

Small Sample Analysis Using Sputter Atomization/Resonance Ionization Mass Spectrometry

W. H. Christie and D. E. Goeringer

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Abstract. We have used secondary ion mass spectrometry (SIMS) to investigate the emission of ions via argon sputtering from U metal, UO_2 , and U_3O_8 samples. We have also used laser resonance ionization techniques to study argon-sputtered neutral atoms and molecules emitted from these same samples. For the case of U metal, a significant enhancement in detection sensitivity for U is obtained via SA/RIMS. For U in the fully oxidized form (U_3O_8), SA/RIMS offers no improvement in U detection sensitivity over conventional SIMS when sputtering with argon.

1. Introduction

Environmental monitoring for trace elements in small samples such as airborne particles requires ultrahigh-sensitivity detection techniques. Depending on particle size and composition, they may contain only picogram to femtogram amounts of any given element. SIMS has been shown to be a useful method for locating and analyzing such small samples in certain instances. Although the sputter-ionization process can be highly controlled by varying the energy, current density, and composition of the sputtering ion beam, the ionization efficiency is generally quite low and is greatly affected by the chemistry of the sputtering region. The sputtered neutral atom and molecule density typically ranges from 2-5 orders of magnitude greater than that for sputtered secondary ions.

The technique of resonance ionization mass spectrometry (RIMS) has recently been developed for isotope ratio measurements. Studies performed in our laboratory by Donohue et al (1982) and Young et al (1984) and elsewhere by Miller et al (1982), Downey et al (1984), and Fassett et al (1984), have been reported for a number of elements using thermal vaporization sources to produce neutral atoms for laser-induced resonance ionization. Other methods of atomization such as glow discharge (Savickas et al 1984), laser ablation (Williams et al 1984), and ion beam sputtering (Winograd et al 1982, Donohue et al 1985), have been reported.

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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 diameter) of selectable mass, complete sample manipulation and viewing capability, and a double-focusing mass spectrometer for mass separation and detection of secondary or laser-generated ions.

2. Experimental

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 (Liebl 1967). In essence, the instrument is two mass spectrometers. In the primary spectrometer, a beam of ions is generated, mass analyzed, and focused onto the surface of interest. Ions sputtered from the sample surface are directed into a double-focusing mass spectrometer where mass analysis is accomplished. Modifications to the ion extraction lens system, which allow discrimination against sputtered ions while allowing efficient collection of resonance ions have been described in another publication (Donohue et al 1985).

2.1 Laser Source and Light Optics

The laser system used in this study was a tunable dye laser (Quanta Ray PDL-2) pumped by a pulsed Nd:YAG laser (Quanta Ray DCR-2A). The dye laser was operated in fifth order resulting in a bandwidth of approximately 0.3 cm^{-1} as determined by a 1 cm^{-1} Fabry-Perot etalon. Rhodamine 610 dye used in our experiments gave a useful tuning range from about 582-598 nm. Dye laser wavelength scans were performed under computer control via a programmable motor controller (Quanta Ray MCI-1) with parallel line interface option. Wavelength calibration was confirmed by recording the optogalvanic spectrum of a Ne-filled uranium hollow cathode lamp.

2.2 Signal Processing/Control Electronics

The signal from the Daly detector's photomultiplier was simultaneously processed by both analog and digital electronic systems. The analog system consisted of a fast current amplifier and gated integrator (Stanford Research Systems SR250). The signal produced by a packet of ions generated from a single laser shot was integrated by the current amplifier into a single pulse approximately $15 \mu\text{s}$ wide. This pulse was sampled by the gated integrator which was triggered by the laser and delayed for the flight time of the ion packet through the mass spectrometer. The resultant dc signal was further processed by the data system (see below). The analog signal from the current amplifier was also used to drive video amplifiers in the standard ARL video display system for real-time observation of mass spectra. The digital system was composed of the standard ARL preamplifier/discriminator, pre-scaler, and fast pulse counting (30 ns pulse-pair resolution) system. The digital system was mainly used to determine relative signal strengths for SIMS signals.

The primary ion beam was pulsed by applying a +450V pulse to opposing alignment plates located at the top of the primary lens column. The ion beam gate width and delay were set by gate/delay generators triggered by the laser flashlamp sync pulse.

Data acquisition and control for the experiments were performed by a microcomputer system (MOB Micro-11) based on the LSI-11/23-Plus (Digital Equipment Corp.) central processing unit and containing a 10 MB Winchester disk and dual floppy disk drives. The system housed an analog-to-digital converter (ADC)/digital-to-analog converter (DAC) interface board; the ADC was used to convert the dc output of the gated integrator, and the DAC was used to control the secondary magnet. Another direct memory access DAC interface was used to drive an x-y scope for real-time display of spectra. A parallel interface was used to control the dye laser motor controller (see above). Spectra could also be sent to a digital plotter (Hewlett-Packard 7475A) via serial line interface for hard copy output.

3. Results and Discussion

Earlier studies in our laboratory demonstrated that argon sputtering of uranium metal in the presence of residual oxygen produced both SIMS and RIMS spectra rich in UO^+ and UO_2^+ as compared to the atomic ion (Donohue et al 1985). The present study shows that for U metal samples the molecular species are essentially eliminated if the partial pressure of oxygen and oxygen-containing species (e.g. H_2O) is sufficiently reduced. To accomplish this in our instrument, the existing 400 L/s ion pump was replaced with a 1200 L/s cryosorption unit. As expected, for any given instrument pressure, primary ion beam current density also affected the UO^+ and UO_2^+ signals seen from U metal targets.

3.1 RIMS Sensitivity Improvement for U Metal Samples

For maximum sensitivity in the SIMS analysis of electropositive metals, oxygen bombardment or oxygen flooding of the sputtering region is commonly used to maximize secondary ion yields. Table 1 presents a comparison of laser-generated U^+ signals using Ar^+ and O_2^+ sputter-atomization of U metal with a time normalized SIMS U^+ signal generated by an O_2^+ primary beam on the same sample. The time normalization for the SIMS signal was done by using the gated integrator/ADC electronics and a gate width (6 μs) identical to that for the RIMS signals rather than the pulse counting system. The primary beams were also run in cw mode for these experiments. As expected, a given flux of Ar^+ primary ions was significantly more effective at generating sputtered neutral U atoms from a U metal target than O_2^+ primary ions were.

Table 1

	SA/RIMS		SIMS
	Ar^+	O_2^+	O_2^+
Primary Beam (10 nA)			
Net Signal	6.44	0.03	0.02
Relative Strength	320	1.5	1.0

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For small sample analysis via SA/RIMS it is necessary to operate the primary sputtering beam in pulsed mode for efficient utilization of the sample. We have found that for highly oxidizable metal samples such as U, the duration of the sputter pulse must be long enough to remove adsorbed impurities that accumulate on the sample surface when the primary beam is not impinging on the sample. Figure 1 shows a low level U^+ resonant ion signal detected when the Ar^+ sputtering beam is $5 \mu s$ long and pulsed 10 times per second in synchrony with the laser pulse. The region of the U metal surface being pulse-sputtered had previously been sputter-cleaned with a cw Ar^+ beam. The primary beam was then switched to pulsed operation and the detected resonance U^+ signal allowed to stabilize as equilibrium was achieved between arrival rate of adsorbable species from the vacuum system and Ar^+ from the pulsed sputtering beam. When the Ar^+ sputtering beam was switched to cw mode, an immediate increase in resonance ion formation was detected. When the sputtering beam was again switched to pulsed mode, the resonance ion signal was seen to decay as the surface was again recovered with chemisorbed impurities.

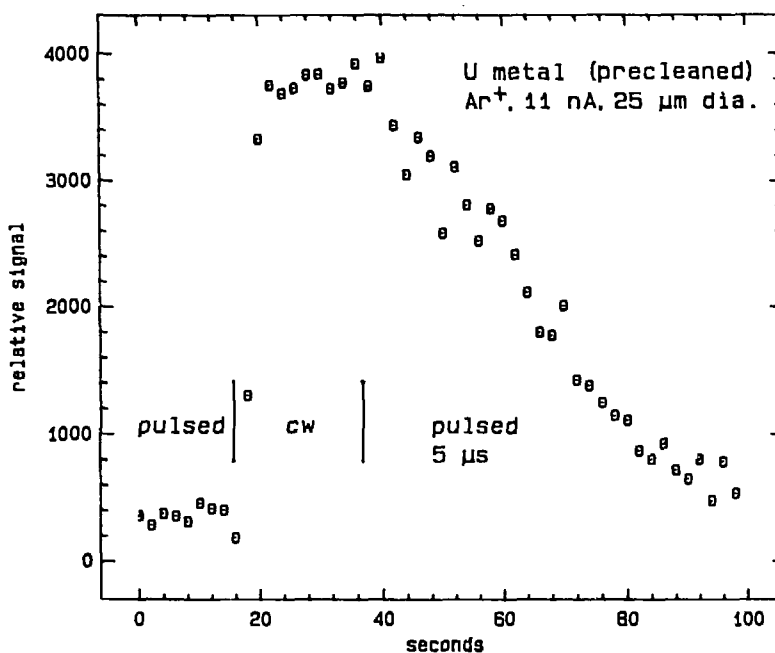


Fig. 1. Effect of adsorbed species on the sputtering of neutral U atoms from U metal target

For the particular Ar^+ current density being used, we show that it takes a pulse width of 120 μs or longer to provide enough presputtering to restore the maximum neutral uranium population that can be sputtered from the surface under these conditions. Samarium is considerably more resistant to oxidation than U. In another experiment, the same Ar^+ beam current was used to sputter a Sm target, but the beam diameter was increased to 60 μm so that the current density was reduced to about 20% of that used in the U experiment. Even with the lowered current density which should enhance surface coverage effects and with only a $5 \mu s$ sputter pulse, the fall off in Sm^+ resonant ion production was much less severe than for U. The results of these experiments reflect the fact that oxide formation on U is considerably faster than on Sm.

3.3 SIMS and RIMS Comparisons in typing on this line

Table 2 compares the SIMS signals determined under similar conditions for U metal, UO₂ and U₃O₈ samples and also compares the resonance ion signals measured under similar conditions for U and UO₂ samples. No data for resonance ion formation on the U₃O₈ sample is shown because no resonant ion signal was obtained under the conditions used for these comparisons. Where UO⁺ and UO₂⁺ signals were seen in the RIMS experiments, they were found to be non-resonant photoionization effects. The U⁺ RIMS signal on the other hand was always sharply tunable with wavelength. The case of U₃O₈ is interesting in that despite the highly oxidized state of the U, it is the U⁺ ion that appears in greatest abundance in the SIMS spectra. Viewed in terms of the RIMS results for U₃O₈, it would appear that relatively little neutral U is sputtered from this sample, and for that matter, little UO⁰ and UO₂⁰. It would appear from these experiments that conventional SIMS offers more sensitivity for the detection of U in this material.

Table 2

Ion	SIMS counts/s x 10			RIMS volt-s x 10	
	U metal	UO ₂ crystal	U ₃ O ₈	U metal	UO ₂ crystal
U ⁺	93	102	750	17.0	0.39
UO ⁺	6	575	90	0.21	6.3
UO ₂ ⁺	2	895	52	-	0.57
UO ₃ ⁺	--	---	0.5	-	-

4. Conclusions

Resonance ionization combined with pulsed Ar⁺ sputtering provides increased detection sensitivity for U from metal samples. From oxidized samples of U it is seen that the population of sputtered neutrals is significantly reduced. At one time it was felt that the laser offered the promise of quantitative SIMS because one could conceivably ionize with 100% efficiency the atomic neutral species sputtered from a surface.

This work clearly indicates that the population of neutrals above a sputtered surface is not always representative in a direct way of the composition of the surface. Just as chemistry in the sputtering region dominates the relative ion yields in SIMS experiments, it also controls the relative neutral yields available for RIMS experiments.

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