

Imaging Analysis of Polymer Cross Sections by Time-of-Flight Secondary Ion Mass Spectrometry

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1. Introduction

Time-of-Flight (TOF) Secondary Ion Mass Spectrometry (SIMS) is one of the few techniques which can provide analysis and imaging of organic materials at $\sim 1\mu\text{m}$ lateral resolution. The technique combines its intrinsic parallel detection capability with high secondary ion transmission and virtually unlimited mass range. It is therefore possible not only to obtain mass spectra but also to acquire "significant" images from surfaces with a minimal amount of primary ion beam damage. Strictly speaking, TOF-SIMS is a *surface* analysis technique since the primary ion beam which causes the emission of substance specific secondary ions has an irreversibly damaging effect on the organic material. This irreversible sample damage will typically occur at primary ion doses around 10^{12} ions/cm². This again stresses that the mass spectrometer needs to be able to detect practically all secondary ions which are generated by the primary ion pulse in order to achieve the highest possible sensitivity.

2. Experimental

The experiments were performed on a *PHI-EVANS TRIFT*TM TOF-mass spectrometer. The instrument is equipped with a Liquid Metal Ion Gun (LMIG) which was operated with Ga as well as In primary ion beams. The LMIG is capable to produce image resolutions of $\sim 750\text{\AA}$ in continuous beam operation and around 1000\AA when the beam is pulsed for TOF analysis at 25keV beam energy. The pulsed, rastered LMIG primary ion beam strikes the sample surface and stimulates the emission of sample specific secondary ions. The secondary ions are electrostatically extracted, injected into the stigmatic imaging, energy compensating TRIFT spectrometer and finally reach the detector. Since all secondary ions are accelerated to the same nominal kinetic energy, ions of different mass will have different velocity. Ions of higher mass will thus take longer to traverse the mass spectrometer to reach the detector than the lighter ions. For every primary ion pulse the detection electronics records the ion flight time (i.e. its mass m) as well as

the raster position of the primary ion beam (i.e. the position (x,y) where the ion was created). This information of (x,y,m) is stored for a large number of primary ion pulses and can be sorted as required by the analytical objectives.

3. Fundamental Limitations of Organic Secondary Ion Imaging

TOF-SIMS provides the best possible utilization of the secondary ions created during primary ion impact. There are, however, some fundamental limitations on the minimum size of an organic structure which can be identified. Although the primary ion beam can provide lateral image resolutions of $<1000\text{\AA}$, this type of image resolution can typically only be achieved in the imaging of inorganic surfaces which are not so prone to the destructive effect of the primary ion beam.

A rather simple estimate can clarify what the minimal size of an organic surface has to be so that it can in fact be unambiguously identified. The limit of lateral resolution in organic ion imaging is related to the secondary ion yield and the primary ion beam damage. In order to estimate the minimum organic structure size which will can be unambiguously identified one needs to assume a typical organic molecular secondary ion yield and the maximum primary ion dose at which the sample surface is altered beyond recognition. In order to have a recognizable peak in the mass spectrum one requires approximately $n=10^2$ secondary ion counts for a given mass. These counts are directly proportional to the organic secondary ion yield $y^{+/-}$, the primary ion dose d_p and the analyzed area A, i.e. $n=A \cdot y^{+/-} \cdot d_p$. For example, with a molecular secondary ion yield of $y^+=10^{-3}$ secondary ions/primary ion, a maximum permissible primary ion dose of $d_{pmax}=10^{13}$ primary ions/cm² and $n=10^2$ secondary ion counts in the mass spectrum, the minimum exposed surface area of an organic structure must be:

$$A=n/(y^{+/-} \cdot d_p)=10^2/(10^{-3} \cdot 10^{13})=10^{-8}\text{cm}^2=1\mu\text{m}^2.$$

The most important limiting factor in organic secondary ion imaging is in fact the secondary ion yield and primary ion beam damage and not the size of the primary ion beam. The organic imaging resolution capabilities in a TOF-SIMS can thus only be improved beyond the μm - region if the product $y^{+/-} \cdot d_{max}$ is reduced. One way to achieve this goal is to utilize microfocused primary ion beams which ionize the analyte more efficiently than Ga.