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Three-Color Resonance Ionization Spectroscopy of Zr in Si

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Abstract. It has been proposed that the composition of the solar wind could be measured directly by transporting ultrapure collectors into space, exposing them to the solar wind, and returning them to earth for analysis. In a study to help assess the applicability of present and future postionization secondary neutral mass spectrometers for measuring solar wind implanted samples, measurements of Zr in Si were performed. A three-color resonant ionization scheme proved to be efficient while producing a background count rate limited by secondary ion signal (5×10^{-4} counts/laser pulse) This lowered the detection limit for these measurements to below 500 ppt for 450,000 averages. Unexpectedly, the Zr concentration in the Si was measured to be over 4 ppb, well above the detection limit of the analysis. This high concentration is thought to result from contamination during sample preparation, since a series of tests were performed that rule out memory effects during the analysis.

1. INTRODUCTION

Resonance ionization spectroscopy (RIS) is characterized by high ionization efficiency and atomic selectivity making it well suited for low-level elemental analysis. It has successfully been used for selective postionization of sputtered neutral species, providing powerful ultratrace analysis capabilities below atomic fractions of 10^{-9}[1-3] while removing only a few monolayers of the substrate. Results obtained using RIS with secondary neutral mass spectrometry (SNMS) are also readily quantifiable.[4]

As continued progress is made to lower detection limits and as a wider variety of systems are studied, increasingly difficult challenges are presented that test the limits of RIS/SNMS capabilities. One such challenge is presented by the needs of the planetary science community to study the composition of the solar wind. It has been proposed that this can be done directly by sending ultrapure collectors into space and exposing them to the solar wind for roughly two years before returning them to earth for analysis.[5] Predictions of the flux and energy of solar wind ions indicate that collectors would receive doses from 10^5-10^{11} ions/cm^2 for elements heavier than Fe, implanted in a shallow distribution less than 100 nm deep.[6] This corresponds to concentrations from 1 ppm to below 1 ppt.
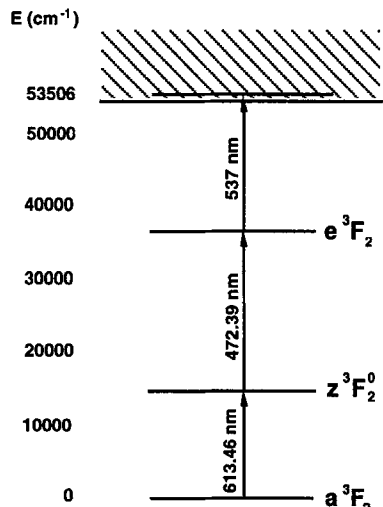
A RIS/SNMS instrument (SARISA IV) developed at Argonne National Laboratory[7,8] is part of a study to determine the applicability of the technique to the solar wind analysis problem. The measurement of Zr in a pure Si sample was used for a test. Si was chosen because it is one of the purest materials available, and is thoroughly characterized by other methods. Zr is an element of interest as a test of solar wind models and has a proven three-color ionization scheme,[9] which can be exploited to minimize background levels.

Results obtained from initial experiments on the Zr/Si system are presented here. A new lower detection limit is reported for the instrument, resulting from

improved suppression of secondary ions. A second, surprising, result was the presence of Zr in the near-surface region well above the detection limit.

2. EXPERIMENTAL

Sputtered neutrals, produced from 2500 V Ar^+ ion bombardment in 800 ns pulses, are postionized in the gas phase ~ 0.5 mm from the target surface from a volume of approximately 10 mm^3. A double hemisphere, energy and angle refocusing time-of-flight (EARTOF) mass spectrometer provides discrimination against secondary ions and other noise sources. Secondary ions are suppressed by applying a voltage to the target during the Ar^+ ion bombardment that imparts sufficient energy to the secondary ions such that the EARTOF prevents their transmission to the detector. The target voltage is pulsed down to the appropriate level just before the postionizing lasers are fired. Atomic selectivity is achieved in Zr by the three-color ionization scheme shown in Fig. 1.[9] To distinguish the resonant photoion signal from background levels, measurements were made with the first laser detuned 0.1 nm to the red of the resonance wavelength. Silicon wafers provided by two independent manufacturers were used as the target materials.
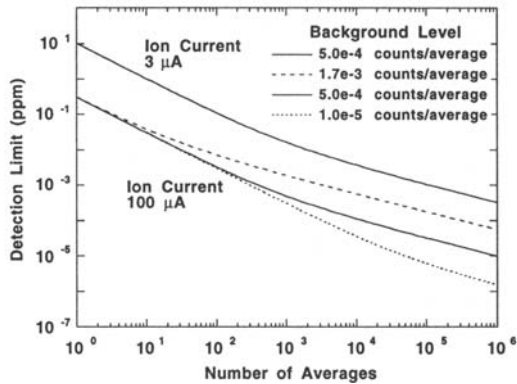
Three depth profiles of Zr concentration in Si were measured on two Si wafers by interleaving analyses with ion beam milling of the sample. The milled area (4 mm^2) was much greater than the sampled area (0.03 mm^2) to ensure that crater-wall effects did not bias the analyses. Each spot was analyzed to a depth of 100 nm. Typically, 25 to 50 measurements were made over the 100 nm range, with each measurement consisting of 10,000 laser shots (5000 signal and 5000 background). Signal from a pure Zr metal target was used to calibrate the instrument, allowing quantitative analyses to be made.[4]

FIGURE 1. Three-color scheme used to resonantly ionize Zr.

3. RESULTS AND DISCUSSION

Using the measured sensitivity and background from the three analyses, an average detection limit for Zr in Si was determined. The top curve in Fig. 2 shows this detection limit as a function of the number of averages. This curve is based on a background count rate of 5×10^{-4} counts/average, obtained by integrating the off-resonance signal over the main Zr isotopes (90-94 Dalton), and assuming a signal-to-noise ratio of unity. The main noise sources were found to be secondary ions traversing the time-of-flight path and scattered ions reaching the detector directly. If nonresonantly ionized species contributed to the background level, their effect was not discernible above these other background sources.

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The measured background is more than two orders of magnitude above the dark count rate of the multichannel plate detector. While it is anticipated that some instrument modifications can be made to reduce the total background, the dark counts alone keep the detection limit above 20 ppt in 10^6 averages using the present primary ion source. By installing a higher current source, however, measurements down to the 1 ppt level are feasible, as is demonstrated by the lower family of curves in Fig. 2. The

FIGURE 2. Detection limit (for Zr in Si) of the SARISA instrument for the present ion source (top curve) and a future ion source (bottom 3 curves). The lowest curve is the limit imposed by the detector dark count rate.

dashed curve corresponds to the present background level scaled linearly with increased ion current, while the solid line is based on a background level independent of source current. Tests conducted to determine how the background will scale with ion current indicated that the actual detection limit will fall somewhere between the two lines. The dotted line in Fig. 2 shows the predicted detection limit if instrument modifications are made that reduce the background level to the detector dark count rate. As can be seen in Fig. 2, the detection limit drops to 1 ppt in 10^6 averages in this case--near the estimated limits required by the solar wind experiment.
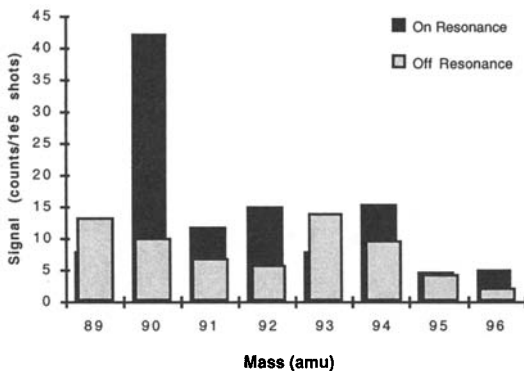
FIGURE 3. Mass spectrum demonstrating the presence of Zr in the Si sample analysis. On resonance signal is greater than off resonance signal for masses corresponding to Zr isotopes (90-92, 94 Dalton).

A quite unexpected result from this study was the unquestionable detection of Zr in the Si samples. Each of the depth profiles revealed a uniform distribution of Zr over the 100 nm depth that was measured. A mass spectrum of the cumulative signal from one of the depth profiles (2.4×10^5 averages) is seen in Fig. 3, where the isotopic signature for Zr is clearly reproduced in the measured mass spectrum. The on-resonance signal is well above background at mass 90, the major isotope of Zr (51%). For the minor

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isotopes of Zr at masses 91, 92, and 94, the net signal is positive in each case though not statistically above the background. The total integrated Zr signal is 4.4×10^{-4} counts/average, corresponding to a concentration of 4 ppb. Similar results were obtained for the two depth profiles on the other sample, although the measured overall Zr concentration was a factor of two lower than for the first target.

The accuracy of the SARISA instrument, when using a pure metal foil for calibration (due to the required dynamic range), is good to within a factor of three,[4] so measured Zr concentrations for these two samples are equal within the analysis uncertainty. Since these high Zr levels were found on samples from different manufacturers, it is believed that the Si wafers were contaminated during the preparation or analysis, not during the manufacturing process. During preparation, wafers were not handled in cleanroom conditions, though precautions were taken so they were not brought into contact with contaminated surfaces.

Contamination during the measurements (memory effect) has been ruled out by several tests performed during the analyses. Typically, a spare piece of pure Si was sputtered for an hour prior to collecting data to cover any Zr in the vacuum system resulting from the calibration. This covering step was eliminated before the second analysis on the second sample, but no change in Zr signal was observed. Secondly, in each analysis the Zr concentration was found to be constant over the measured depth. This would not be expected if Zr was being deposited onto the sample. In addition, at the end of the depth profile, no increase in Zr signal was observed when the sample surface was reanalysed at a new location. All of these results indicate that Zr on nearby surfaces was well covered and not being redeposited onto the Si sample. Therefore, it is believed that the contamination of the Si samples is occurring prior to their introduction into the SARISA instrument.

ACKNOWLEDGMENTS

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