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Ion Microprobe Mass Spectrometry Using Sputtering Atomization and Resonance Ionization

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1. Introduction

Resonance ionization mass spectrometry (RIMS) has recently been developed into a useful technique for isotope ratio measurements. Studies performed in our laboratory [1-6] have been reported for a variety of elements using thermal vaporization sources to produce the atom reservoir for laser-induced resonance ionization.

A commercial ion microprobe mass analyzer (IMMA) has been interfaced with a tunable pulsed dye laser for carrying out resonance ionization mass spectrometry of sputtered atoms. The IMMA instrument has many advantages for this work, including a micro-focused primary ion beam (2 μm in diameter) of selected mass, complete sample manipulation and viewing capability, and a double-focusing mass spectrometer for separation and detection of the secondary or laser-generated ions. Data were obtained demonstrating the number and type of ions formed along with optical spectral information showing the wavelengths at which resonance ionization occurs.

2. Experimental

IMMA. The secondary ion mass spectrometer used in this work was manufactured by Applied Research Laboratories (Sunland, CA) and is based on the design of LIEBL [7]. Modifications to the ion extraction lens system were made to allow discrimination against sputter ions while allowing efficient collection of resonance ions. For this work the secondary mass analyzer was operated at mass resolutions ($M/\Delta M$) on the order of 200. Primary ions were generated by using a mixed gas consisting of approximately 2 atom % Ar, 34 atom % N_2 and 64 atom % O_2 in the duoplasmatron ion source. This allowed the sputter targets to be bombarded with operator-selected mass analyzed ion beams of Ar^+ , N_2^+ or O_2^+ .

3. Laser Source and Light Optics

The laser source used in this study was a Chromatix CMX-4 flashlamp-pumped dye laser with a bandwidth of approximately 3 cm^{-1} and an optical pulse width of about 1 μsec . A useful wavelength range of approximately 580-610 nm was generated with the Rhodamine-6G dye used in all the experiments. The pulse energy measured directly at the laser output was about 5 mJ with the available energy above the sample surface estimated to be from 10-50 times less.

The laser beam was spatially filtered and focused to approximately a 0.01 cm diameter spot directly above the sample with

a beam expander assembly housing a 10 μm pinhole. The horizontal and vertical positions relative to the sample surface were varied by an adjustable mirror mount. The elevation of the laser beam was lowered to a plane parallel and just above the sample surface by a periscope assembly mounted in the sample chamber.

Signal Processing. Photomultiplier anode pulses produced by bundles of ions reaching the Daly detector were processed by a preamplifier and pulse-shaping amplifier. The output pulse was sampled by a gated integrator triggered by the sync pulse from the laser; the gate delay was adjusted to coincide with the output pulse which occurs approximately 25 μsec after the laser sync pulse.

4. Samples

Samples consisting of natural U and Sm metal embedded in low vapor pressure epoxy were polished until a smooth metallographic finish was obtained. The cross-sectional area of each metal sample was approximately 0.1 cm^2 .

5. Results and Discussion

Sensitivity. The ion bundle produced in a single laser pulse (nominally 1 μsec long) was found to be 3 ± 1 μsec wide at the detector following a delay of 23 μsec (for Sm) or 30 μsec (for U) due to time-of-flight through the secondary mass spectrometer. The number of ions in each bundle could be counted using a fast oscilloscope to monitor the output of the ion multiplier preamplifier. The largest signals obtained for ^{238}U using Ar^+ bombardment were found to have > 100 ions per pulse while those for ^{152}Sm were found to have 40 ions per pulse.

An estimate of the sampling efficiency can be obtained from the conditions which gave > 100 U^+ ions per laser pulse. The current of Ar^+ ions incident on the surface was 21 nA, or 1.3×10^{11} ions/sec. However, due to the pulsed nature of the laser, only a small fraction of this current was effective in producing U atoms for the resonance ionization process. This fraction is determined by the average transit time of atoms through the laser volume (for short duration laser pulses) or by the actual length of the laser pulse (for pulse lengths of > 100 nsec). The above argument assumes a 0.1-0.01 cm laser beam diameter and an average kinetic energy of 10 eV for the U atoms. In the case reported here, the nominal laser pulse duration was 1 μsec , which means that 1.3×10^5 Ar^+ ions incident on the surface resulted in > 100 U^+ ions being detected. Therefore, the gross efficiency of the sputtering-resonance ionization process was 1 ion detected for every 1300 Ar^+ ions striking the sample.

Mass Spectra. It was of interest to know what ionic species are produced by the laser beam. Therefore, mass spectra were scanned over the mass range 0-300 amu near the resonant wavelengths for U and Sm. At the resonant wavelength of 591.4 nm, the U^+ peak is observed. At higher mass, the UO^+ peak

appears with almost equal intensity in spite of the fact that Ar^+ was the bombarding species. In fact, the UO^+ peak occurs at all wavelengths produced by the dye laser, indicating a nonresonant ionization process. The effect of detuning the laser 0.2 nm resulted in the disappearance of the U^+ signal with no change in the UO^+ intensity. A similar effect was observed for Sm. Both Sm^+ and SmO^+ signals were observed with the SmO^+ signal occurring at all wavelengths produced by the laser, whereas the resonant Sm^+ signal was sharply tunable.

These results suggest that residual oxygen is interacting with the sample to produce metal oxide species which are sputtered and ionized by the laser in a non-resonant process. The SIMS spectra of these metals under Ar^+ bombardment also show strong MO^+ and MO_2^+ peaks. This phenomenon will be the subject of further study.

6. Future Studies

Future work will involve refinements of the ion optical system to obtain higher extraction and transmission efficiency of the laser generated ions. The use of pulsed ion beam sputtering is being pursued in order to maximize the efficiency of atom production. In addition, a more powerful laser system is being acquired to produce saturated resonance ionization over a larger volume. Investigations of different sample types will involve use of resin beads and small particles of Sm or U oxides, to test the capability of the technique for measuring real-life samples.

7. References

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