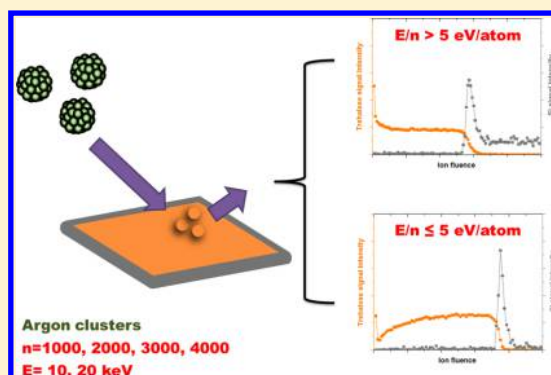


## Molecular Depth Profiling with Argon Gas Cluster Ion Beams

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## S Supporting Information

**ABSTRACT:** Argon gas cluster ion beams (Ar-GCIBs) are remarkable new projectiles for secondary ion mass spectrometry (SIMS) depth profiling of organic materials. However, the optimal cluster size and kinetic energy to provide the best quality of depth profiles, in terms of high ionization efficiency of the target molecules, little chemical damage, and short experiment time, for organic materials is not fully understood. Hence, the effect of cluster size and kinetic energy on the quality of molecular depth profiling is investigated on a simple platform composed of trehalose thin films to acquire more fundamental information about the ion/solid interaction. The results suggest that the sputter yield ( $Y/n$ ) of argon clusters is linearly dependent upon kinetic energy per atom ( $E/n$ ). When  $E/n > 5$  eV/atom, normal depth profiles are obtained with relatively high sputter yields. When  $E/n \leq 5$  eV/atom, however, distorted depth profiles in the steady state region are observed, which exhibit a low sputter yield and variable ionization efficiency. As a consequence of these observations, it was concluded that high kinetic energy increases the useful molecular ion yield of trehalose and that  $\text{Ar}_n^+$  clusters with a small  $E/n$  value minimize ion beam bombardment induced chemical damage. Hence optimal conditions for molecular depth profiling will be obtained using the highest kinetic energy with the largest clusters while maintaining a value of  $E/n$  near a threshold value of 5 eV/atom. In general, this study provides insight into selecting optimal Ar-GCIB characteristics for molecular depth profiling of organic materials.



## INTRODUCTION

Secondary ion mass spectrometry (SIMS) has been used as an in-depth characterization method for inorganic materials, particularly semiconductors, for many years.<sup>1–3</sup> To expand the scope of this technique into the investigation of organic samples, there has been a growing emphasis on the development of cluster ion sources, such as  $\text{Au}_3$ ,<sup>4,5</sup>  $\text{Bi}_3$ ,<sup>6</sup>  $\text{SF}_5$ ,<sup>7</sup> and  $\text{C}_{60}$ .<sup>4</sup> These probes, particularly  $\text{C}_{60}$ , are more effective than the traditional atomic ion sources, because less chemical damage is accumulated during the interaction of the projectiles with the solid. Molecular depth profiling of a variety of organic materials is now possible,<sup>8–11</sup> providing an important new characterization modality for SIMS. Recently, argon gas cluster ion beams (Ar-GCIBs)<sup>12</sup> have generated a great deal of excitement, because they appear to yield better depth resolution and produce less chemical damage than  $\text{C}_{60}$ ,<sup>13–16</sup> broadening the scope of this technology even further.

There is flexibility associated with the implementation of GCIBs. For example, the nature of the chemical composition of these clusters can be varied, consisting of water clusters<sup>17,18</sup> or Ar clusters doped with other species such as  $\text{CO}_2$ <sup>15</sup> and  $\text{CH}_4$ ,<sup>19</sup> or other molecules such as  $\text{N}_2$ <sup>20</sup> and  $\text{C}_2\text{H}_5\text{OH}$ .<sup>21,22</sup> The idea behind many of these experiments is to increase the ionization efficiency of the target molecules by providing a source of protons for making  $[\text{M} + \text{H}]^+$  ions. Other dopants such as  $\text{CO}_2$  appear to provide a stabilizing effect on the cluster, yielding better focusing properties for imaging.<sup>15</sup>

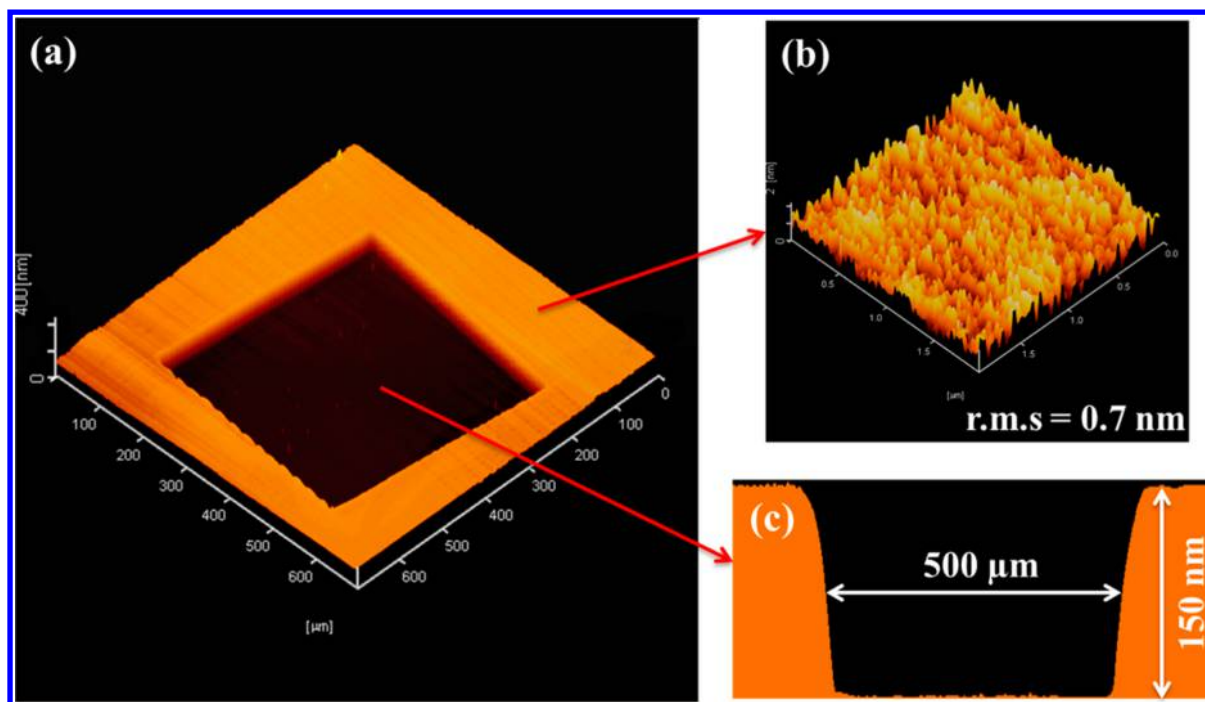
At a more basic level, however, it is also possible to vary the cluster size, mass, and kinetic energy over wide ranges. There have been attempts to predict how the sputtering yield and the ionization probability depend upon these parameters using both fundamental<sup>23</sup> and empirical<sup>24,25</sup> approaches that have helped to begin to organize available data in a consistent fashion. In addition, there have been several Ar-GCIB studies that have focused on how the depth resolution obtained during molecular depth profiling of multilayer structures depends upon cluster size and kinetic energy.<sup>26,27</sup> To achieve a molecular depth profile in the shortest time, with the best ionization efficiency and with the fewest sputter-induced artifacts, there surely exists a complex interplay between these parameters that has yet to be worked out.

Here, we examine depth profiles of 150 nm spin-cast thin films of trehalose deposited onto Si wafers. The profiles were obtained under various conditions using the Ar-GCIB projectile for sputtering and for analysis. We limited the study to pure Ar-GCIBs to avoid chemical effects associated with reactive species. Trehalose is chosen as a model substrate because it has been extensively used by us to determine appropriate conditions for  $\text{C}_{60}$  depth profiling and it has been successfully characterized with an erosion dynamics model to measure the thickness of the

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**Figure 1.** AFM images of a trehalose film bombarded by a 40 keV  $C_{60}^+$  ion beam. Image a shows the bombarded region of the film in three dimensions. Image b shows that the unbombarded region of the film has a 0.7 nm rms roughness. Image c shows a line scan taken across the bombarded region of the film, which indicates that the film has a thickness of 150 nm.

altered layer at the surface, depth resolution, sputtering yield, and damage cross section.<sup>28–30</sup> Following this methodology, we examine depth profiles obtained using kinetic energies of 10 and 20 keV with cluster sizes of  $Ar_{1000}$ ,  $Ar_{2000}$ ,  $Ar_{3000}$ , and  $Ar_{4000}$ . With this approach, it is possible to quantitatively determine how the important parameters affect the shape and the intensity of the depth profile. Perhaps most importantly, this study suggests that the best situation results from using the highest kinetic energy and the largest possible cluster with an  $E/n$  value slightly larger than 5 eV/atom. This finding is in agreement with recently published studies in the static SIMS regime, which state that high energy and larger clusters are beneficial for increasing the molecular ion yield of organic materials.<sup>15,18</sup>

## EXPERIMENTAL SECTION

**Material and Sample Preparation.** Presliced 5 mm  $\times$  5 mm Si wafers (Ted Pella Inc., Reading, CA, USA) were used as substrates for all films. The substrates were piranha etched (3:1  $H_2SO_4/H_2O_2$ ) for 20 min and rinsed with deionized water three times to remove contaminants from the substrates and make the substrate surface hydrophilic. (*Extreme caution must be exercised when using piranha etch. An explosion-proof hood should be used.*) Trehalose (Sigma-Aldrich Co., St. Louis, MO, USA) films were prepared by spin-casting 50  $\mu$ L of a 0.5 M aqueous trehalose solution in 10  $\mu$ L aliquots onto the cleaned Si wafers. Each aliquot was allowed to spin for 30 s at 5000 rpm before the subsequent aliquot was applied. A uniformly colored film with a glassy appearance is normally obtained. The freshly prepared films were immediately transferred to the ToF-SIMS instrument for measurement to minimize surface contamination.

**Instrumentation.** Sample analysis was performed using a J105 3D Chemical Imager (Ionoptika Ltd., Chandlers Ford, UK), the design of which has been described previously.<sup>31</sup> The instrument is equipped with a 40 kV  $C_{60}$  primary ion beam and a 20 kV Ar-GCIB system. Unlike conventional ToF-SIMS

instruments that operate alternatively between data acquisition cycles in pulsed mode and erosion cycles in DC mode, this J105 instrument uses a continuous primary ion beam to generate a continuous stream of secondary ions. The secondary ions are collected in a buncher and then accelerated into a ToF analyzer. This design allows for continuous data collection and ensures that no sample information is lost. In this study, trehalose films were first investigated with a 40 keV  $C_{60}^+$  ion beam. SIMS images of  $64 \times 64$  pixels and corresponding mass spectra were collected from an area of  $500 \mu\text{m} \times 500 \mu\text{m}$  with an ion fluence of  $\sim 1.3 \times 10^{12}$  ions/ $\text{cm}^2$  per image. Depth profiles and ion intensity measurement were collected from the central  $13 \times 13$  pixels of each image, thus eliminating the crater edge effects. The gathered sputter yield and beam-induced chemical damage information were compared to earlier measurements<sup>30</sup> that were carried out on a traditional ToF-SIMS instrument. The design and characteristics of the 20 kV Ar-GCIB system have been described in detail elsewhere.<sup>13</sup> In the Ar-GCIB experiments, the cluster size distribution can be checked by pulsing the ion beam and measuring the flight time of the primary ions between the pulser and the sample stage (see S1 in the Supporting Information). From the known flight distance and kinetic energy, the flight time spectrum can be used to determine the average cluster size of the beam and a Wien filter is used for selecting cluster ions of the desired size. In this study, we have  $Ar_{1000}$ ,  $Ar_{2000}$ ,  $Ar_{3000}$ , and  $Ar_{4000}$  cluster ions at kinetic energies of 10 and 20 keV, respectively. For each gas cluster, the primary ion beam current was measured using a Faraday cup, and the beams used were all adjusted to provide  $\sim 90$ – $120$  pA beam currents. The experimental setup was the same as described above except that the ion fluence applied here was higher,  $\sim 5.5 \times 10^{12}$  ions/ $\text{cm}^2$  per image. Note that in this study all of the depth profiling experiments were performed in negative ion mode at room temperature and no sign of sample charging was noticed.

**Atomic Force Microscopy (AFM) Measurements.** The trehalose film thickness was measured by an AFM (Nanopics 2100, KLA-Tencor, San Jose, CA, USA). This unique type of AFM offers a maximum scanning area of 0.8 mm  $\times$  0.8 mm in contact mode, allowing a convenient one-step measurement of the entire eroded crater. An AFM image of a trehalose film eroded by a 40 keV  $C_{60}^+$  ion source is illustrated in Figure 1. The AFM measurement indicates a 0.7 nm root-mean-square (rms) film roughness and a 150 nm film thickness. Note that the erosion rate of Si is significantly slower than that of trehalose. Therefore, the removed Si thickness should be negligible. This AFM was also employed to determine sputtering yields via the formation of a wedge-shaped crater.<sup>32</sup>

## RESULTS AND DISCUSSION

**Negative Secondary Ion Depth Profiles of Trehalose Films Bombarded by  $C_{60}^+$ .** The negative secondary ion depth profile for a 150 nm trehalose film on Si bombarded by 40 keV  $C_{60}^+$  is shown in Figure 2a, where the trehalose molecular ion ( $M - H$ )<sup>-</sup> at  $m/z$  341 and substrate signal at  $m/z$  168 for  $Si_6^-$  are plotted as a function of  $C_{60}^+$  ion fluence. A total ion fluence of  $\sim 1.05 \times 10^{14}$  ions/cm<sup>2</sup> is used to etch through the film before reaching the Si substrate. The sputter yield volume of trehalose is calculated from the known fluence and film thickness and is

presented in units of sputtered material volume per projectile ion. In this case, one  $C_{60}^+$  primary ion removes 143 nm<sup>3</sup> of material, a value consistent with earlier measurements.<sup>30</sup> In addition, an erosion model developed by Cheng et al.<sup>29</sup> is used to fit the trehalose molecular ion decay profile to quantify the ion beam bombardment induced chemical damage, as shown in Figure 2b. According to the model, the dependence of the secondary ion signal  $S$  on ion fluence  $f$  is governed by

$$S(f) = S_{ss} + (S_0 - S_{ss}) \exp\left[-\left(\frac{Y}{d} + \sigma_D\right)f\right] \quad (1)$$

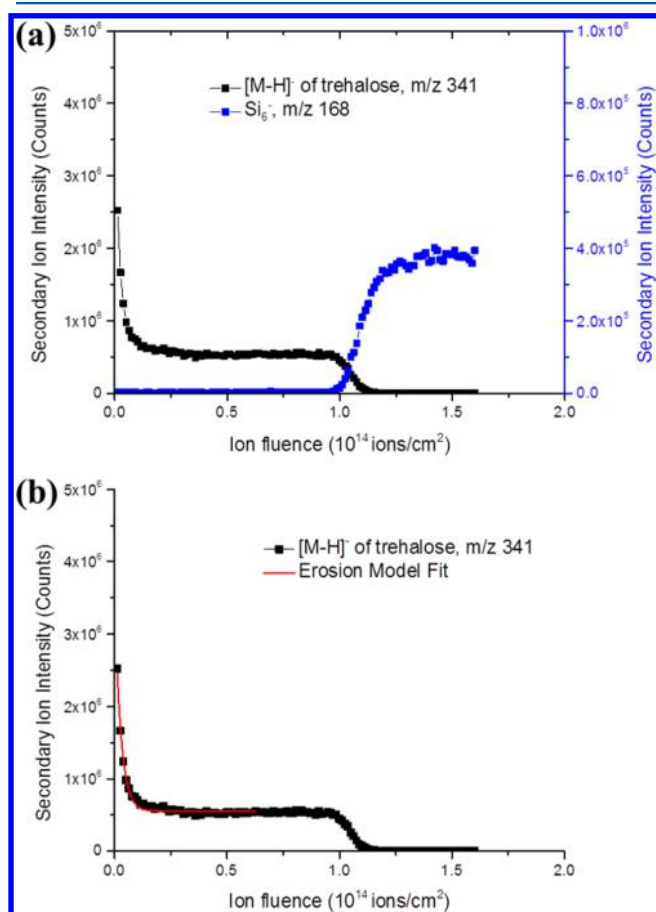
where  $S_0$  is the signal intensity at zero fluence,  $S_{ss}$  is the signal intensity at steady state,  $Y$  is the sputter yield volume,  $d$  is the altered layer thickness,  $\sigma_D$  is the damage cross section, and  $f$  is the primary ion fluence. The value of  $S_{ss}$  is also related to  $Y$  and primary ion beam induced damage as

$$S_{ss} = S_0 \frac{Y}{Y + d\sigma_D} \quad (2)$$

The two variables associated with chemical damage,  $d$  and  $\sigma_D$ , can then be extracted from eqs 1 and 2. For our sample,  $d$  and  $\sigma_D$  are calculated to be  $\sim 25$  and  $\sim 30$  nm<sup>2</sup>, respectively. These values are slightly higher than our earlier results,<sup>30</sup> which is probably associated with the intrinsic water content of the deposited films, as explained by Lu et al.<sup>33</sup> Trehalose films with less water content have a larger ratio value between the initial and steady state signal, indicating an enhanced damage cross section during the ion bombardment, which is the case for the trehalose films investigated in this study. Note that in the previous work, trehalose thin films were all analyzed in positive ion mode, where the trehalose molecular ion peak  $[M + H]^+$  at  $m/z$  343 is of low intensity and the two most abundant trehalose molecule related peaks are quasi-molecular ions  $[M - OH]^+$  at  $m/z$  325 and the sodium adduct  $[M + Na]^+$  at  $m/z$  365. There is less interference of trehalose molecular ion information in negative ion mode, where the only predominant peak of trehalose molecule is  $[M - H]^-$  at  $m/z$  341.

**Negative Secondary Ion Depth Profiles of Trehalose Films Bombarded by Ar-GCIBs.** Eight negative secondary ion depth profiles of the trehalose films obtained using different kinetic energies ( $E$ ) and Ar cluster sizes ( $n$ ) are presented in Figure 3. Depth profiles shown in Figure 3, panels a–c and e, exhibit a shape similar to the one obtained with  $C_{60}^+$ ; namely, the trehalose molecular ion falls quickly into a steady state value. The depth profiles shown in Figure 3, panels d and f–h, however, are distinctly different. In these cases, the trehalose signal initially decreases and then slowly increases to reach a steady state. Note that these unusual depth profiles appear only when  $E/n \leq 5$  eV/atom. Speculation about the reasons behind this behavior is discussed below.

Values of the trehalose sputter yield volume at different kinetic energies and Ar cluster sizes are summarized in Table 1. These results clearly indicate that the sputter yield volume is affected by a combination of kinetic energy and Ar cluster size. Briefly, as shown in Figure 4, the trehalose sputter yield volume decreases with increasing Ar cluster sizes at a given kinetic energy. Moreover, for the same cluster size, the sputter yield volume increases with increasing kinetic energy. Seah<sup>24</sup> has introduced a universal equation for Ar gas cluster sputtering yields to organize the experimental data and to allow rational comparisons to be made. The universal equation that describes the relationship



**Figure 2.** (a) Depth profile of a 150 nm trehalose film obtained with a 40 keV  $C_{60}^+$  ion beam. The secondary ion intensities of the trehalose molecular ion peak at  $m/z$  341  $[M - H]^-$  and substrate signal at  $m/z$  168 for  $Si_6^-$  are plotted as a function of  $C_{60}^+$  ion fluence. (b) Erosion model fit (red line) for the trehalose molecular ion signal in the depth profile of a 150 nm trehalose film bombarded by 40 keV  $C_{60}^+$ .



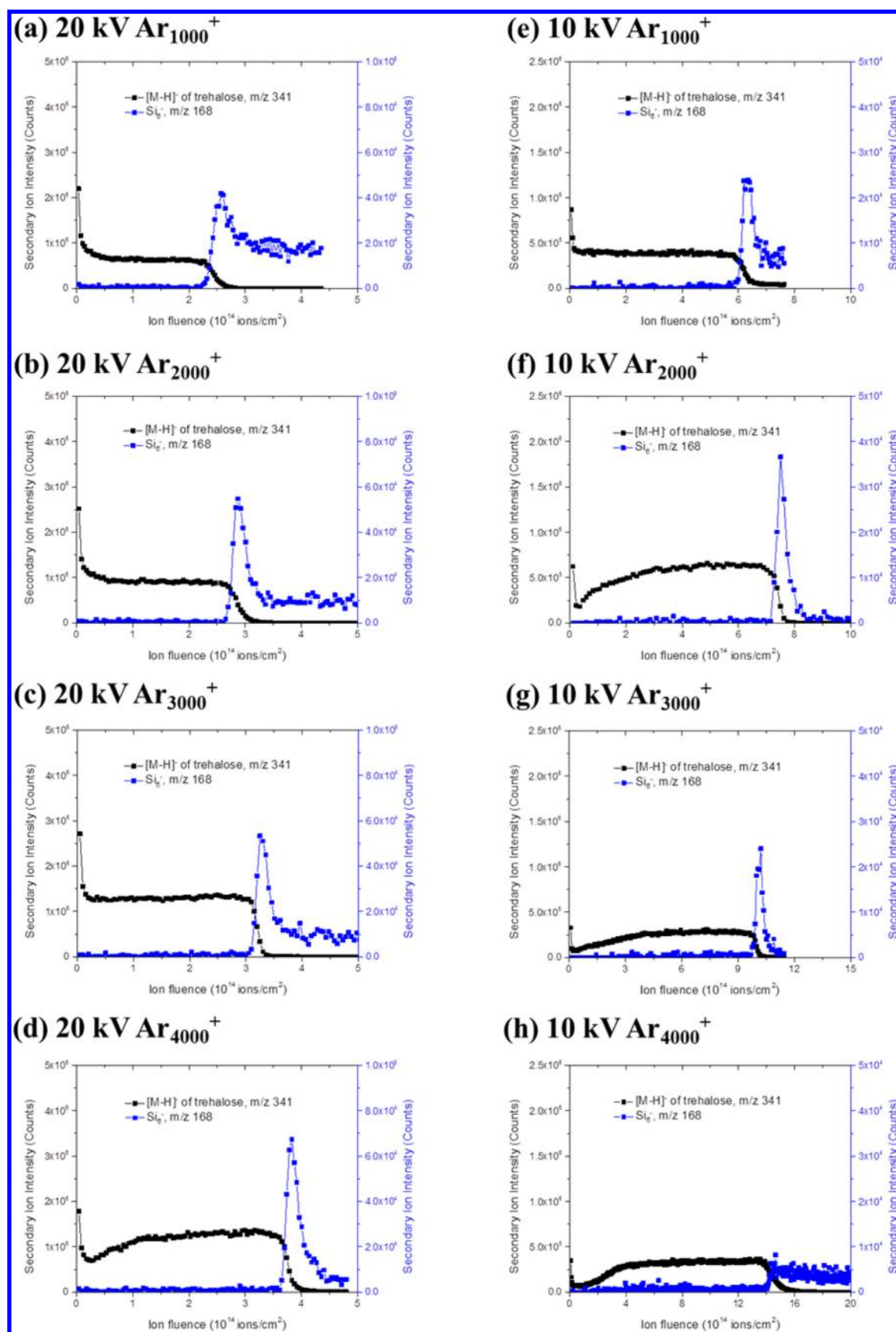


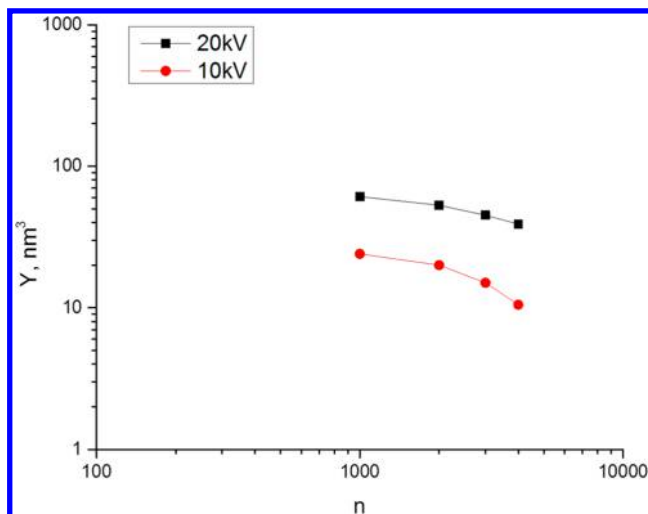
Figure 3. Depth profiles of the 150 nm trehalose films obtained with 10 kV and 20 kV  $\text{Ar}_n^+$  ion beams.

between sputter yield volume per atom ( $Y/n$ ) and the kinetic energy per atom ( $E/n$ ) is defined as

$$Y/n = B(E/An)^q / [1 + (E/An)^{q-1}] \quad (3)$$

**Table 1.** Measured Trehalose Sputter Yield Volume for Different Kinetic Energies and Cluster Sizes of Ar-GCIBs

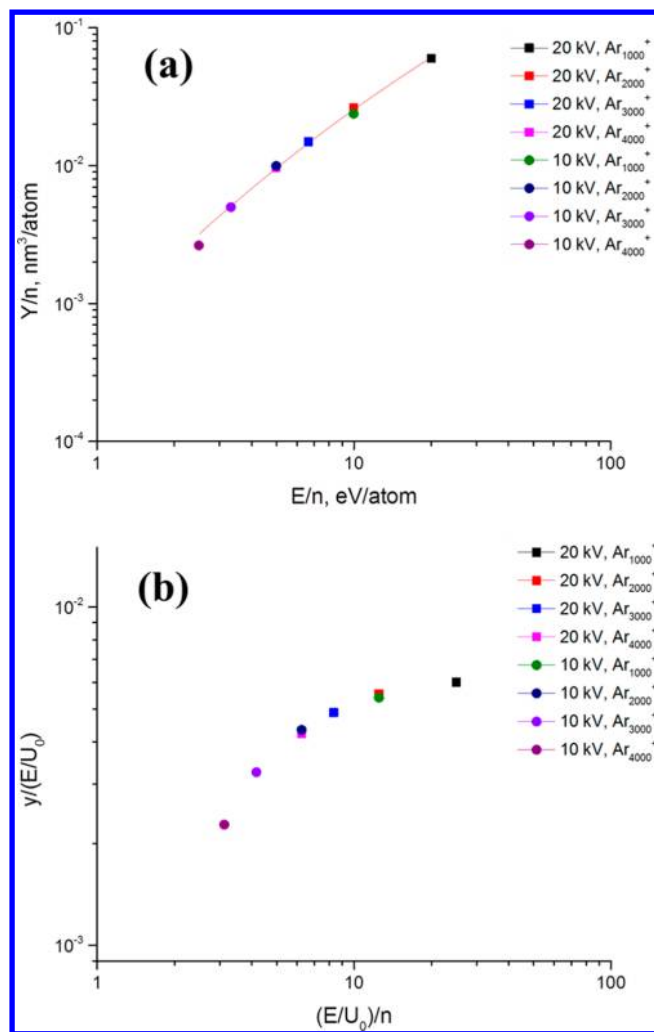
kinetic energy (kV)	sputter yield volume (nm <sup>3</sup> )			
	Ar <sub>1000</sub> <sup>+</sup>	Ar <sub>2000</sub> <sup>+</sup>	Ar <sub>3000</sub> <sup>+</sup>	Ar <sub>3000</sub> <sup>+</sup>
20	61	53	45	39
10	24	20	15	10

**Figure 4.** Dependence of sputter yield volume ( $Y$ ) on cluster size ( $n$ ) for  $\text{Ar}_n^+$  cluster bombardment of trehalose films.

where the parameters  $B$ ,  $A$ , and  $q$  can be determined by fitting eq 3 to the experimental data. Our results show that  $Y/n$  exhibits a nearly linear dependence on  $E/n$  and the parameters  $B$ ,  $A$ , and  $q$  have values of 0.018 nm<sup>3</sup>, 4.8 eV, and 2.0, respectively. These values are close to the ones reported for other organic materials.<sup>24,34</sup>

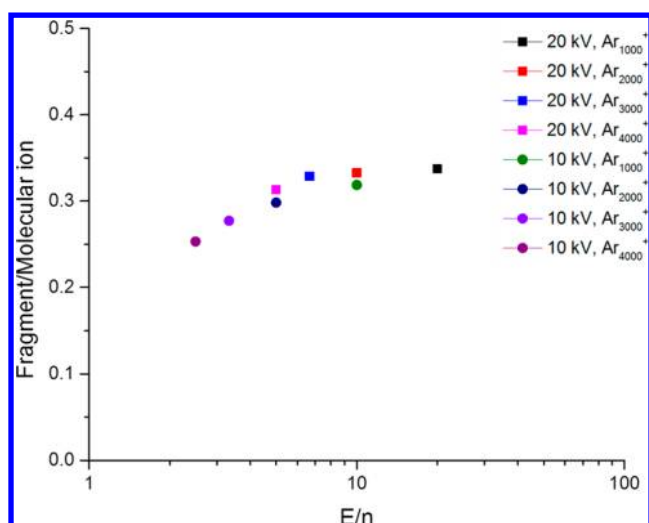
Using a more fundamental approach, Paruch et al.<sup>23</sup> have recently suggested taking cohesive energy ( $U_0$ ) of the analyte into consideration. Therefore, our data were replotted as  $y/(E/U_0)$  versus  $(E/U_0)/n$ , as shown in Figure 5b. Note that  $y$  is the sputter yield in units of sputtered material molecules per projectile ion and  $U_0$  is defined as the energy needed to free a molecule from the substrate. For trehalose, it is mainly the intermolecular hydrogen bond attractions that hold the substance together, and its cohesive energy is estimated to be  $\sim 0.8$  eV for a trehalose molecule. The estimation is based on the assumption that the cohesive energy is equal to the heat of sublimation.<sup>35,36</sup> The plot shows that in the low  $(E/U_0)/n$  portion, the sputter yield is low and increases with increasing energy, whereas when it passes the threshold value ( $(E/U_0)/n = S/U_0$ ), the sputter yield remains almost constant. The low sputter yield in the low  $(E/U_0)/n$  portion is probably associated with the unusual depth profiles shown in Figure 3d,f–h. We will come back to this issue below.

The next step is to gain a better understanding of the molecular sputtering process of the trehalose films under  $\text{Ar}_n^+$  cluster bombardment, specifically regarding the creation of chemical damage. The erosion model mentioned earlier can be successfully applied to those normal trehalose molecular ion depth profiles shown in Figure 3a–c,e. The calculated  $d$  and  $\sigma_D$  values are  $\sim 5$  and 17 nm<sup>2</sup>, 17 and 17 nm<sup>2</sup>, 13 and 19 nm<sup>2</sup>, and 10 and 23 nm<sup>2</sup> for 10 kV Ar<sub>1000</sub><sup>+</sup>, 20 kV Ar<sub>1000</sub><sup>+</sup>, 20 kV Ar<sub>2000</sub><sup>+</sup>, and 20 kV Ar<sub>3000</sub><sup>+</sup>, respectively. It appears that for the same cluster ( $\text{Ar}_{1000}^+$ ), higher kinetic energy yields a higher  $d$  value, whereas

**Figure 5.** (a) Dependence of  $Y/n$  on  $E/n$  for  $\text{Ar}_n^+$  cluster bombardment of trehalose films. The red line represents a fit to the universal equation (eq 3) for argon gas cluster sputtering yields proposed by Seah.<sup>24</sup> (b) Dependence of  $y/(E/U_0)$  on  $(E/U_0)/n$  for  $\text{Ar}_n^+$  cluster bombardment of trehalose films.

$\sigma_D$  remains nearly constant. Moreover, the results show that the  $d$  value is decreasing with increasing cluster size at 20 kV ( $\text{Ar}_{1000}^+ < \text{Ar}_{2000}^+ < \text{Ar}_{3000}^+$ ), whereas  $\sigma_D$  is increasing with increasing cluster size. It seems that  $\sigma_D$  is related to the actual size of the cluster. Therefore, a larger cluster will have a higher  $\sigma_D$  value. The  $d$  value is mainly associated with  $E/n$ . At the same kinetic energy, a larger cluster has a lower value of  $E/n$ , so the energy is deposited closer to the surface, which results in a smaller  $d$  value.

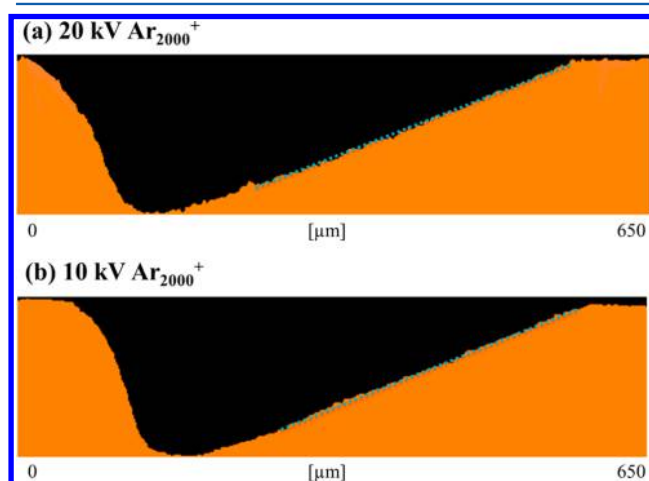
The intensity of the first data point of each depth profile acquired with  $\text{Ar}_n^+$  is shown in Figure 6 as a function of  $E/n$ , and one finds that  $\text{Ar}_n^+$  with a smaller  $E/n$  value has a smaller fragment to molecular ion ratio, which indicates less damage. This finding can be further confirmed from the trehalose molecular ion depth profiles shown in Figure 3, where the span between trehalose molecular ion intensity at the first data point and the steady state becomes narrower as the  $E/n$  value decreases. Note that the signal level of the first acquired data point on the freshly prepared trehalose film is quite reproducible and no significant fluctuation is observed. In principle, the unusual shape of the profiles shown in Figure 3d,f–h can also be interpreted in terms of the erosion dynamics model, if the assumption of a constant total sputter yield is dropped.<sup>37</sup> If the



**Figure 6.** Dependence of the ratio of the intensity of the trehalose fragment at  $m/z$  179 to the trehalose molecular ion at  $m/z$  341 from the first data point of each depth profile as a function of  $E/n$ .

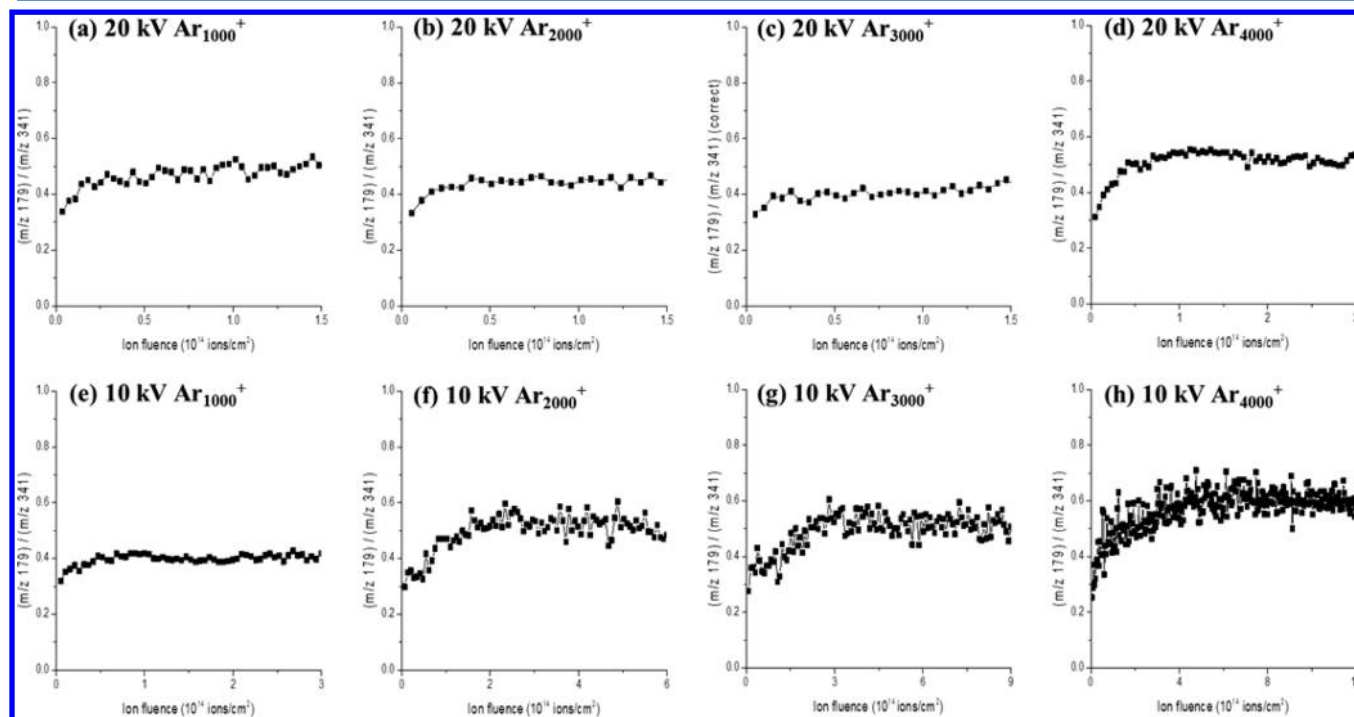
yield variation is slow, the system will follow eq 1 into a quasi-steady-state regime, where the molecular ion signal follows a gradual change of  $Y$  via eq 2. The observed signal rise would then correspond to an increasing sputter yield, which leads to a faster removal of the fragmentation debris produced by a projectile impact. As a consequence, the accumulated damage should be reduced and one should observe a decreasing signal of fragments as compared to the molecular ion. The ratio of the intensity of the trehalose fragment at  $m/z$  179 to the trehalose molecular ion at  $m/z$  341 as a function of primary ion fluence is displayed in Figure 7. It is evident that the ratio increases with increasing fluence, indicating the buildup of more damage while the molecular ion signal increases. To examine the role of possible

sputter yield variations further, a wedge crater was eroded as shown in Figure 8. Briefly, the wedge crater was created by

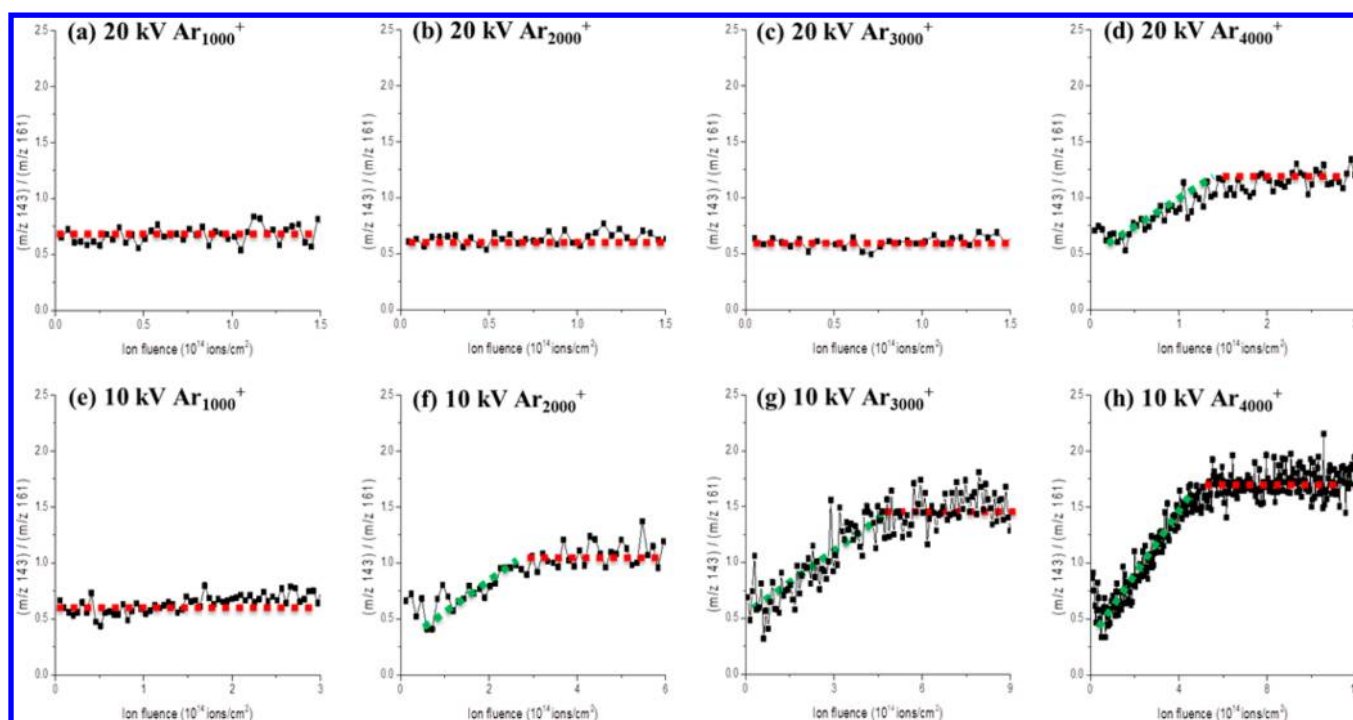


**Figure 8.** AFM image of the wedge crater eroded into a 150 nm trehalose film by (a) a 20 kV  $\text{Ar}_{2000}^+$  ion beam and (b) a 10 kV  $\text{Ar}_{2000}^+$  ion beam. Note the slope of the bevel remains as a straight line before the crater reaches the Si substrate.

repeating the raster as many times as there are pixels in one line or lines in one raster frame. In each of these raster frames, one more line was skipped. In our case, the beam was scanned across a  $500 \mu\text{m} \times 500 \mu\text{m}$  area using a  $64 \times 64$  pixel raster. The raster was repeated 64 times, scanning 64 lines in the first frame, 63 lines in the second frame, etc., until the last scan was only over a single line. One set of these wedge frames therefore consists of 64 rasters. The dwell time on each pixel was set to about 20  $\mu\text{s}$ , which is the minimum dwell time that ensures stable beam position on a pixel. The number of wedge frame sets during a



**Figure 7.** Ratio profiles of the intensity of the trehalose fragment ( $m/z$  179) to the intensity of trehalose molecular ion ( $m/z$  341) as a function of ion fluence under different  $\text{Ar}_n^+$  bombarding conditions.



**Figure 9.** Ratio profiles of the intensity of two characteristic trehalose fragments ( $m/z$  143 to  $m/z$  161) as a function of ion fluence under different  $\text{Ar}_n^+$  bombarding conditions.

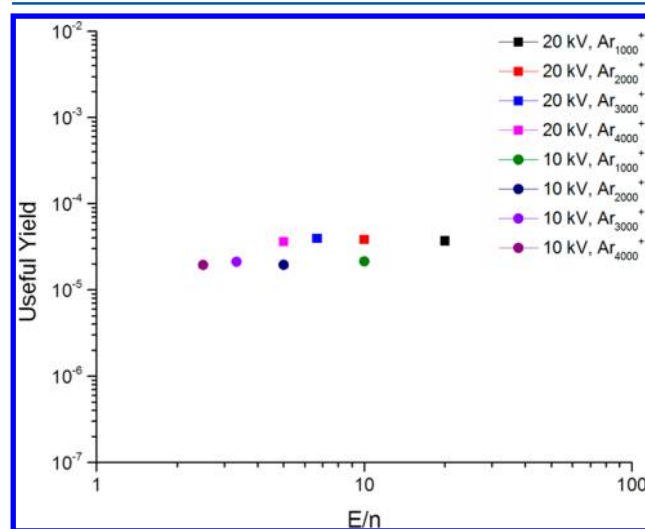
sputter erosion step was calculated such that the set total sputtering time in an erosion cycle was reached. As outlined in detail elsewhere, a fluence-dependent sputter yield variation manifests itself as a curved crater bottom in such an experiment.<sup>38</sup> Because all craters observed in Figure 8 exhibit a straight line profile, the unusually shaped depth profiles are not caused by a variation in sputter yield.

Now, the remaining question is what factor leads to the two different shapes of trehalose molecular ion depth profiles shown in Figure 3. If sputter yield changes are excluded, possible explanations for the observed increase of the molecular ion signal are that there is an increasing survival probability against fragmentation or that there is an enhanced ionization of the sputtered molecules. To examine this further, the ratio of the intensity of two characteristic trehalose fragments ( $m/z$  143 to  $m/z$  161) is plotted as a function of ion fluence for each  $\text{Ar}_n^+$  bombarding condition, as presented in Figure 9. For those normal trehalose molecular ion depth profiles shown in Figure 3a–c,e, this ratio remains virtually constant, see Figure 9a–c,e, which confirms that a true steady state is reached under these conditions. Note that for all of these conditions,  $E/n > 5$  eV/atom. However, for the unusual depth profiles shown in Figure 3d,f–h, the ratio between the two fragments increases throughout the same fluence interval where the molecular ion signal increases, until it finally reaches a steady state, as shown in Figure 9d,f–h. In connection with Figure 7, this finding indicates that the observed increase of the molecular ion signal is accompanied by increasing fragmentation as well. Hence, this signal increase must be attributed to an increasing ionization probability of the emitted molecules. Note that the mass difference ( $\Delta m$ ) between the two fragments is 18, which indicates that there could be a water content change during the depth profiling. The extra water can cause trehalose ionization probability to increase during the experiments.<sup>33</sup>

Finally, it is possible to acquire information about the useful yield of trehalose under different  $\text{Ar}_n^+$  bombarding conditions. Here, the useful yield is defined as the ratio of the number of detected molecular ions to the number of the sputtered molecule equivalents, and its value is estimated via

$$\text{useful yield} = S_1/[f \times A \times y] \quad (4)$$

where  $S_1$  is the molecular ion signal intensity at the first data point,  $f$  is the primary ion fluence used to take the spectra,  $A$  is the data analysis area, and  $y$  is the sputter yield in units of sputtered molecule equivalents per projectile ion. Note that the amount of signal transmission loss in the mass spectrometer is not considered here. As shown in Figure 10, the useful molecular



**Figure 10.** Dependence of useful molecular ion yield of trehalose on  $E/n$  for  $\text{Ar}_n^+$  cluster bombardment of trehalose films.



ion yield of trehalose increases with increasing kinetic energy but remains almost the same with increasing Ar cluster sizes at a given kinetic energy, indicating that the useful yield is dependent only upon kinetic energy.

## CONCLUSION

The effect of projectile size and kinetic energy of Ar-GCIBs on the molecular depth profiling of trehalose thin films has been investigated with the purpose of finding the optimal cluster size and cluster energy to improve the quality of depth profiles for organic materials. Our results suggest that when  $E/n > 5$  eV/atom, normal depth profiles could be obtained with relatively high sputter yield, whereas when  $E/n \leq 5$  eV/atom, unusual depth profiles, which show ionization efficiency variation, are acquired with low sputter yield. However, this observation does not imply that  $E/n$  values should be as high as possible. In fact, the  $E/n$  value should be kept above but close to the threshold value (5 eV/atom in our case) because ion beam bombardment induced chemical damage is limited.

Although this study has focused upon using trehalose as a model system, we believe the conclusions can be generalized for many other organic materials. In preliminary studies, we have found similar behavior for other organic thin films including sucrose, dipalmitoylphosphatidylcholine (DPPC), and Gly-Gly-Tyr-Arg (GGYR) (see S2 in the Supporting Information). It will be of interest to determine how much the threshold value for creating depth profiles without artifacts changes with molecule type. In general, however, our study shows that high kinetic energy increases the useful molecular ion yield of trehalose. Hence, a combination of high kinetic energy and large cluster size will ultimately optimize molecular depth profiling experiments with SIMS.

## ASSOCIATED CONTENT

### Supporting Information

Depth profiles of sucrose, DPPC, and GGYR thin films obtained with a 20 kV Ar<sub>4000</sub><sup>+</sup> ion beam. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b03482.

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### Notes

The authors declare no competing financial interest.

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