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Materials Analysis Using Secondary Ion Mass Spectrometry: Challenges and Opportunities

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Secondary ion mass spectrometry (SIMS) has evolved over a long period of time (the first reports of sample sputtering by gaseous ions were in the mid-nineteenth century). Early SIMS spectra contained fragment and cluster ions that were used for elemental analysis of surfaces particularly to obtain accurate atomic distributions as a function of sample depth (commonly termed "depth profiles"). In the late 1960s Benninghoven and co-workers introduced static SIMS [1]. In this method one can softly ionize the surface layer leading to the ejection of molecular and large cluster ions. However, in the 1980s and 1990s SIMS was largely overshadowed by other mass spectrometric techniques, including ESI and MALDI, because in SIMS it was difficult to desorb ions with $m/z > 500$.

In recent years SIMS has undergone a resurgence with the development of commercially available cluster ions beams, such as Au_n^+, Bi_n^{x+}, SF_5^+, C_{60}^+ and gas cluster ion beams (GCIB) (in particular Ar_n^+, typically $n \geq 1000$). Today SIMS is employed to obtain both elemental- and molecular- specific (two-dimensional (2d)) images, depth profiles and most recently three-dimensional (3d) chemical images.

In SIMS an ion beam strikes a sample surface leading to the ejection of secondary species – neutrals, positive and negative ions, and electrons. The ejected ions are then detected by a mass analyzer. In time-of-flight secondary ion mass spectrometry (TOF SIMS), acquisition of spectra and images is normally achieved by moving a focused, pulsed ion beam across the sample surface. Thus, in TOF SIMS the spectral or image quality is determined in large part by the signal intensity. For many years Ga^+ liquid ion beams were employed in TOF SIMS because they could be focused to spot sizes as small as 10 nm. However, this type of ion beam does not efficiently eject and ionize molecular species with $m/z \geq 100$, resulting in image resolutions of > 1μm [1, 2]. The introduction of cluster ion beams, such as Au_n^+ and Bi_n^{x+}, led to the reduction of experimental lateral resolution from > 1 μm to ~400 nm [3]. This is because cluster ion beam sources, such as Au_n^+ and Bi_n^{x+} produce secondary ions with a much higher efficiency (the ratio of the secondary ion yield to the disappearance cross-section), up to 3 orders of magnitude larger than Ga^+, particularly at high mass-to-charge ratios [4-6].

Polyatomic ion beams, particularly SF_5^+, C_{60}^+ and Ar GCIB, have enabled the development of molecular depth profiling for organic materials, such as polymers and molecular layers [7, 8], and led to improvements in the depth profiling of inorganic materials by reducing preferential sputtering and surface roughening effects [9]. When a primary ion strikes a substrate, material is sputtered from the outermost 10-20 Å, and upon repeated striking the same spot multiple times SIMS can provide chemical information as a function of depth (a "depth profile") if the rate of sample erosion is known. Using atomic primary ions molecular depth profiles could not be obtained because the collision cascade caused by the primary ion impact penetrated deep into the sample leading to chemical damage and intermixing of the layers. Cluster ion beams do not penetrate as deep into the samples and have high sputter rates leading to less interlayer mixing and significantly reduced chemical damage [9]. The unique properties of cluster ion beam SIMS - greatly reduced sample damage, relatively flat crater bottoms and significantly enhanced secondary ion production – have also led to the development of 3d chemical imaging in which SIMS two-dimensional SIMS imaging and depth profiling have been combined [2].

However, there are still multiple issues that must be addressed. Further improvement of secondary ion intensities will extend the mass range of SIMS allowing the detection of polymers, proteins and other species, which greatly improves the utility of SIMS. The secondary ion intensity is the product of the sputter and ionization yields. However, it is unclear that further significant improvements can be achieved in the sputter yield [10]. We have recently developed a matrix-enhanced SIMS (ME SIMS) using ionic liquid matrices which is suitable for imaging applications [11]. Using this method molecular the ionization probability is greatly enhance and so ion intensities are increased by up two orders of magnitude for a wide variety of analytes including polymers and other large organic molecules. Further, the detection limit of these analytes was improved by approximately three orders of magnitude.

SIMS produces a large amount of data which are inherently multivariate. For example, a SIMS mass spectrum is a composite of mass spectra from each species present in top 10-20 Å of the sample. Chemometric methods, such as principal component analysis (PCA), are sometimes employed to extract information from SIMS data but the results are often hard to interpret. Recently we have developed a new analysis method based on maximum a posteriori (MAP) reconstruction against physically motivated models, rather than statistical dimensionality-reduction techniques such as PCA [12, 13]. This allows us to quantitatively measure concentrations of species, and extract their mass spectra and sample topography. Further, for the first time this model can be used to investigate matrix effects present.

In summary, SIMS is a widely applicable technique which is capable of obtaining mass spectra, depth profiles, and 2d and 3d chemical images. There are a number of challenges remaining for the quantitative analysis of samples such as understanding matrix effects. However, perhaps the biggest challenge for the wider implementation of SIMS is the perception in the scientific community that SIMS is principally concerned with fundamental measurements in desorption and ionization. To address this issue, in addition to methodological development more work is needed to apply SIMS to solve real world problems in areas including in forensic science, biotechnology and conservation science.

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