



Three-dimensional molecular imaging using mass spectrometry and atomic force microscopy

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ABSTRACT

We combine imaging ToF-SIMS depth profiling and wide area atomic force microscopy to analyze a test structure consisting of a 300 nm trehalose film deposited on a Si substrate and pre-structured by means of a focused 15-keV Ga⁺ ion beam. Depth profiling is performed using a 40-keV C₆₀⁺ cluster ion beam for erosion and mass spectral data acquisition. A generic protocol for depth axis calibration is described which takes into account both lateral and in-depth variations of the erosion rate. By extrapolation towards zero analyzed lateral area, an “intrinsic” depth resolution of about 8 nm is found which appears to be characteristic of the cluster-surface interaction process.

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1. Introduction

Since the advent of cluster ion beams as projectiles for SIMS has opened up the possibility of molecular sputter depth profiling, a number of studies have been devoted to the combination of imaging analysis and sputter erosion for 3D characterization of molecular samples [1–4]. A key question in these experiments regards the accurate conversion of the projectile ion fluence into eroded depth. In principle, both composition variations as well as surface topography can influence sputter erosion rates, thus making the depth scale calibration a tedious task. In this paper, we investigate the role of such inhomogeneities on a patterned test sample and describe a protocol to correct for the observed effects. Similar to an approach reported by Wagter et al. [5], the surface topography is examined before and after acquisition of a depth profile, allowing the total eroded depth at each pixel of the image to be separately determined.

2. Experimental

The experiments were performed using an imaging ToF-SIMS instrument described in detail elsewhere [6]. The system is equipped with a liquid metal ion source as well as a microfocus fullerene ion source. Secondary ion images were acquired using a pulsed, mass selected 40-keV C₆₀⁺ ion beam of about 20 pA current, 50 ns pulse length and roughly 1 μm spot size impinging under 40° with respect to the surface normal.

The sample was a 300-nm layer of trehalose doped with a 1% concentration of a peptide (GGYR) which was spin-cast onto a Si substrate [7]. The film was patterned using a focused 15-keV Ga⁺ ion beam, and the resulting surface structure was characterized by a wide area atomic force microscope (AFM) [8]. First, a uniform ion fluence of 1.5×10^{15} Ga⁺/cm² was applied by rastering the dc beam across an area of 160 μm × 200 μm, creating a shallow crater of 30 nm depth. Then, deep trenches were etched into parts of this crater by scanning the focused dc beam along predefined lines forming the letters “PSU”. More details about this pattern have been reported previously [8].

After patterning and AFM inspection, the sample was subjected to imaging depth profile analysis using the 40-keV C₆₀⁺ cluster ion beam. The depth profile was acquired by alternating between sequential data acquisition and sputter erosion cycles. During data acquisition, a chemical image of the surface was recorded by raster scanning the pulsed C₆₀⁺ ion beam in a digital pattern of 256 × 256 pixels over an area of 280 μm × 200 μm. A total of 20 ion pulses were directed to each pixel. During the erosion cycles, the C₆₀⁺ beam was operated in dc mode and rastered using a TV-like analog pattern with a scan area nearly equivalent to the scan area utilized during image acquisition. Each erosion cycle comprised a bombardment time of 10 s, corresponding to an ion fluence averaged over the entire raster area of about 2×10^{12} C₆₀⁺/cm² per cycle.

3. Results and discussion

In order to convert the acquired stack of SIMS images into a true 3-D distribution of analyte species, the initial surface topography before depth profiling was determined by an AFM image taken

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prior to the depth profile analysis (see insert in Fig. 2). In order to calibrate the depth scale as a function of projectile ion fluence, the surface topography was examined again after completion of the depth profile. The total eroded depth was then determined at each pixel by carefully registering the resulting AFM image with both the ToF-SIMS images and the AFM image taken before.

Surprisingly, it is found that, depending upon the exact location within the analyzed surface area, the “eroded” depth, i.e., the height difference between both profiles, varies between values of about +300 nm to –50 nm. While the former corresponds to the removal of the organic overlayer, the latter reveals deposition of material rather than erosion as a consequence of ion bombardment. It is obvious that in these areas the definition of a depth scale is problematic.

In the “virgin” portions of the film that have not been exposed to the Ga⁺ ion beam, depth profiles should closely resemble those measured on unstructured films [7,9]. In this lateral area (“region 1”), the depth scale can be calibrated by linear interpolation between the erosion rates \dot{z}_{Tre} and \dot{z}_{Si} of the trehalose film and of the Si substrate according to

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

with weighing factors c_{Tre} and c_{Si} being determined from the measured SIMS signals I_{Tre} ($[M-OH]^+$ at m/z 325) and I_{Si} (Si^+ at m/z 28) as

$$c_X = \frac{I_X/I_X^{max}}{\sum_Y I_Y/I_Y^{max}} \quad (X, Y = Tre, Si), \quad (2)$$

where 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 (0.01 nm/s), the value of \dot{z}_{Tre} can then be determined from the measured crater depth (280 nm) by integrating Eq. (1) over the entire depth profile. For the different parts of the unstructured trehalose film, this results in $\dot{z}_{Tre} = 0.37 \pm 0.1$ nm/s.

The second important lateral area (“region 2”) includes those portions of the film which have been subjected to Ga⁺ ion pre-bombardment within the shallow crater outside of the deep trenches. A Ga⁺ secondary ion signal is clearly visible in this region, which disappears after C₆₀⁺ bombardment to a fluence of about $8 \times 10^{13} \text{ cm}^{-2}$. At the same time, the signal characterizing the trehalose film rises to the same level as the undisturbed film (region 1), thus indicating that the surface layer modified by the Ga⁺ pre-bombardment has been removed and the original film underneath is being analyzed, until eventually the substrate is reached. Assigning an erosion rate $\dot{z}_{Tre/Ga}$ to the altered surface layer,

$$\dot{z} = c_{Ga} \cdot \dot{z}_{Tre/Ga} + c_{Tre} \cdot \dot{z}_{Tre} + c_{Si} \cdot \dot{z}_{Si}. \quad (3)$$

Inserting \dot{z}_{Tre} and \dot{z}_{Si} from above, it is now possible to integrate Eq. (3), compare with the total eroded depth in this area (250 nm) and solve for $\dot{z}_{Tre/Ga} = 0.13$ nm/s. Averaging the erosion rate during the removal of the entire altered layer, a value of 0.18 nm/s is obtained which is significantly lower than that of pure trehalose, indicating that either the chemical damage induced by the Ga⁺ pre-bombardment or the implantation of Ga into the film leads to a pronounced reduction of the sputtering yield.

Using Eqs. (1) and (3), the sputter time can be converted into eroded depth. In order to compare depth profiles taken from the two regions, the depth scale zero was set at the original, virgin film surface, and a constant value z_0 was added to the sputtered depth to account for Ga⁺ pre-erosion. The resulting depth profiles are shown in Fig. 1. The actual value of z_0 was fitted to ensure that the film-substrate interface is located at the same depth in both regions, resulting in $z_0 = 29$ nm in good agreement with the AFM

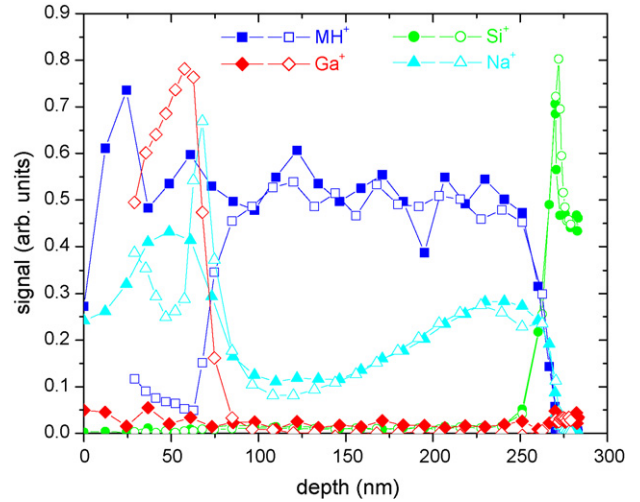


Fig. 1. Depth profile obtained from the virgin region (closed symbols) and the Ga pre-bombarded region (open symbols). Signals are normalized to the number of pixels in each region.

data. It is seen that a surface layer of about 42 nm thickness has been altered by the 15-keV Ga⁺ bombardment.

The depth resolution is assessed by the measured Trehalose-Si interface width. In principle, this value can be determined from either the decay of film related or the rise of substrate related signals. For the data displayed in Fig. 1, $\Delta z = 17$ (16) nm and 15 (14) nm are obtained for the two different regions, if the 84–16% transition of the $(M-OH)^+$ trehalose signal (Si^+ substrate signal) is analyzed.

In judging these values, it is of note that the signals have been integrated over a certain lateral area of the acquired images. Therefore, the measured interface width may in principle contain contributions arising from lateral inhomogeneities of either the trehalose overlayer thickness or the erosion rate. In order to investigate the significance of such effects, surface areas of different sizes were defined within region 1 and the procedure described above was repeated with the signals integrated over the corresponding pixels. The resulting variation of the interface width is displayed in Fig. 2. It is clearly seen that there is an area effect, contributing about half of the interface width determined from the data of Fig. 1. If extrapolated to zero area, the data indicate an “intrinsic” depth resolution of about 8 nm, which appears to be

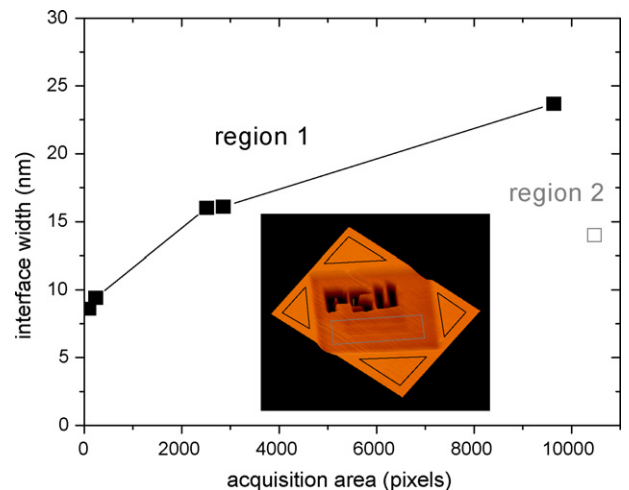


Fig. 2. Interface width vs. number of pixels contained in the analyzed surface area.

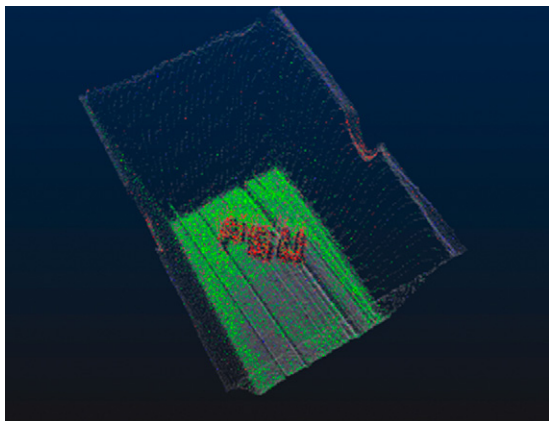


Fig. 3. True 3D representation of peptide MH^+ (blue), Si^+ (green) and Ga^+ (red) ToF-SIMS signals while crossing the interface between trehalose film and Si substrate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

characteristic of the cluster-surface interaction process. This finding can be compared with model simulations of C_{60} impinging onto silver, indicating an altered layer of several nm increasing nearly linearly with impact energy [10]. Extrapolating these results to 40 keV, one obtains a value of about 7 nm, which is in good agreement with the “intrinsic” depth resolution obtained here.

The origin of the observed area effect becomes clear if the full 3D information is utilized. In order to achieve a true 3D representation of the acquired ToF-SIMS data, the depth scale calibration outlined above was applied to each pixel of the imaged area separately. Details of this procedure have been described elsewhere [8]. As a result, the 3D-representation of one single SIMS image acquired within the interface region is shown in Fig. 3. It is clearly seen that the silicon substrate is already exposed within about half of the crater area, whereas the remaining area still exhibits the trehalose related peptide signal. Moreover, traces of

the initial, Ga^+ beam induced surface topography are still visible at the silicon substrate interface.

4. Conclusion

The data presented here clearly demonstrate that the assumption of a constant sputter erosion rate, both laterally and in-depth, might be very misleading. The described protocol allows correction for these differential sputtering effects, transforming the projectile ion fluence to a realistic depth scale.

It is evident that measured interface widths are easily broadened by artifacts arising from lateral inhomogeneities, even if the analyzed area within the eroded crater is restricted. If corrected for such effects, the “intrinsic” depth resolution appears to agree with model simulations of the altered surface layer formed under cluster ion bombardment.

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