Optimizing 3D molecular imaging with ToF-SIMS: A comparison between C_{60} single beam and Bi_n/C_{60} dual beam depth profiling

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Statement of Purpose: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful imaging technique due to its high surface sensitivity, molecular specificity, and lateral resolution. It is capable of acquiring 3D molecular images by etching the sample in between imaging sequences. In practice, many ToF-SIMS 3D molecular images are acquired in the dual beam mode, where a high-energy analysis beam (e.g., Ga^+ or Bi_n^+ at 25keV) is used at low fluence for image acquisition, and is combined with a low-energy beam for sputtering/etching (e.g., C_{60}^{n+} at 10 keV, Cs^+ at 250 eV). Because the fluence of the analysis beam is kept below the static limit, the effect of its high-energy bombardment is sometimes neglected in the data interpretation, with the chemical damage entirely attributed to the etching beam. However, since imaging of organic and biological samples requires the detection of large molecules, which are fragile and highly prone to loss of molecular information, this chemical damage needs to be minimized to create a high quality 3D image. The influence of the analysis beam on the quality of ToF-SIMS depth profiles has been studied for inorganic samples [1], but no systematic study has been reported for organic samples. Because organic samples, and especially biological tissues and cells, are complex and fragile, a systematic study is necessary to understand, quantify, and model the influence of the ToF-SIMS parameters on the quality of ToF-SIMS 3D molecular images. These parameters include the species, fluence, energy, bombardment angle, and charge state of each primary ion beam.

Methods: In this paper, multiple depth profiles of an organic film (155 nm thick trehalose spun cast on Si) were performed in the single beam mode (C_{60}^+ for analysis and etching) and compared to those obtained in the dual beam mode (Bi_1^+ or Bi_3^+ for analysis and C_{60}^+ for etching). For all depth profiles the same parameters were used for the etching beam (i.e., C_{60}^+ at 10 keV, 500 x 500 μm^2 etching area, 2.5 x 10^{12} ions/cm^2 of fluence per etching cycle) and the analysis conditions were varied (i.e., ion species and fluence per analysis cycle). The intensity of the molecular ion fragment ([M-OH] at *m/z* 325) was monitored as a function of fluence, and later calibrated to the thickness of the film as measured by AFM. The quality of the depth profiles were quantitatively assessed by comparing their respective depth, lateral, and mass resolutions, and also by their efficiencies and steady state intensities.

In addition, the implantation depths of Bi^+, Bi_3^+, Bi_3^{++}, and Bi_5^{++} (accelerated at 25 kV) in a trehalose film were investigated to understand how different species of Bi_n^{q+} contribute to differences in the accumulation of damage during depth profiling. 10^{12} ions/cm^2 of Bi_n^{q+} were implanted into the film with a raster size of 100 x 100 μm^2 area, and the same spot was depth profiled in the single beam mode to obtain an average implantation depth for each Bi ion. The film thickness was measured by AFM.

Results: Changing the analysis conditions could significantly improve or degrade the quality of ToF-SIMS depth profiles. At very low fluence (≤ 3% of the total primary ion fluence for both Bi_1^+ and Bi_3^+), no additional damage is incurred to the sample relative to C_{60} single beam depth profiling. In fact, Bi_n^+ actually improves the quality of the ToF-SIMS 3D images because of its higher lateral resolution. Also, the depth resolution for both beams was the same as C_{60} single beam (9 nm). At higher Bi_n^+ fluences, the high clean up efficiency of the C_{60} beam [2] can no longer remove the chemical damage induced by the analysis beam and the quality of ToF-SIMS data (steady state intensities and depth resolution) degrades with increasing Bi_n^+ fluence (or decreasing C_{60} fluence); the depth resolution went from 9 to 15 nm when the analysis beam fluence reached 20% of the total fluence.

Implantation depth depended on both the incident kinetic energy and nuclearity of the primary ion. For example, increasing the number of Bi atoms from 1 to 3 for 25 keV single charged ions decreased the average implantation depth from 16 to 8 nm. When the ion energy was increased from 25 keV Bi_3^+ to 50 keV Bi_3^{++} the average implantation depth increased from 8 to 12 nm.

Conclusions: The research investigates the utility of dual beam depth profiling on the acquisition of quality 3D molecular images by controlling the accumulation of damage while exploiting the high lateral and mass resolutions of Bi_n^+. Results suggest that at very low fluence (roughly 3% of the total primary ion fluence for Bi_1^+ and Bi_3^+), the accumulation of damage can be neglected, and dual beam depth profiling rivals the depth resolutions and steady state intensities obtained in the single beam mode. Furthermore, the implantation data suggest that the deeper implanting ion species causes a more significant decrease in the steady state intensities as a function of analysis beam fluence.

References:

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