

# Molecular depth profiling of multi-layer systems with cluster ion sources

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## Abstract

Cluster bombardment of molecular films has created new opportunities for SIMS research. To more quantitatively examine the interaction of cluster beams with organic materials, we have developed a reproducible platform consisting of a well-defined sugar film (trehalose) doped with peptides. Molecular depth profiles have been acquired with these systems using  $C_{60}^+$  bombardment. In this study, we utilize this platform to determine the feasibility of examining buried interfaces for multi-layer systems. Using  $C_{60}^+$  at 20 keV, several systems have been tested including Al/trehalose/Si, Al/trehalose/Al/Si, Ag/trehalose/Si and ice/trehalose/Si. The results show that there can be interactions between the layers during the bombardment process that prevent a simple interpretation of the depth profile. We find so far that the best results are obtained when the mass of the overlayer atoms is less than or nearly equal to the mass of the atoms in buried molecules. In general, these observations suggest that  $C_{60}^+$  bombardment can be successfully applied to interface characterization of multi-layer systems if the systems are carefully chosen.

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## 1. Introduction

With the development of cluster ion sources, molecular depth profiling has been shown to be feasible in many cases. For example, Gillen and co-workers [1–3] used  $SF_5^+$  to profile polymer films by monitoring specific fragment ions in the range of  $m/z$  100. More recently, a similar strategy has allowed the study of multi-layer polymer films [4]. Wucher et al. [5] have also depth profiled through ice doped with histamine using  $C_{60}^+$  bombardment and concluded that there was minimal damage accumulation during sputtering. Similar data have been reported by the Vickerman group [6,7]. More details about the significance of these developments are presented in an accompanying paper [8]. At this point, we define a successful molecular depth profile as one whereby the molecular ion signal intensity of interest reaches a non-zero steady state value ( $S_{ss}$ ) as a function of primary ion dose, assuming of course that the species of interest is distributed evenly throughout the film.

Recently, we have developed a simple analytical expression [9] that identifies some of the parameters that affect  $S_{ss}$ , relative to the signal acquired from a virgin surface ( $S_0$ ) as:

$$\frac{S_{ss}}{S_0} = \frac{Y_{tot}}{Y_{tot} + nd\sigma_d} \quad (1)$$

where  $Y_{tot}$  is the total sputtering yield,  $n$  is the molecular density,  $d$  is the depth associated with any damage or disruption created by the primary beam and  $\sigma_d$  is the damage cross section of the target molecule. Obviously, the best depth profiles are achieved when  $Y_{tot} \gg nd\sigma_d$ . To test this model in detail, we have developed a platform of uniform thin films composed of trehalose or trehalose doped with peptides [10]. Molecular depth profiles with peptide molecules of up to  $m/z$  830 have been reported [9,10].

One advantage of this platform is that a certain parameter can be changed in making or analyzing the film and correlated with specific properties of the depth profile such as sputter yield, sputter rate, ionization yield, interface width and degree of chemical damage accumulation. In previous studies, we have bombarded films with peptides of different molecular weights, at different temperatures using primary ions of various kinetic energy and mass. In this report, we explore the capability of  $C_{60}^+$  to perform molecular depth profiling on multi-layer

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samples with the aim of evaluating the prospects for characterizing buried interfaces.

## 2. Experimental

### 2.1. Materials and film preparation

The materials and film preparation have been described in detail in another paper [10].

### 2.2. Metal and ice deposition

Al and Ag films were deposited onto the sample held at 100 K through a vacuum metal deposition chamber. A quartz crystal microbalance was connected to monitor the thickness of the deposition. For the deposition of ice, the sample was also cooled to 100 K and water vapor was introduced into the vacuum chamber at about  $10^{-5}$  torr for 2 min. The temperature was then retained at 100 K while the sample was sputtered and analyzed.

### 2.3. Depth profiling

For depth profiling, the  $C_{60}^+$  ion beam was operated in dc mode to sputter through the film at an area of  $300 \mu\text{m} \times 300 \mu\text{m}$  followed by the acquisition of TOF mass spectra after each sputter cycle using  $C_{60}^+$  at an ion fluence of  $10^{10} \text{cm}^{-2}$  into a zoomed area inside the crater in order to avoid side effect. This process is also described in detail elsewhere [10].

### 2.4. Instrumentation

The SIMS equipment and the  $C_{60}$  ion source have been described in detail [10]. Crater depths, edge profiles and

calculated sputter rates were determined using a KLA-Tencor Nanopics2100 atomic force profilometer. Resolution in the Z and X/Y ranges are ca. 3 Å and 2 nm, respectively.

## 3. Results and discussion

For the first series of experiments, trehalose films were prepared either on Si or on Al-coated Si substrates and subsequently coated with either 4 or 500 Å of Al. Aluminum was chosen because it has a light mass and is unlikely to form islands during deposition. Since the deposition was carried out at cryogenic temperature, we believe that the intrinsic Al/trehalose interface is very sharp. Moreover, other artifacts such as Al penetration into the sugar are considered unlikely to occur since previous studies of Al deposition onto –OH terminated self-assembled monolayers [11] suggest simple formation of –OAl bonds. The results for all of these profiles are presented in Fig. 1. For the 4 Å Al film (Fig. 1b), the critical molecular ion peaks reach a steady state value in the trehalose layer. The intensity of the  $m/z$  325 peak is reduced by a factor of 5, however, relative to the control (Fig. 1a). For the thicker Al film (Fig. 1c), protein molecular ions are seen to appear in the trehalose layer, but the interface widths are quite large, preventing the establishment of a steady state signal.

Although we do not yet fully understand those results, it is instructive to view the data in terms of Eq. (1). Apparently, the presence of only 4 Å of Al reduces the value of  $S_{ss}/S_0$  through its effect on  $Y_{\text{tot}}$  or  $d$ . It is possible, for example, that a small amount of Al is knocked into the trehalose film, reducing the yield of trehalose molecules. Beam induced chemical reactions between Al and trehalose are also possible. The resulting effect would be increased chemical damage accumulation, from which the system is unable to recover. A similar argument could

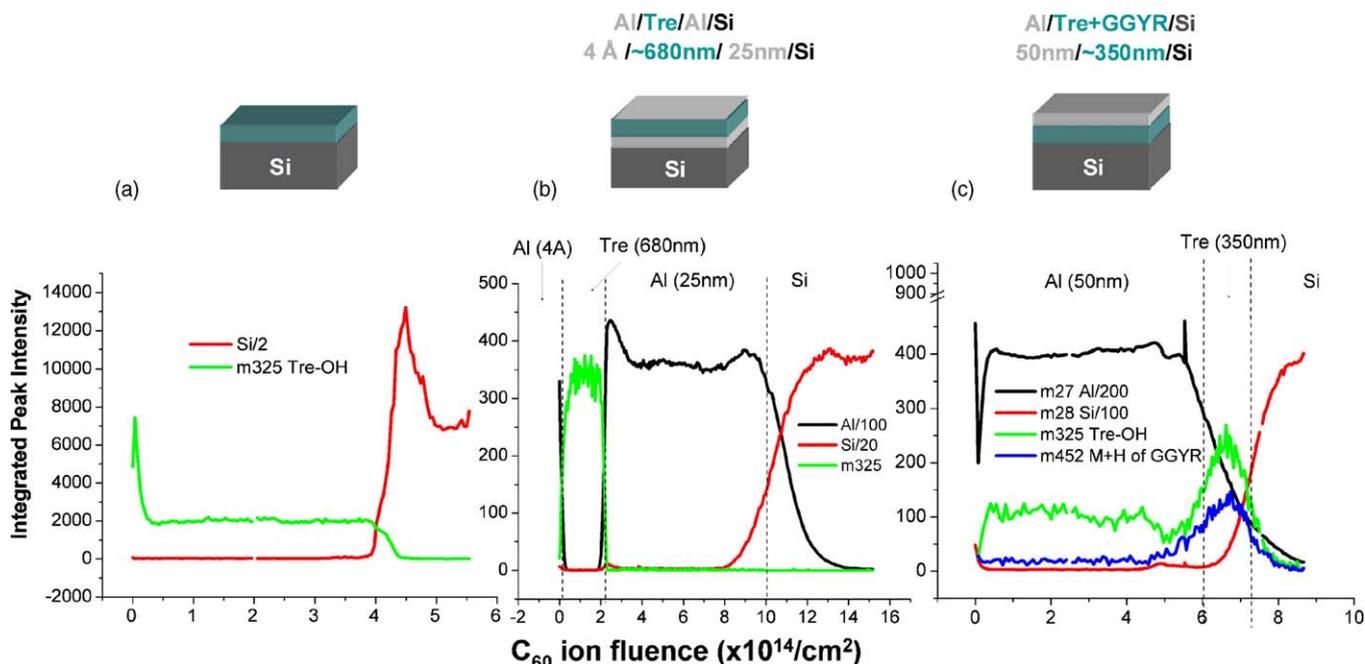


Fig. 1. Depth profiles of secondary ion intensities vs.  $C_{60}^+$  ion fluence of (a) trehalose, (b) Al/Tre/Al/Si film and (c) Al/Tre + GGYR/Si film. The Tre + GGYR film was prepared with a concentration of 1% (molar) GGYR in trehalose. Note: the dramatic difference in erosion rate for Al relative to trehalose.

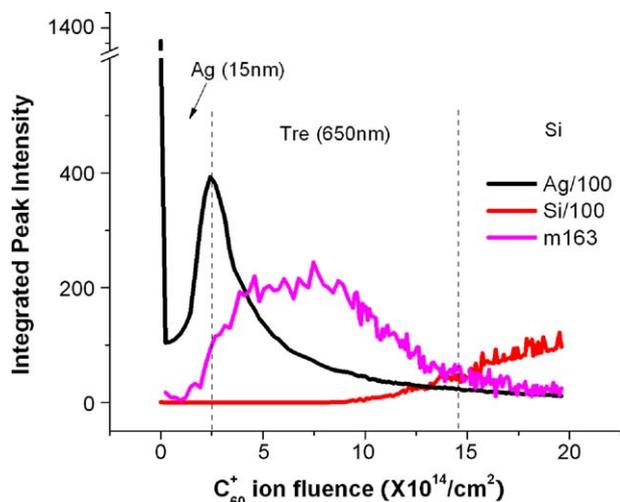


Fig. 2. Depth profiles of secondary ion intensities vs.  $C_{60}^+$  ion fluence of Ag/Tre/Si film. The signal of  $m/z$  163 is a typical fragment ion of trehalose and used here as an indicator of the trehalose film. The major trehalose peak at  $m/z$  325 overlaps with the  $Ag_3$  isobaric interference and is not shown here.

be employed to understand the behavior of the thicker Al overlayer film.

Silver deposition presents an even more complicated picture as shown in Fig. 2. The Ag-related ion intensities increase at the metal/trehalose interface, presumably due to matrix ionization effects and are observed to be present throughout the sugar film. Although there is a semblance of a steady state formed by the organic ions, the intensity is about an order of magnitude lower than expected. These data suggest that ion-beam mixing and the influence this effect exerts on the parameters in Eq. (1) is again responsible for the convoluted profiles.

Finally we investigated a trehalose film with an ice overlayer. Ice is important because in most biological tissue or cell studies in vacuum, water-ice is a major component once the sample is frozen to keep biological integrity. In our experiment, a 1.73  $\mu\text{m}$  film of amorphous ice was deposited onto a 450 nm film of trehalose. In Fig. 3, ratios of signal

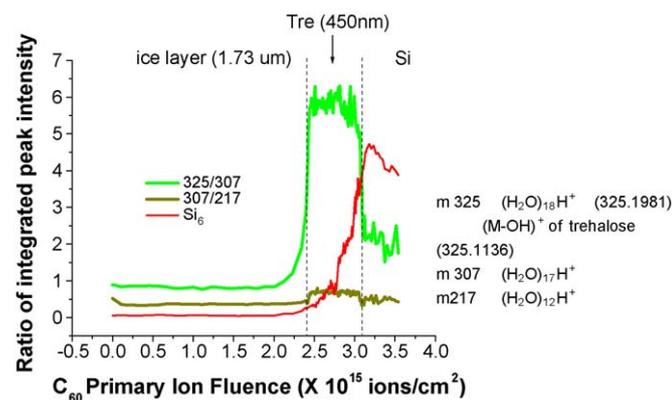


Fig. 3. Depth profiles of ratios of signal intensities vs.  $C_{60}^+$  ion fluence of ice/Tre/Si film. Ratios are plotted in order to remove the interference of ice cluster peak at  $m/z$  325. The  $Si_6$  peak is picked instead of Si to avoid the interference of hydrocarbon peaks at  $m/z$  28.

intensity are plotted against primary ion dose since at  $m/z$  325 there is an isobaric interference between the ice cluster  $(H_2O)_{18}H^+$  and  $(M-OH)^+$  of trehalose. The trend of the trehalose signal is illustrated by comparing the ratio of  $m/z$  325 and an ice cluster peak at  $m/z$  307  $((H_2O)_{17}H^+)$ , and the ratio of two ice cluster peaks at  $m/z$  307  $((H_2O)_{17}H^+)$  and  $m/z$  217  $((H_2O)_{12}H^+)$ . The thickness of the ice layer is calculated from an independent study of sputter yield of ice by 20 keV  $C_{60}^+$  [5] while the thickness of the trehalose layer is determined by AFP after the sample is warmed back to room temperature in the vacuum. We estimate that the intensities of the trehalose ions are very close to those observed in the control sample. The influence of the lighter water molecule does not negatively impact the physical structure of the trehalose film during bombardment and the parameters of Eq. (1) are preserved. The result is intriguing since after depth profiling through a layer of almost 2  $\mu\text{m}$  of ice, the molecular signal of trehalose can still be obtained and remains stable until a sharp trehalose/Si interface is reached. Hence, the ice must be removed without the formation of significant topography and interface mixing is insignificant for this case.

It is interesting to compare the behavior of the four systems reported above. For the overlayers,  $Y_{\text{tot}}$  of Al and Ag are on the order of 200 atoms/ $C_{60}^+$  projectile at 20 keV. For water,  $Y_{\text{tot}}$  is about 2500 molecules/ $C_{60}^+$ . It is likely that the variation of behavior between the systems is a combination of these yield effects through the influence of Eq. (1) and the likelihood of interface mixing between the overlayer and the trehalose film driven by the relative masses.

#### 4. Conclusions

By examining a series of multi-layer systems, we have shown that depth profiling of multi-layers is possible but not straightforward. There are many possible complications. For example, the depth profiling of A/B could be very different than that of B/A, if A and B have very different masses or different yields. This is an extremely important problem, however, and will require considerably more research to map out the appropriate strategies.

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