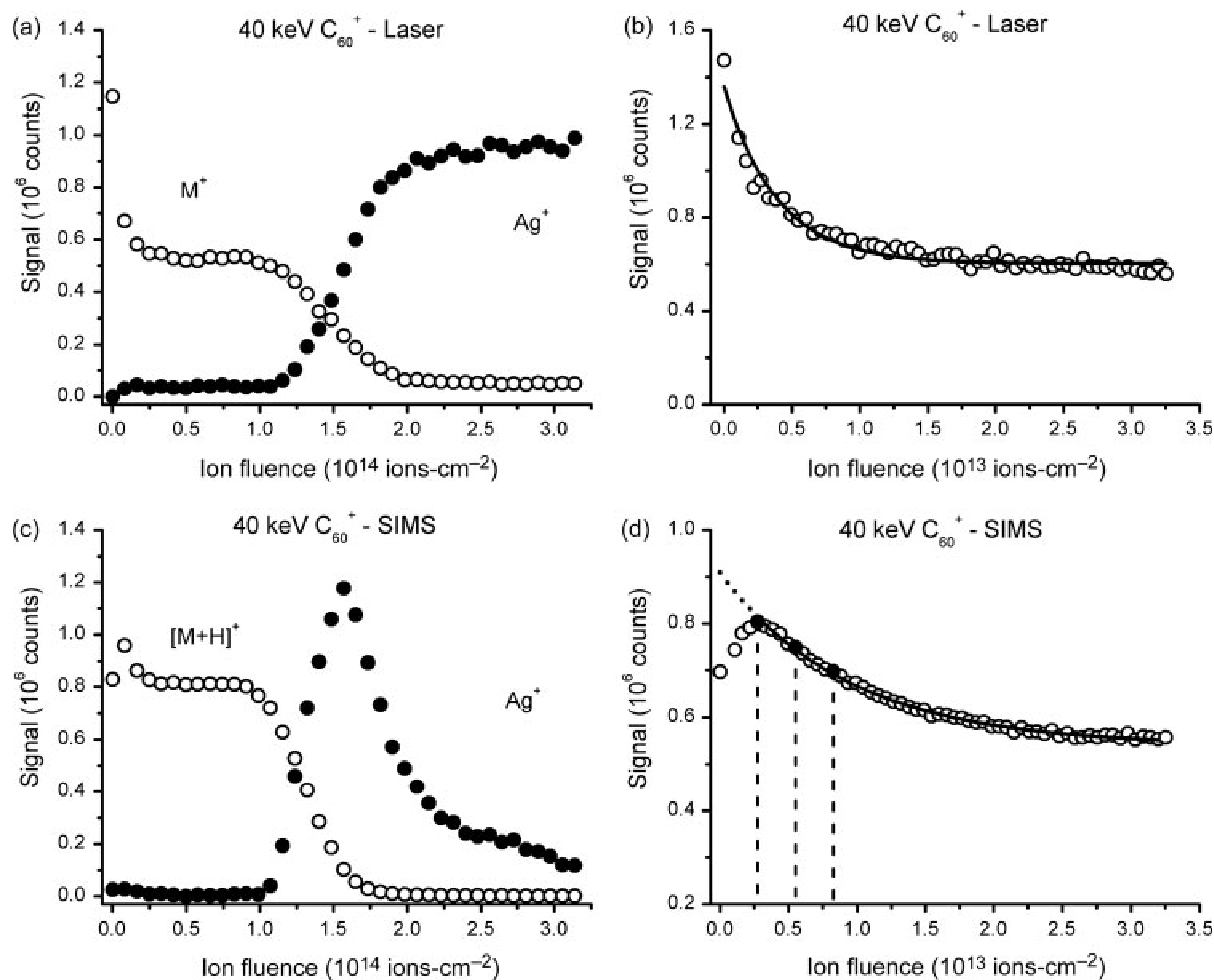

Figure 1. Molecular depth profiles of a guanine thin film generated by monitoring the signal intensity of (a) the photoionized M° (open) and Ag° (black) neutral species, and (c) the secondary $(M+H)^+$ (open) and Ag^+ (black) ions as a function of ion fluence. Near-surface molecular depth profiles generated by monitoring (b) the photoionized M°, and (d) the secondary $(M+H)^+$ ion signal intensities as a function of ion fluence. Exponential decay fits (solid lines) following the form of Eqn (1) are shown in (b and d). Data limits (black with dashed dropdown lines) and extrapolated data (dotted line) are shown in (d).

with ∼150 nm of Ag. A simple masking lithography technique was applied to the guanine films leaving ∼5% of the Ag-coated shard bare on each end. The samples were electrically grounded from the bare Ag-coat to a Cu sample block using Ag paste, shown to successfully eliminate charging effects within organic films of such thickness within our lab. The trehalose thin films were prepared by spin-coating a 1 M aqueous solution of trehalose onto the previously mentioned Si shards at ∼3200 rpm. Both methods produce homogenous coverage indicated by uniform color associated with the optical interference pattern created within the films.

Results and Discussion

The primary goal of this research is to acquire a depth profile of an organic thin film utilizing not only the secondary ions, but also the neutral component of the sputtered flux. Comparison of the ion and neutral components of the depth profile yield useful information about chemical damage accumulation and changes in the molecular ionization probability as a function of ion fluence. In addition, the fundamental knowledge gained from samples amenable to laser photoionization may be applied to other molecular systems where only SIMS data are available.

The neutral and ion components of a molecular depth profile of a guanine thin film are shown in Fig. 1a and c. In addition, near-surface neutral and ion depth profiles are shown in Fig. 1b and d in order to emphasis surface-specific changes in the molecular ionization probability. It is important to note that the ionization probability of desorbed guanine molecules increases by roughly a factor of two during the first few sputter cycles. In an attempt to quantify this surface fluctuation, an exponential decay function described by the erosion dynamics model[6] is fitted to both the neutral and ion components of the near-surface depth profile. The form of this function is

$$S = S_{ss} + (S_o - S_{SS})exp(-\sigma f) \quad (1)$$

where S is the molecular ion signal, S_{SS} the steady state signal, S_o the initial signal, and f the primary ion fluence. The resulting value for the disappearance cross-section σ (∼25 nm^2) fits well with similar data obtained on other systems. In the case of the SIMS profile, the exponential decay fit was performed using three different ion fluences marked by the drop-down lines in Fig. 1d. In

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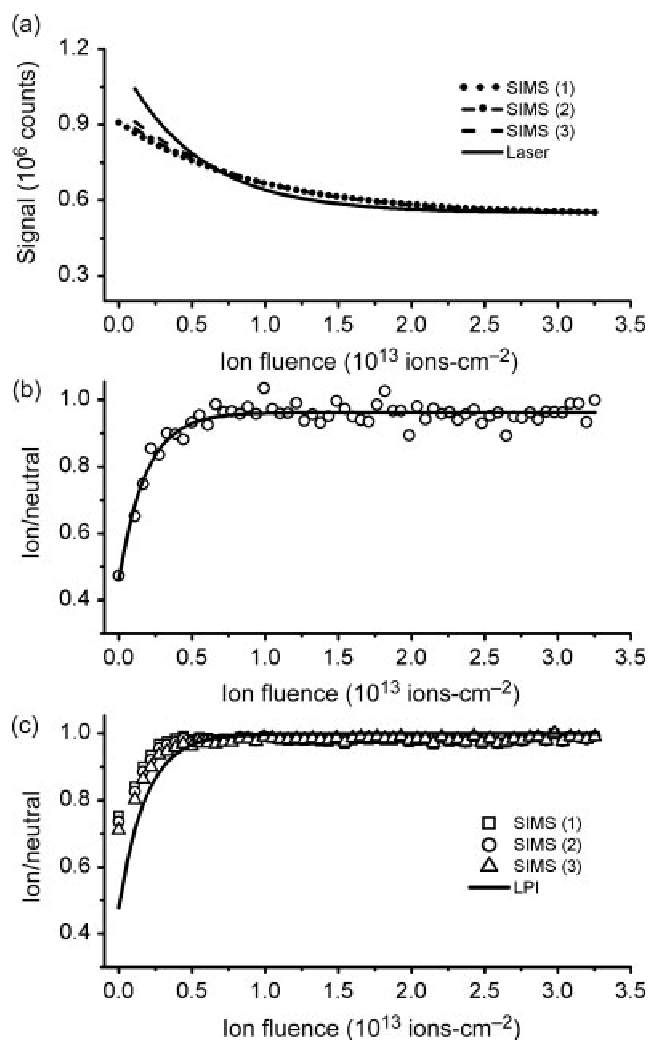

Figure 2. Exponential decay fits taken from SIMS (dotted, dash/dot/dash and dashed) and photoionization data (solid) obtained from near-surface guanine depth profiles are compared in (a). The ion ratio for the guanine $(M+H)^+$ secondary ion signal over the M° photoionized neutral signal is plotted as a function of ion fluence in (b). An exponential fit (solid) to this data follows the form of Eqn (2). Data generated from the SIMS fits (open) are compared (c) to the exponential fit (solid) from (b).

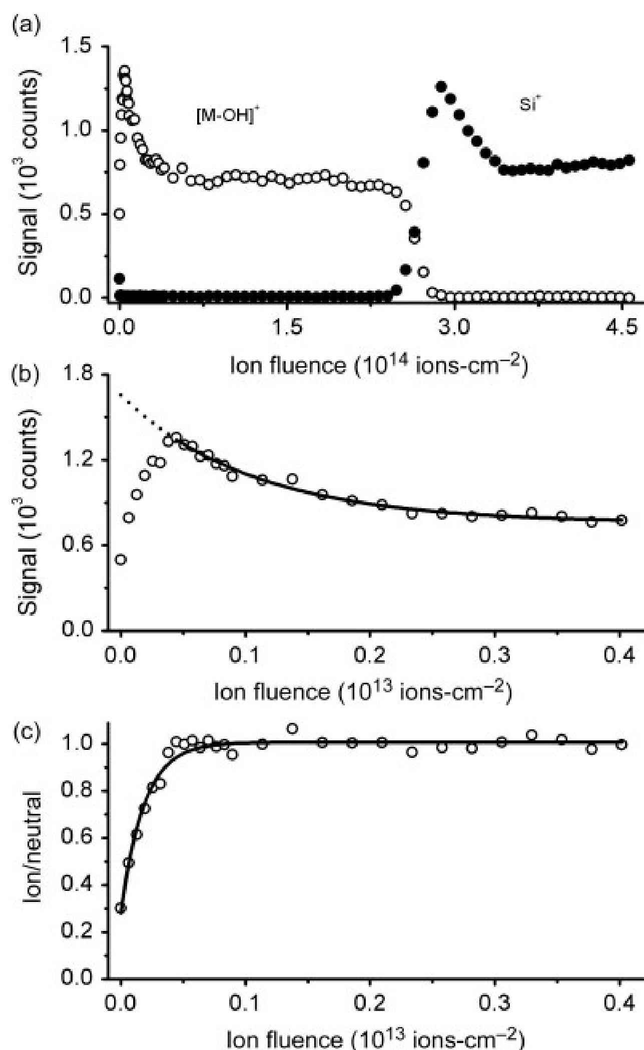

Figure 3. Molecular depth profile of a trehalose thin film created by plotting the signal intensity of (a) the secondary $(M-OH)^+$ (open) and Si^+ (black) ions as a function of ion fluence. Near-surface molecular depth profile created by plotting the signal intensity of (b) the secondary $(M-OH)^+$ ion as a function of ion fluence. An exponential decay fit (solid line) following the form of Eqn (1) and extrapolated data (dotted line) are shown in (b). The ion ratio for the trehalose $(M-OH)^+$ secondary ion signal over data generated from the exponential fit in (b) is plotted as a function of ion fluence in (c). An exponential fit (solid) to this data follows the form of Eqn (2).

addition, the exponential decay function is extrapolated back to the initiation of the profile marked by the dotted line in Fig. 1d. In this manner, it is possible to simulate the laser photoionization data from the SIMS data.

It is of interest to determine whether or not fitting the SIMS near-surface profile data using the erosion dynamic model accurately describes the actual signal obtained by laser photoionization of the neutral component. Therefore, three different fits of Eqn (1) to the SIMS data at fluences above the three limiting data points illustrated in Fig. 1d are shown in Fig. 2a in comparison with the fit obtained from the laser photoionization data. Clearly, the SIMS data do not exactly fit the laser photoionization data, and the apparent disappearance cross-section comes out by about a factor of two lower, but the agreement is fairly good considering that the erosion dynamics model does not predict the initial rise in the protonated molecular secondary ion signal of guanine.

It is possible to examine the initial increase in the protonated molecular secondary ion signal of guanine by dividing the secondary ion signal by the neutral signal obtained by laser photoionization of intact neutral guanine molecules. The result is shown in Fig. 2b and is essentially a characterization of the increase in ionization probability within the first few cycles of the depth profile. These data can also be fit to a function

$$\alpha^+ = \alpha_{ss}^+ - (\alpha_{ss}^+ - \alpha_o^+)exp(-\sigma_i f) \qquad (2)$$

where α^+ is the ionization probability with $\alpha_o{}^+$ and $\alpha_{ss}{}^+$ being its initial and steady-state values, respectively, and f is the primary ion fluence. Interestingly, the apparent ionization enhancement cross-section σ_i entering Eqn (2) is by about a factor of two larger than the disappearance cross-section determined from Fig. 1b, indicating that ionization enhancement and chemical damage do not follow the same behavior. A further discussion of this point requires a physical model to describe the ionization enhancement

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which is currently not available. On the other hand, the SIMS signal decay results from a convolution of both processes occuring on comparable fluence scales, thus leading to the discrepancy of the secondary ion and neutral fit curves in Fig. 2a.

Nevertheless, it is still possible to get a feeling for transient ionization phenomena by dividing the SIMS profile data by hypothetical data generated from the extrapolation of the high-fluence exponential decay fits. Figure 2c shows a comparison between the simulated ionization probability plots obtained from SIMS data using the three fits indicated in Fig. 2a to the actual data derived from the laser photoionization experiments. Once again, the resulting data do not exactly match the exact behavior of the ionization probability, but the general trend is clearly revealed.

The protocol established in the previous discussion may be applied to SIMS molecular depth profiles that exhibit similar surface fluctuations, but do not benefit from comparable laser photoionization data. For example, Fig. 3a shows depth profiling data obtained from a spin-coated trehalose thin film on a Si substrate. Surface fluctuations similar to those of the guanine depth profile can be observed in Fig. 3b. Following the previously described analytical protocol, the trehalose molecular secondary ion signal may be fit using Eqn (1) and extrapolated back to zero. From this fit and the secondary ion signals, a simulated plot of the change in ionization probability as a function of ion fluence can be generated as seen in Fig. 3c. By fitting Eqn (2) to these data, we obtain values of $\sim$70 nm^2 and $\sim$500 nm^2 for σ and σ_i, respectively. Apparently, in this case, the ionization enhancement and damage decay occur on very different fluence scales, and the simulated data should, therefore, much more accurately predict the changes in the ionization probability even in the absence of laser photoionization data.

Conclusion

The results presented herein illustrate that molecular secondary ion depth profiles may be distinctly influenced by variations in the ionization probability of sputtered neutral particles. Specifically, the transients observed both at the original surface and at interfaces between different layers of the sample can be significantly influenced by these types of matrix effects. Laser photoionization techniques aimed at detecting neutral molecules desorbed from the ion-bombarded surface have proven to be of considerable value. The significance of these types of measurements lie not only with the ability to directly compare the secondary ion and neutral components of a depth profile, but also with a wider-reaching applicability to molecular depth profiles where ample laser photoionization data may not be available.

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