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This article was submitted to American Society of Mass
Spectrometry Conference, Orlando, Florida June 2-6, 2002

May 31, 2002

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Accelerator-Based Surface Chemistry by Combined Time-of-Flight Mass Spectrometry (TOF-MS) and Particle-Induced X-ray Emission (PIXE)

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Keywords: Particle-Induced Desorption, Particle-Induced X-ray Emission, Surface Chemistry

Abstract

We describe the development of a new capability for performing microscopic chemical analysis in the near surface of a sample. The technology uses a focused high-energy ion beam from an accelerator to cause characteristic elemental x-rays to be emitted and, simultaneously, molecules and fragments to be desorbed from the surface of the sample. Spectroscopic analysis of the fluoresced x-rays provides quantitative trace element information of the sample volume probed by the beam. The elemental data are subsequently used to identify peaks in the mass analysis of the desorbed species, thereby providing a detailed description of the local surface chemistry. High-resolution (micron-scale) chemical imaging is possible by scanning the beam over the sample.

Introduction

Incident ions with energies on the order of 1 MeV/amu induce many ion-atom interactions in the near surface (50 Å to 100 μm depth) of a sample. Detection and interpretation of the signals produced by these interactions has led to the development of many methods for elemental and isotopic analysis. However, important chemical information concerning ion valence and chemical bonding has generally not been accessible using mega volt ions because the physical processes involved occur at the electronic or nuclear level. Many other techniques for chemical speciation have been developed; with mass spectrometry probably the most commonly used method. In general, mass spectrometry alone can not be considered quantitative due to variations in the ionization efficiency of various analytes and also because of matrix effects. Improved quantitation is commonly achieved by comparing to reference spectra where the amounts of a given compound are known or by using internal standards, but these techniques assume the sample is uniform and compositionally similar to the standards.

We are developing a new approach for quantitative surface microchemistry that takes advantage of combined elemental and mass analyses. The method is based on using a focused MeV-energy ion beam to desorb various ionic species and fragments from the surface of the sample, while simultaneously generating characteristic x-rays from the elements present in the near surface. The x-ray data are used to quantify the elements present in the sample and this information is then used in the mass analysis to set bounds on the chemical state. The desorption process is of particular interest in high energy ion beam analysis for three reasons: 1) it can provide sensitive chemical information at each beam scan point, 2) it can provide trace element and isotopic data complementing the x-ray fluorescence data, and 3) it assures minimum perturbation of the sample since only a very small number of species are desorbed.

Background

The spectrometry of ion beam-induced x-rays, commonly referred to as particle-induced x-ray emission or PIXE, is a well-established technique for trace element analysis. A beam of ions is used to excite inner shell electrons from atoms in the target material. Outer shell electrons can fill the inner shell vacancies, simultaneously emitting x-rays whose energies are characteristic of the particular atom (element). The highest energy K-line transitions result from filling the innermost shell. Similarly, lower energy L-line transitions arise from filling the next shell and so on. The x-ray energy spectrum is collected by a photon detector and consists of the x-ray peaks for all elements of $z > 10$ superimposed on a bremsstrahlung background. This background, however, is substantially lower than the one produced by an electron beam, so quantitative analysis of trace elements is performed routinely. Analysis software is used to deconvolute the acquired x-ray spectrum into individual, absolute amounts of the elements

excited by the ion beam. Because of the low bremsstrahlung background, detection sensitivities can be in the part-per-million range especially for thin samples, i.e., when the ion beam can pass completely through the sample. The range of MeV-energy ions is a few microns to several hundred microns.

The same incident ions producing characteristic x-rays also cause atomic and molecular species to be desorbed from the surface of the sample (particle-induced desorption mass spectrometry, or PIDMS). Since PIXE provides a quantified analysis of the elements and their concentrations, it can be used to simultaneously identify and set upper limits for the peaks in the mass spectrum of desorbed species in the same area of the sample. As the incident ion beam slows down and electronic ionizations occur, the energy loss function depends on the ion's effective charge; higher charge states of an ion at a particular energy produce larger desorption yields. The ions and fragments are collected by a mass spectrometer while the x-rays are collected with an energy dispersive x-ray detector. Time-of-flight mass spectrometry allows rapid data collection over a broad mass range that is compatible with the fast scanning capability for PIXE imaging. The spectral data and the spatial coordinates of each beam scan point are stored in a computer and the spectra are post-analyzed for the chemical information.

Results

The particle-induced x-ray emission (PIXE) spectra are collected with as many as four high purity germanium detectors and analyzed for elemental information with in-house developed software (see Figure 1). Mass spectra are acquired with an in-house designed and built linear time-of-flight detector incorporating an electrostatic mirror and microchannel plate detector (see Figure 2). The start signal for the time-of-flight is determined either by pulsing the ion beam from the accelerator or by applying positive and negative potentials to alternate wires of a gating grid inside the spectrometer. We began our tests using focused 3-MeV protons, which is the usual mode for PIXE analysis. These protons deposit most of their energy deep



Figure 2. Photo of the time-of-flight mass spectrometer installed on sample analysis chamber.

inside the sample (the proton range is several tens-of-microns in most materials), so only a small number of ions were desorbed from the surface. To improve the desorption yields, we switched over to a 6-MeV oxygen (O^{3+}) beam. Figure 3 shows the PIXE elemental x-ray spectrum (Fig. 3a) and the PIDMS mass spectrum (Fig. 3b) from a cesium chloride sample. The mass spectrum was collected for 1 hour with a 1 mm diameter oxygen beam having a current of 30 nA. From preliminary data, we determined the mass resolution of our instrument to be 675 at 540 m/z.



Figure 1. Photo of accelerator-based ion microbeam system. In the foreground is the sample analysis chamber with four x-ray detectors for PIXE analysis.

Summary

We have demonstrated a new method for performing quantified surface chemistry with micron-scale spatial resolution. The data presented in this paper are preliminary and we will be improving our data collection and analysis. Experiments are planned to fully determine the secondary ion yields, sensitivity, and detection limits, and to interpret the correlation and quantification of combined elemental/mass analysis. We also plan to explore Fourier frequency domain analysis to increase the duty cycle of the spectrometer.

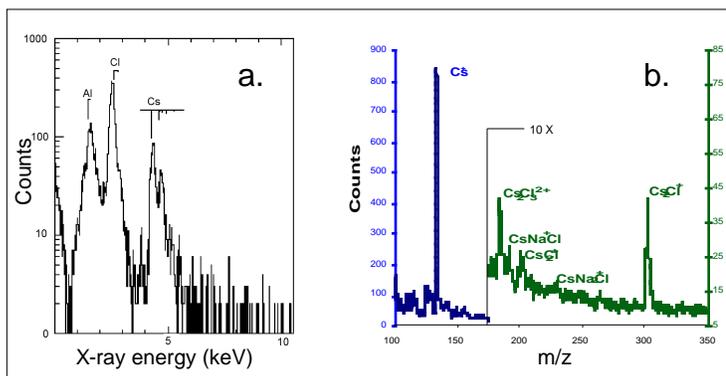


Figure 3. PIXE and PIDMS spectra from a cesium chloride sample obtained with a 6-MeV oxygen beam.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Sandia Corporation, a Lockheed Martin Company, under Contract No. DE-AC04-AL85000 and by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.