

Resonance Ionization of Sputtered Atoms - Progress Toward a Quantitative Technique*

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ABSTRACT: The combination of RIMS and ion sputtering has been heralded as the ideal means of quantitatively probing the surface of a solid. While several laboratories have demonstrated the extreme sensitivity of combining RIMS with sputtering, less effort has been devoted to the question of accuracy. Using the SARISA instrument developed at Argonne National Laboratory, a number of well-characterized metallic samples have been analyzed. Results from these determinations have been compared with data obtained by several other analytical methods. One significant finding is that impurity measurements down to ppb levels in metal matrices can be made quantitative by employing polycrystalline metal foils as calibration standards. This discovery substantially reduces the effort required for quantitative analysis since a single standard can be used for determining concentrations spanning nine orders of magnitude.

1. INTRODUCTION

Since the demonstration that atomic selectivities of 10^{19} could be achieved by resonance ionization spectroscopy (Hurst, 1977), the field has rapidly grown as researchers have attempted to exploit this unique capability. One arena where these endeavors have been particularly fruitful is surface analysis where resonance ionization mass spectrometry (RIMS), in combination with ion sputtering, has been employed to analyze for trace impurities on the surfaces and in the bulk of a solid by probing the material ejected into the gas phase during ion bombardment. Here, the selectivity of resonance ionization is used to separate the element of interest from the bulk material that is sputtered and a mass spectrometer is used for noise discrimination and detection. At least three different laboratories have reported detection capabilities below atom fractions of 10^{-9} (1 appb) employing this technique (Young, 1986; Pappas, 1989; Thonnard, 1989; Pellin, 1990).

In addition to selectivity, RIMS of sputtered atoms has the potential for making quantitative measurements with ease. This is derived from the fact that sputtering of clean metals by noble gas ions produces a flux dominated by ground state neutral atoms and the fact that there is a large data base on the rate of removal for most metals due to sputtering. By knowing sputtering rates and instrument transmissions, it is possible to draw quantitative conclusions

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regarding impurity concentrations if the degree of ionization is known. Thus, RIS is unique in that complete ionization of a species is possible without extraordinary efforts.

One of the difficulties associated with quantitative analysis is the development of standards. This is particularly true for techniques that are attempting to extend detection limits to heretofore unobtainable levels. To better define the usefulness of surface analysis by resonance ionization of sputtered atoms (SARISA) for quantitative analysis, a series of samples has been analyzed for various impurities at levels that can be confirmed by other techniques. The experiments that have been completed to date are presented herein.

2. EXPERIMENTAL

RIMS experiments have been performed to determine the concentration of Fe, Cu, and Mo in Si. Pure Si wafers were dipped into solutions containing Cr, Cu, Ni, and Fe in order to produce contaminated samples. These samples were then analyzed by total reflection x-ray fluorescence (TXRF). Each wafer was then split in half, one half being analyzed by secondary ion mass spectrometry (SIMS) and the other half by SARISA. In addition, two targets were prepared by ion implanting 200 keV Mo into Si wafers at doses of $3.0 \times 10^{13}/\text{cm}^2$ and $1.0 \times 10^{11}/\text{cm}^2$.

The TXRF that was used was an Atomika model XSA 8000 located at Siemens, Munich, Germany. The SIMS instrument was the CAMECA IMS 3f located at the Technical University, Vienna, Austria. SARISA is a one-of-a-kind laser postionization secondary neutral mass spectrometer built and operated by Argonne National Laboratory, USA. Both the TXRF and SIMS are commercially available instruments and require no further description. Details of SARISA can be found in past publications (Pellin, 1988; Pellin 1987).

For Cu and Mo in Si, simple two-color/two-photon ionization schemes produce good discrimination between signal and background. In the SARISA analyses, the Cu resonance transition at 327.40 nm ($^2S_{1/2} \rightarrow ^2P_{3/2}$) was utilized. A dye laser containing DMT and pumped with a KrF excimer laser was employed for the resonance step and a XeCl excimer laser (308 nm) was used to access the ionization continuum. For Mo RIMS, the z^7P_0 state is accessed from the ground state (a^7S_3) by a dye laser tuned to 386.41 nm and then ionized with light from a XeCl excimer laser. For Fe in Si, a three-color/three-photon scheme was employed in order to minimize isobaric interference from nonresonantly ionized Si dimers (Gruen, 1991). This ionization scheme requires three dye lasers tuned to 344.06, 640.00, and 510.0 nm in order to access the z^5P_3 , e^5D_4 and an autoionizing state of Fe, respectively, in a stepwise fashion.

In order to make quantitative determinations, the SARISA instrument was calibrated before and after analysis of the unknown sample. This was accomplished by determining the transmission of the instrument by measuring the signal from a pure metal foil of the element being investigated. For a constant ion current and instrument transmission, this signal, S , from the pure, p , elemental target is then used to calculate the concentration of that element, $[M]$, in an unknown sample, u , through the equation,

$$[M] = \frac{S_u Y_p G_p}{S_p Y_u G_u} \quad (1)$$

where Y is the sputtering yield and G is the gain of the detector.

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3. RESULTS AND DISCUSSION

Both SIMS and SARISA have the capability to determine elemental concentrations as a function of depth. This is accomplished by monitoring signal for the element of interest as an ion beam mills into the target. Typical results for the SARISA instrument are shown in Figures 1 and 2 for Cu and Mo, respectively. As can be seen in Figure 1, the Cu is clearly a surface contaminate that falls off with depth. This is in contrast to the Mo sample shown in Figure 2. Here, the Mo depth profile shows the typical shape expected for an ion-implanted target. The peak at 200 nm in Figure 2 is in agreement with that depth for 200 keV Mo implanted into Si.

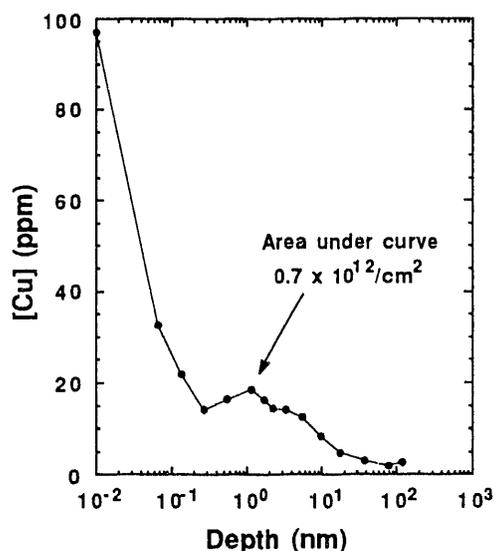


Fig. 1 SARISA analysis showing the Cu in Si concentration as a function of depth. Integration of the data from 0 to 15 nm yields a total Cu content of $0.7 \times 10^{12}/\text{cm}^2$.

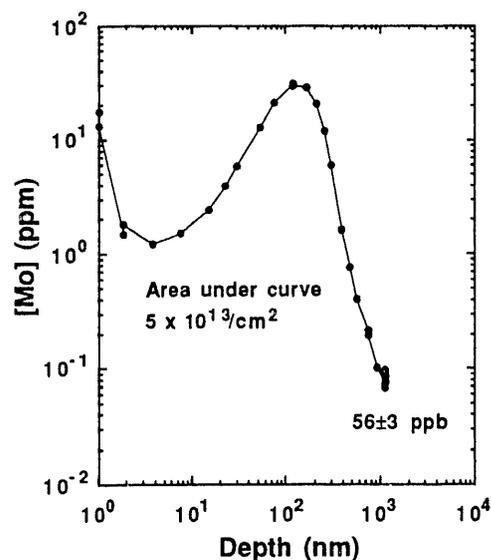


Fig. 2 SARISA analysis showing the Mo in Si concentration as a function of depth. Integration of the entire curve yields a total Mo content of $5.0 \times 10^{13}/\text{cm}^2$.

TXRF instruments are unable to produce concentration versus depth data but rather measure the total concentration of contaminants in the near-surface region. For Si targets, this corresponds to about 15 nm. Thus, TXRF is capable of measuring surface contamination such as shown in Figure 1 but is unable to determine the concentration of implanted species as shown in Figure 2. In order to compare the SARISA measurements with TXRF data, concentration versus depth data must be integrated over the depth of TXRF sensitivity. Similarly, depth profile data of ion implanted standards must be integrated over the entire concentration peak in order to compare the SARISA measured results with the known ion dose. Integrations of SARISA depth profiles have been performed and are listed in Table I along with results from TXRF measurements and from implanted targets of known ion doses. Also listed in Table I are results of the SIMS analyses. Since SIMS data is difficult to quantify, results from these analyses are expressed only as to whether or not real signal above interferences could be observed.

As can be seen in Table I, agreement is reasonably good when various types of instruments are used to analyze the same sample. To date, only Cu analyses have been performed on identical Si samples by SARISA, SIMS, and TXRF. Unfortunately, the SIMS analysis suffered from an isobaric interference that, when suppressed, reduced the sensitivity of the

measurement to the point that no Cu could be detected. Only SIMS analyses of Fe and Cr had confirmed signal above levels of isobaric interferences, but the SARISA analyses for these samples are yet to be performed. The agreement between the TXRF and SARISA measurements indicate that either may be used to measure surface contaminations. However, TXRF is unable to furnish the concentration versus depth information that SARISA can produce. In addition, SARISA has been shown to have a detection limit below 1 ppb while maintaining near monolayer resolution (Pellin, 1990).

Table I. Comparison of impurity concentrations in Si as determined by various analytical methods. All concentrations are given in atoms/cm². For SIMS analysis, yes and no indicate whether an element was detected.

Element	SARISA	TXRF	SIMS	Ion Implant
Mo	5.0×10^{13}	-	-	3.0×10^{13}
Mo	2.5×10^{11}	-	-	1.0×10^{11}
Fe	4.0×10^{12}	8.0×10^{12}	-	-
Fe	-	0.6×10^{12}	yes	-
Cu	0.8×10^{12}	1.3×10^{12}	no	-
Cu	-	0.3×10^{12}	no	-
Cr	-	0.3×10^{12}	yes	-
Ni	-	1.1×10^{12}	no	-

A point regarding the accuracy of the SARISA measurements that should be emphasized is the method of calibration as described in the experimental section. Simple metallic foils were used as standards for these measurements, yet the accuracy appears to be good to within a factor of 3. As shown here for Si and observed in our laboratory for other metals, Equation 1 is valid down to at least ppb levels for metallic targets. The only other information required to make quantitative determinations in this manner is knowledge of the sputtering yields for the metal and the unknown substrate, and knowledge of the detector gain curve. Thus, it is possible to perform trace analyses with SARISA without the laborious task of developing and fabricating calibration standards specific to the substrate of interest.

4. REFERENCES

- Gruen D M, Calaway W F, Pellin M J, Young C E, Spiegel D R, Clayton R N, Davis A M and Blum J D 1991 *Nucl. Instrum. Methods Phys. Res. B* **58** 505
Hurst G S, Nayfeh M H and Judish J P 1977 *Appl. Phys. Lett.* **30** 229
Pappas D L, Hrubowchak D M, Ervin M H and Winograd N 1989 *Science* **243** 64
Pellin M J, Young C E, Calaway W F, Burnett J W, Jørgensen B, Schweitzer E L and Gruen D M 1987 *Nucl. Instrum. Methods Phys. Res. B* **18** 446
Pellin M J, Young C E and Gruen D M 1988 *Scanning Microsc.* **2** 1353
Pellin M J, Young C E, Calaway W F, Whitten J E, Gruen D M, Blum J D, Hutcheon I D and Wasserburg G J 1990 *Phil. Trans. R. Soc. Lond. A* **333** 133
Thonnard N, Parks J E, Willis R D, Moore L J and Arlinghaus H F 1989 *Surf. and Interface Anal.* **14** 751
Young C E, Pellin M J, Calaway W F, Jørgensen B, Schweitzer E L and Gruen D M 1986 *Inst. Phys. Conf. Ser.* **84** 163

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