

adequate spatial resolution. Using depth profiling, i.e. acquiring series of secondary ion signals at specific time intervals during the sputtering process, the distribution of elements within a microvolume near the surface is obtained.

A drawback of this technique is that it is impossible to determine a priori the exact location of subsurface features. To overcome this problem we have combined a Cameca-3f SIMS with a KONTRON IPS digital image processing system.

In the SIMS instrument, the mass filtered secondary ion image is formed on a phosphorus screen in combination with a micro-channel plate. The images are registered at 30 frames per second with a high sensitivity TV camera. Images are digitized with a resolution of 512×512 or 256×256 pixels at 8 bits per pixel (256 gray levels). The image processor allows real time integration and averaging of images. Combined with the control over the gain of the channelplate and the camera sensitivity, this allows for a dynamic range of 6 orders of magnitude, including single ion detection.

Since each successive image represents the lateral distribution of the element of interest at greater depth, the 3 dimensional elemental distribution in the analyzed volume can be reconstructed by "stacking" series of images.

The use of the digital image processing system makes it possible to convert the secondary ion intensity images into concentration images at the pixel level by applying standard SIMS quantification procedures such as "Matrix Ion Species Ratio" or "Sensitivity Factors". An overall accuracy of 10% can be obtained in this way.

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Ion-molecule reaction rates in laser-generated plumes

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Mass spectra indicate the presence of various ion-molecule reactions in expanding laser generated plumes [1]. Important classes of these reactions like electron transfer, proton transfer and heavy particle rearrangement were considered and the corresponding reaction rates were evaluated.

In our model the laser heats the surface of the target material leading to fast evaporation. The evaporated material expands into the vacuum getting fragmented and ionized by further laser heating. Simultaneously heterogeneous and homogeneous reactions occur giving rise to a large variety of ions. At low irradiances target surface temperature patterns provided the basis to estimate desorption and reaction rates. At high irradiances we obtained spatial temperature, velocity and density distributions for the electrons, ions and neutrals by solving our one-component one-dimensional (1C-1D) hydrodynamic model [2, 3].

Electron transfer reaction rates were calculated using the Rapp-Francis version of the impact parameter method [4, 5], whereas proton transfer and particle rearrangement processes were described by the Gioumousis-Stevenson [6] and the average dipole orientation (ADO) [7] theories.

Results on electron transfer reactions show monotonous increase in rate constant with increasing relative velocity of the reaction partners. Since particles are gaining essentially the same hydrodynamic velocity in the expansion the external accelerating field is responsible for the velocity difference of ions and neutrals. The cloud of ions drifting in the ion source gains relative velocity compared to the cloud of neutrals.

The enormous variability of laser generated mass spectra depending on experimental conditions could be rationalized observing ion-molecule reaction rates among other factors. At elevated temperatures orientation of permanent dipoles is overruled by the averaging effect of intense rotation. Expansion and cooling of the plume can lead to dipole orientation and thus to the onset of other reaction channels. Therefore, target heating, plume hydrodynamics and laser focusing is strongly coupled to the variety of ionic reaction products and consequently to the resulting mass spectra.

References

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Oxide and doubly charged ion peaks in ICP-MS

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In Inductively Coupled Plasma Mass Spectrometry the mass spectrum does not only show peaks from singly charged ions but also from secondary ion species, mainly oxide and doubly charged ions. If accurate and precise data are to be obtained with this technique, the study of these oxide and doubly charged ions is of importance since they may lead to spectral overlap interferences due to the low resolution of the quadrupole mass spectrometer.

In this study, using a commercially available VG Plasma-Quad, ratios of doubly charged ions to singly charged ions and of oxide (and hydroxide) ions to singly charged ions were determined for a large number of elements. These were selected to cover a wide range of atomic masses, first and second ionisation potentials and chemical properties. In most cases the level of hydroxide ions was observed to be very low. The correlation between the ratios of MO^+/M^+ and M^{2+}/M^+ with the M-O bond strength and the difference between the second and the first ionisation potential respectively is discussed. The short and long term stability of these ratios were investigated. The influence of the matrix on the levels of oxide and doubly charged ions was studied. Moreover we have investigated the influence of several variable parameters associated with sample introduction and plasma operation (plasma power, nebuliser flow rate, auxiliary flow rate, sample uptake rate, temperature of the water-jacketed spray chamber, lens settings and condition of the cone and the skimmer) on the magnitude of the M^+ signal and M^{2+}/M^+ and MO^+/M^+ ratios. Conclusions concerning system optimisation are drawn.