Molecular depth profiling of trehalose using a C_{60} cluster ion beam

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ABSTRACT

Molecular depth profiling of organic overlayers was performed using a mass selected fullerene ion beam in conjunction with time-of-flight (TOF-SIMS) mass spectrometry. The characteristics of depth profiles acquired on a 300-nm trehalose film on Si were studied as a function of the impact kinetic energy and charge state of the C_{60} projectile ions. We find that the achieved depth resolution depends only weakly upon energy.

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1. Introduction

The advent of cluster ion beams as projectiles for SIMS has opened up the possibility of molecular depth profiling [1]. A key issue is the depth resolution achievable under bombardment of molecular surfaces with energetic cluster ions. A number of studies have addressed this question mainly by determining the measured width of interfaces between different organic films [2,3] or an organic film and the substrate [4–11]. A fundamental problem occurs in such analysis if the sputter erosion rate strongly varies between the different layers. Different interpolation schemes have been used in order to calibrate the relationship between projectile ion fluence and depth in the interface region [5,12], leading to a relatively broad scatter of published interface width data. In this paper, a more general approach is proposed for depth scale calibration across an interface, which is based on the variation of both the film and the substrate related signals. This method is then applied to a data set of depth profiles measured on a 300 nm trehalose film on Si with different projectile energies and charge states.

2. Experimental

The experiments were performed using an imaging TOF-SIMS instrument described in detail elsewhere [13]. The system is equipped with a microfocus fullerene ion source delivering a mass selected C_{60} ion beam which can be accelerated to 40 keV, focused into a sub-μm spot size and impinges under $40°$ with respect to the surface normal. Depending on the selected charge state, the impact energy of the projectile ions can be chosen up to 120 keV. Secondary ion mass spectra were acquired using the ion beam in a pulsed mode with pulse duration of about 50 ns. The ion extraction field was also pulsed and switched on shortly ($\sim$100 ns) after the projectile pulse in order to ensure that the sample was always at ground potential during the ion bombardment.

Depth profiles were acquired by alternating between sequential data acquisition and sputter erosion cycles. During the erosion cycles, the C_{60}^+ beam was operated in dc mode and raster scanned across a surface area of about 200 μm $\times$ 280 μm using a TV-like analog pattern. Each erosion cycle comprised a bombardment time of 1 s during the first 10 and 6 s thereafter, corresponding to an ion fluence averaged over the entire raster area of about 2×10^{12} and 1.2×10^{13} C_{60}^+/cm^2 per cycle, respectively. During data acquisition, the pulsed ion beam was raster scanned across a surface area of half the side length in both dimensions centered within the sputter crater. A total of 10^4 ion pulses were accumulated during acquisition of each mass spectrum, thus keeping the associated ion fluence below 10^{10} C_{60}^+/cm^2.

The sample was a 300-nm layer of trehalose ($C_{12}H_{22}O_{11}$) spin-cast onto a Si substrate. Details of the preparation procedure have been described elsewhere [5]. The film was inspected for uniformity both optically and by atomic force microscopy (AFM). The volume of the eroded crater was determined after the analysis using a large-view (800 μm $\times$ 800 μm) AFM.

3. Results and discussion

The raw data of a sputter depth profile obtained under bombardment with 40-keV C_{60}^{1+} projectile ions is shown in Fig. 1. The $(M-OH)^+$ secondary ion signal at m/z 325 representing the trehalose film exhibits a fast initial increase, followed by an exponential decrease to a steady state, which then persists during

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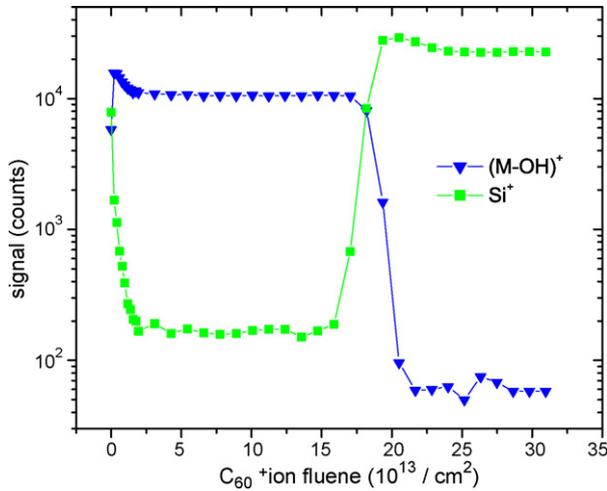E-mail address: andreas.wucher@uni-due.de (A. Wucher).

Fig. 1. Integrated intensity of (M−OH)⁺ trehalose signal (m/z 325) and Si⁺ substrate signal (m/z 28) vs. fluence of C_{60}^+ projectile ions of 40 keV.

the removal of the entire overlayer. The interface to the underlying Si substrate is clearly visible by the decay of the trehalose signal and the rise of the Si⁺ signal.

The width of the film–substrate interface represents an important quantity characterizing the depth resolution. An accurate determination of the interface width requires calibration of the eroded depth as a function of projectile ion fluence. For that purpose, the total eroded depth was determined by examining the surface topography after completion of the depth profile by AFM. In establishing the depth scale, care must be taken since the erosion rate strongly varies between the trehalose film and the substrate. In our earlier work, we used a linear interpolation of the erosion rate using the measured Si⁺ substrate signal normalized to its interface maximum as a weighting factor between the erosion rates $\dot{z}_{Tre}$ and $\dot{z}_{Si}$, respectively [5]. This procedure was adopted from a similar approach used by Wagner [12]. It bears, however, ambiguity since one could in principle also use the trehalose signal (normalized to its steady state value) for the same purpose. As shown in Fig. 2, this may significantly influence the depth scale calibration throughout the interface region, thus altering the measured width of the film–substrate interface. Therefore, we

choose here to interpolate the erosion rate according to

$$\dot{z} = c_{Tre} \cdot \dot{z}_{Tre} + c_{Si} \cdot \dot{z}_{Si} \qquad (1)$$

with weighting factors c_{Tre} and c_{Si} being determined from *both* signals I_{Tre} and I_{Si} as

$$c_X = \frac{I_X/I_X^{max}}{I_{Tre}/I_{Tre}^{max} + I_{Si}/I_{Si}^{max}}. \qquad (2)$$

I_{Tre}^{max} and I_{Si}^{max} denote the respective signal maxima detected throughout the depth profile. Using a known substrate erosion rate of Si—measured independently by eroding craters into the bare Si substrate, the value of $\dot{z}_{Tre}$ can then be determined by integrating Eq. (1) over the entire depth profile and equating the result to the measured crater depth. The value $\dot{z}_{Tre}$ determined in this way is then inserted into Eq. (1) to calculate the depth corresponding to a specific erosion time or ion fluence.

In order to evaluate the depth resolution, the interface width Δz between the trehalose film and the Si substrate is determined from the transition of measured SIMS signals. In principle, both the decay of a film related signal or the rise of a substrate related signal can be used for that purpose. An expanded view of the interface region in Fig. 1 is shown in Fig. 3. Assuming a Gaussian response function, the interface width is determined from 84 to 16% transition of the respective signal. The resulting values of Δz obtained from either the trehalose (M−OH)⁺ or the Si⁺ signal are depicted in Fig. 3. Although the difference is apparently small, it should be noted that larger differences between both values have been observed for other bombarding conditions.

When determining the measured depth, it is important to account for possible artifacts arising, for instance, from a lateral inhomogeneity of the erosion rate or the overlayer thickness. Although a gating method was implied by taking spectral data only from a field of view that had half the dimension of the erosion area, the measured interface width may still be broadened by such effects. In fact, imaging depth profiles taken with the same experimental setup and on the same system investigated here have revealed that the interface width decreases if the lateral area over which the mass spectrometric signal is acquired becomes smaller. Based on this observation, a "true" interface width of about 8 nm was determined by extrapolating the measured interface width to zero acquisition
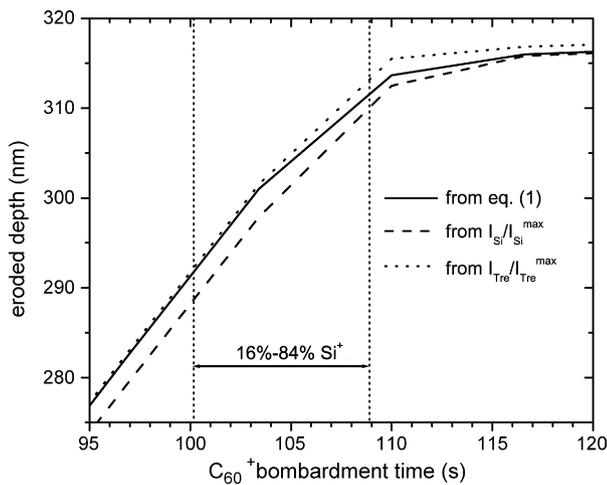

Fig. 2. Depth scale calibration obtained from the data in Fig. 1 using either the normalized Si signal (dotted line), the normalized trehalose signal (dashed line) or the values c_{Tre} and c_{Si} as weighing factors between trehalose and silicon erosion rates.
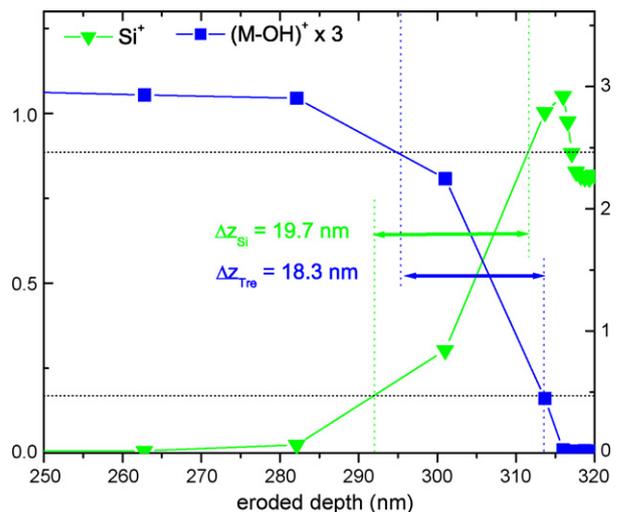

Fig. 3. Interface region of data plotted in Fig. 1 after depth scale calibration and interface width. Dotted lines: 84 and 16% of maximum signal.
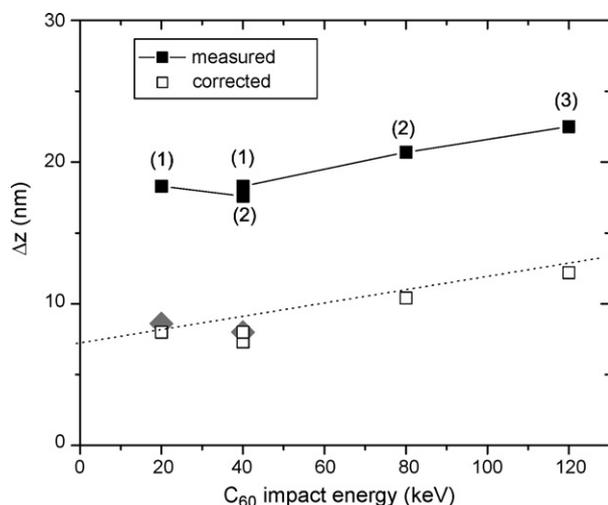
Fig. 4. Interface width vs. impact energy of C_{60} projectile ions. Closed symbols: measured values; open symbols: corrected for crater effect. The numbers in brackets denote the charge state of the projectile ion.

area [14]. We therefore conclude that about half of the apparent interface width determined in Fig. 3 is produced by such artifacts.

In order to further characterize the depth resolution, we have repeated the experiment for different impact energy of the impinging C_{60} clusters. This experiment was performed by (i) varying the ion acceleration voltage between 40 and 20 kV and (ii) varying the projectile charge state q between $q = 1$ and $q = 3$. The resulting depth profiles were subjected to the same data reduction process as described above. Details regarding, for instance, the impact energy dependence of the trehalose erosion rate will be published elsewhere [15]. The resulting interface width determined from the trehalose signal is displayed in Fig. 4 (full symbols). In light of the discussion stated above, we assume the same artifact to be superimposed on the measured data and therefore subtract 9 nm from each measured value. The resulting corrected interface widths are depicted as open symbols. Several observations are notable. First, the data taken for (40 kV, $q = 1$) are practically identical to those obtained for (20 kV, $q = 2$). This finding is expected, since both conditions produce the same impact energy of 40 keV. It is nevertheless notable since it indicates that at least for the system investigated here the projectile charge state does not seem to be important. Second, the depth resolution deteriorates only slightly with increasing impact energy. The apparent slight increase of the interface width from 40 to 20 keV is within the experimental reproducibility and therefore not statistically

relevant. The validity of the crude correction procedure is corroborated by the data point shown as a diamond, which was obtained from an earlier depth profile obtained with a previous version of the C_{60} ion source, using the same data evaluation procedure as describe above except the correction.

4. Conclusion

In contrast to most applications on inorganic samples, molecular sputter depth profiling of organic thin films often involves strongly varying erosion rates between different layers. A protocol is described to correct for theses changes and convert the projectile ion fluence into corrected eroded depth. Using this script, it is found that the interface width characterizing the depth resolution during profiling a 300-nm trehalose overlayer on Si exhibits only a weak dependence on the cluster impact energy. If corrected for lateral inhomogeneity, the data indicate an intrinsic depth resolution of about 8–9 nm which appears to be rather independent of impact energy below 40 keV. The physical origin of this value is unclear at the present time. It does, however, agree with model simulations of the altered surface layer formed under bombardment of metals with energetic C_{60} projectiles.

References

[1] N. Winograd, Anal. Chem. 77 (2005) 142A.
[2] A.G. Sostarecz, S. Sun, C. Szakal, A. Wucher, N. Winograd, Appl. Surf. Sci. 231/232 (2004) 179.
[3] M.S. Wagner, Anal. Chem. 77 (2005) 911.
[4] J. Cheng, N. Winograd, Appl. Surf. Sci. 252 (2006) 6498.
[5] J. Cheng, N. Winograd, Anal. Chem. 77 (2005) 3651.
[6] C. Mahoney, A. Fahey, G. Gillen, Anal. Chem. 79 (2007) 828.
[7] C. Mahoney, S. Roberson, G. Gillen, Anal. Chem. 76 (2004) 3199.
[8] M.S. Wagner, G. Gillen, Appl. Surf. Sci. 231/232 (2004) 169.
[9] J.S. Fletcher, X.A. Conlan, N. Lockyer, J.C. Vickerman, Appl. Surf. Sci. 252 (2006) 6513.
[10] E.A. Jones, J.S. Fletcher, C.E. Thompson, D.A. Jackson, N.P. Locklyer, J.C. Vickerman, Appl. Surf. Sci. 252 (2006) 6844.
[11] X.A. Conlan, I.S. Gilmore, A. Henderson, N.P. Lockyer, J.C. Vickerman, Appl. Surf. Sci. 252 (2006) 6526.
[12] M.S. Wagner, Anal. Chem. 76 (2004) 1264.
[13] R.M. Braun, P. Blenkinsopp, S.J. Mullock, C. Corlett, K.F. Willey, J.C. Vickerman, N. Winograd, Rapid Commun. Mass Spectrom. 12 (1998) 1246.
[14] A. Wucher et al., these proceedings.
[15] A. Wucher, J. Cheng, N. Winograd, J. Phys. Chem. (2008), submitted.