Journal of Radioanalytical and Nuclear Chemistry, Vol. 263, No. 3 (2005) 691–696

Use of combined NAA and SIMS analyses for impurity level isotope detection

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(Received April 6, 2004)

Neutron activation analysis (NAA) offers advantages for detecting impurity levels of select isotopes that have suitable neutron cross sections. Secondary ion mass spectrometry (SIMS) on the other hand detects most isotopes, but suffers various molecular interferences and covers only a small beam size volume per run. These two methods are combined here to study a large number of isotopes in titanium thin films in an electrolytic cell experiment. Nine isotopes are covered by NAA and over 50 with SIMS. An overlap in the data sets allows a normalization of SIMS data to the more accurate NAA measurements.

Introduction

Earlier studies of thin-film metal coated microspheres electrolyzed in a Patterson Power Cell™ discovered possible nuclear transmutation products.[1] Various metal coatings of 500–2000 Å thick Ni and Pd were used in that work. Here, we report a new study on a Ti thin film, intended to extend the earlier database and also further refine the analysis technique.

A combination of SIMS and NAA was employed for this effort. The NAA is time consuming and was limited to measurement of nine elements with appropriate cross sections where referenced standards were available. SIMS, with ultra low detection limits, could detect all isotopes rapidly. However, it provides relative isotope concentrations and abundance ratios more precisely determined than absolute concentrations. Thus the SIMS concentration values were normalized to the more accurate NAA results.

The electrolysis system is similar to conventional units, but it contained the metallic cathode material sputtered onto microspheres forming a packed bed configuration. The polystyrene (PS) microspheres aid resistance to flaking due to the compressibility of the polystyrene core material. The use of a thin film coating follows the earlier swimming electron layer (SEL) theory,[2] whereby the Fermi energy levels of metals equalize at the interface by creating an electron layer. Shielding by this electron layer enhances the reaction probability.

Experimental

The experiments were carried out in a flow-type electrolysis unit described in Reference 1. The electrolysis cell held a packed bed of ~1000 microspheres, (~1 cm^3 total volume) with parameters shown in Table 1a. The microspheres were manufactured by sputtering the Ti on while the microspheres were "fluidized" in a vibrating shaker unit to obtain a uniform coating. As the electrolyte, 4M lithium sulfate was used along with a Ti anode and the run lasted for 260 hours. The present study focused on reaction product identification rather than excess heat studied in earlier experiments.

Secondary ion mass spectrometry

A dual focusing SIMS (CAMECA IMS 5f) was employed to obtain a reasonably high sensitivity combined with ease of operation. SIMS uses a primary beam of ions incident on the sample to sputter ions out of it, for analysis in an associated mass spectrometer.[3] A microsphere was mounted on the SIMS sample holder using a carbon-based adhesive tape (for good conductivity while avoiding metallic tape contamination). The sample was far enough from the sample holder material to avoid contamination by any material sputtered off of the holder. The runs were carried out using 10 nA of O_2^+ primary ions at 14.5 keV, 300–5000 mass of resolution modes and a field aperature of 400 μm with a contrast diaphragm aperature of 150 μm. The O_2^+ bombardment beam was selected to maximize the positive ion yield. Most electronegative species (gaseous state at room temperature) were not of direct interest and hence allowed to diffuse out of the Ti coating in a high vacuum (~10^{-10} Torr) during the runs.

The magnetic sector analyzer used separate species of similar mass numbers but different actual masses, thus aiding the resolution and minimizing mass interferences.[3,4] A double focusing type analyzer reduced the secondary beam energy spread. A Faraday cup and electron multiplier detectors were used with ion currents of 10^{-8} to 10^{-14} A. This gave detection limits (set by stray species background) for most trace elements between 10^{-6} and 10^{-9} g/g. Either a "low" or a "high" resolution can be used depending on the adjustment of the entrance slit, field aperture, energy slit

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0236–5731/2005/USD 20.00
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and exit slit.[3] Low-resolution scans were first performed using ion currents of ~10 nA. Based on the analysis of that data, a decision was made regarding which isotopes require high resolution scans due to possible interferences. Then, a typical resolving power ($M/\Delta M$; where M is the mass of the isotope and ΔM is its deviation from the interference species mass) of ~5,000 was achieved (Fig. 1).

To obtain Fig. 1, the mass scale was first calibrated for high resolution with a standard copper sample to obtain a positive identification of ^{63}Cu (mass of 62.929 amu). This procedure was also used in isotope ratio analysis, i.e., ^{65}Cu was also analyzed by a high resolution scan.

Molecular interference is largely eliminated with the energy discrimination using a 60 V offset. A typical mass spectrum of an unreacted sample with the offset (Fig. 2) had only a dozen lines vs. over a hundred without the offset applied.

Several other possible uncertainties in SIMS analyses were considered in evaluating error limits. Multiple SIMS analysis on a similar sample may show differences due to variations in the sample orientation with respect to the secondary ion optic axis, and variations in electric field near the sample. Such variations were reduced by normalizing the intensities of the matrix element.[5] Sputtering in SIMS is known to exhibit a mass fractionation effect, i.e., one isotope in an element may be preferentially sputtered vs. the other.[6] It is estimated that this could result in a maximum isotope shift of 4% in present experiments. Sampling over regions with non uniform concentrations could also introduce errors. However the broad surface SIMS "maps" for Cu, Zn, and Ni suggest a good uniformity (±10%) of concentration of key elements around these microsphere surface. In this case, the SIMS was tuned to a particular mass and the beam was then scanned over a wider area of the sample.

Table 1. Sample and analysis data. (a) Parameters for Ti-coated microspheres from sputtering batch #65, (b) Parameters for NAA methods, (c) NAA result of microspheres prior to run #15, (d) NAA result of microspheres after run #15, (e) RSF calculated from NAA data

(a)	Layer	Diameter, cm	Layer volume, cm^3	Layer volume, cm^3	Density, g/cm^3	Layer mass, g	No. of atoms
	PS	1.06E-01	6.22E-04			6.09E-04	
	Ti (1400A)	1.06E-01	6.22E-04	4.93E-07	4.51E+00	2.23E-06	2.80E+16

(b) Method	Irradiation facility (neutron flux, n·cm^{-2}·s^{-1})	Analytical procedure		
		Irradiation	Decay	Counting
Thermal, short-lived	PS (3.7·10^{12})	10–300 s	5–20 m	10–20 m
Epithermal, medium-lived	CLNAT (2.1·10^{11})	2–8 h	2–5 d	1–10 h
Thermal, long-lived	LS (3.4·10^{12})	2–6 h	15–35 h	3–6 h

(c)	Element	Concentration, ppm	Error, ppm	Detection limit, ppm
	Ag	1.88	0.14	0.02
	Al	40.66	2.75	1.6
	Cu	<DL		24.6
	V	<DL		0.2

(d)	Element	Concentration, ppm	Error, ppm	Detection limit, ppm
	Ag	5.53	0.38	0.47
	Al	39.17	3.24	4.21
	Cu	141.54	26.79	79.10
	V	1.02	0.15	0.32
	Fe	1528.83	59.93	135.47
	Cr	722.79	7.63	3.81
	Co	18.23	0.29	0.21
	Ni	1123.88	18.46	24.99

(e)	Isotope	At. wt., AW	IP, eV	SIMS, *I*, counts	NAA, ppm	± Error NAA, ppm	RSF, atom/cm^3
	Fe(56)	55.93	7.87	832	382384.10	14989.68	1.80E+23
	Ni(58)	57.94	7.64	150	189516.80	3113.35	4.78E+23
	Zn(64)	63.93	9.39	124	194873.93	2471.87	5.38E+23
	Cr(52)	51.94	6.77	2259	164942.06	1740.02	3.08E+22
	Cu(63)	62.93	7.73	32	24017.61	4545.68	2.65E+23
	Al(27)	26.98	5.99	72	10760.97	890.54	1.21E+23
	Co(59)	58.93	7.86	15	5009.41	79.95	1.24E+23
	Ag(107)	106.91	7.58	1	759.11	52.67	3.11E+23
	V(51)	50.94	6.74	5	280.33	41.60	2.41E+22

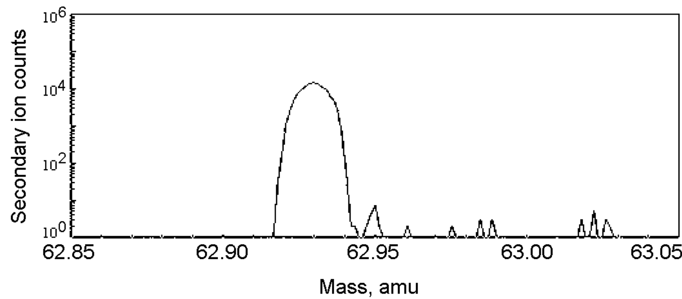

Fig. 1. High-resolution mass spectrum for ^{63}Cu isotope identification.
The mass range analyzed is 62.85 to 63.05 amu, with a total of 150 channels, giving $M/\Delta M$ of ~4625

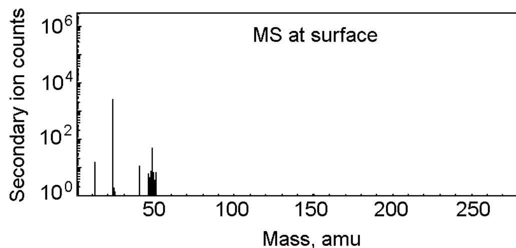

Fig. 2. Mass spectrum of a microsphere from batch #65 with a –60 V offset

The sputtering yields depend on atomic composition, chemical state, crystallographic orientation, surface gases, etc. of the target, collectively called the "matrix" effect.[7] Thus, the sensitivity of the SIMS differs for different elements in a sample. Relative Sensitivity Factors (RSFs), discussed later, are used to process SIMS data to compensate for these effects.

Neutron activation analysis

NAA provides the unique ability to obtain absolute yields of key elements in a sampling of 100–1000 microspheres, vs. the local data from SIMS using single beads. Like SIMS, NAA offers impurity-level detection limits (10^{-4}–10^{-3} ppm) and excellent isotope detection with immunity from matrix effects and easy conversion of counting data (intensities) into concentration values.

Sample irradiations were performed at the University of Illinois 1.5-MW Triga reactor (now out of operation), under conditions shown in Table 1b. Elements whose product nuclide from the (n,γ) reaction had a short half-life (Ag, Al, Cu and V) were analyzed by the thermal short-lived method, while the thermal long-lived method was used for Fe, Cr, Co, Ni and Zn.

The γ-ray detector system contained a liquid N_2 cooled, high purity germanium (HPGe) crystal detector with eighteen percent relative efficiency (1.9-keV resolution for the 1332-keV photopeak of ^{60}Co) plus a large NaI(Tl) crystal ring detector outside the main detector and an Ortec ADCAM PC-based mutichannel analyzer. Compton suppression was employed to further minimize the background.[8] A reference standard method was used to determine element concentrations. This technique used simultaneous irradiation and γ-counting of a prepared NIST sample (one standard sample for each element) along with the test sample. The γ-spectrum data was processed using the Neutron Activation Data Analysis (NADA) code.[9] The NADA code automatically accounts for flux variations, large deadtime corrections, counting geometry, spectral and nuclear interference, as well as uranium fission interferences.

Results from these NAA study were used to determine the concentrations of nine elements in a sample, providing a calibration for the corresponding SIMS data as described next. This is, in effect, equivalent to using the ion-implant method commonly used as a standard for the SIMS. However, this method is much simplier and less costly.

Normalization of SIMS to NAA

The relative SIMS intensities were converted to absolute isotope quantities using RSF values. The RSF value is used to convert the secondary ion intensity (I_1) to an atom density (c_1) using data from a reference sample as follows:[3]

$$c_1 = \frac{I_1}{I_2} \cdot RSF \cdot A_2$$

where c_1 is in atom/cm^3, I_2 is the reference matrix isotope secondary ion intensity in counts, RSF is the relative sensitivity factor for the element 1, in the matrix 2, in atom/cm^3, and A_2 is the fractional abundance of the reference matrix isotope. This expression can be rearranged to give:

$$\frac{RSF_1}{RSF_2} = \frac{ppm_1}{ppm_2} \cdot \frac{AW_2}{AW_1} \cdot \frac{I_2}{I_1} \tag{1}$$

Here, ppm_i is the concentration (measured by NAA) of the isotope, i, in the metal coating [µg/g equals ppm (part-per-million)], and AW_i is the atomic weight of the isotope of species i, in amu. The above relation can be used to calculate the RSF of isotope 1 in the test sample when the concentration for the reference sample (isotope 2) is determined from the NAA. The corresponding RSF_2 is determined using a SIMS measurement on the reference under conditions identical to the test sample.

Statistical analysis

Since microsphere samples were only analyzed once in the SIMS, the technique for estimating errors for a single measurement as explained in Reference 10 was adopted. This assumes that the value of the secondary ion intensity for a mass number can be represented by a Gaussian or Poisson distribution. Then, the error formula applied to calculate the deviation $\sigma_{CM\%}$ in normalized $CM\%$ is shown in the equation below, where the nomenclature follows Reference 10. For the unreacted microspheres, the RSF vs. IP relation used ^{51}V as a reference. ^{56}Fe was selected as the reference element for the reacted microsphere data analysis. This choice was based on the observation that ^{56}Fe had the highest concentration from NAA, a low RSF, and a high SIMS intensity:

$$\sigma_{CM\%} = \sqrt{\left[\left(\frac{\sigma_{ppm_R}\cdot I}{I_R}\right)^2 + \left(\frac{\sigma_I \cdot ppm_R}{I_R}\right)^2 + \left(\frac{\sigma_{I_R}\cdot I\cdot ppm_R}{I_R^2}\right)^2\right]}\cdot \cdot\left[\frac{RSF\cdot AW\cdot 10^{-2}}{RSF_R\cdot AW_R\cdot \sum_{\text{all isotopes}} CM\%.}\right] \quad (2)$$

Results

Results for the nine NAA elements are given in Tables 1c and 1d for the unreacted and reacted samples, respectively. The concentrations shown are based on the total microsphere volume. Concentrations in the thin film metal given in later comparisons are based on AES thickness measurements of the coatings. Table 1e shows the RSF values calculated from the c_1 definition given earlier for the nine NAA elements.

The data from these tables are plotted in Fig. 3, which is used to obtain RSF values for interpretation of the SIMS count data. Equation (1) was used to calculate the RSFs using ^{56}Fe as the reference isotope. A fit of this data to an exponential function is also shown. For comparison, the RSFs measured by WILSON et al.[11] with implants in a Ti matrix in a planar target are included in Fig. 3 along with a corresponding fit. The present NAA-based result is in close agreement with the WILSON et al.[11] data, even though the samples differed in matrix material and geometry. This general agreement gives added confidence to the present results. In contrast, use of a "general" RSF with a slope of 0.92 decade/eV, suggested in Reference 11 as a "rough approximation" is quite different from these more precise determinations. These RSF values are used next to find isotope concentrations along with isotope ratios, and production rates.

Isotope shifts

The atoms of an isotope produced in a run is calculated by subtracting the atoms of the isotope present before the run from that after the run. This difference is then converted to Y, the atomic yield of an isotope per 100 initial nucleons:

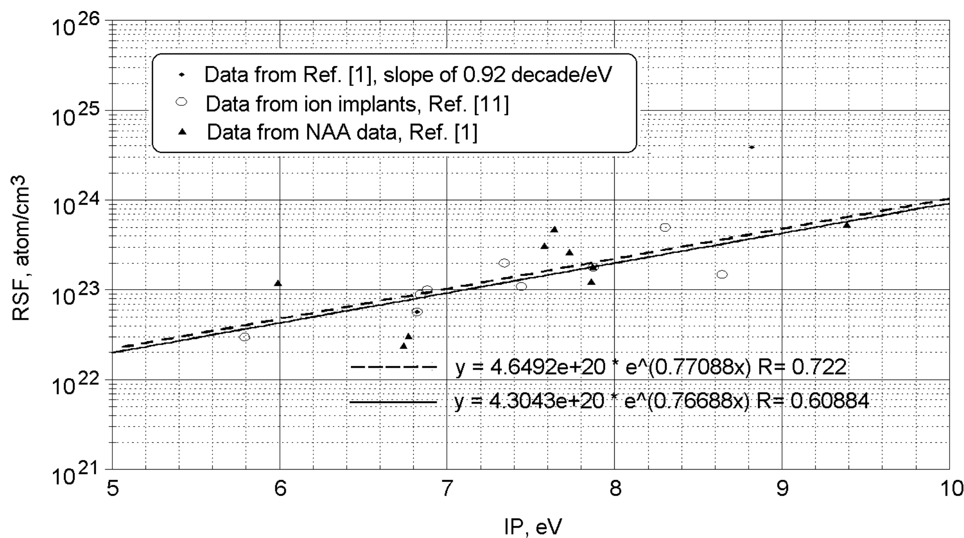

Fig. 3. RSF plotted vs. IP (- - -) fit to NAA data; (——) fit to Reference 11 data

$$Y = \frac{CN\%_{AR} - CN\%_{BR}}{A} \qquad (3)$$

where $CN\%$ is the percent concentration of nucleons of an isotope in the metal film and A is the mass number (total number of nucleons) in an atom of the isotope. Subscript BR denotes the metal film before the run and AR afterwards. The average atomic production rate, shown in Fig. 4, PR_i of isotope i in atom/s·cm^3, is calculated by dividing by the run duration. The resulting rates represent run average values. Periodic sampling might be used to determine possible time variations, but first a method must be found to extract beads without perturbing the run itself.

The isotope shifts (deviations of measured abundance from natural values) are shown in Fig. 5. The standard deviations were derived from application of the standard error propagation formula. If the error bar shown does not cross zero, the shift can be considered as potentially significant.

Discussion and conclusions

This research has developed a unique combined NAA-SIMS analysis technique for the study of impurity level isotopes in thin films. High precision analytical techniques were needed to characterize the isotopic concentrations. Ion implanted samples typically used as a SIMS reference were not convenient to manufacture because of the specialized facilities required, the high cost, and the difficulty of matrix reproduction between samples and reference thin film coatings. Thus, a NAA technique was developed to normalize the SIMS *RSF* values.

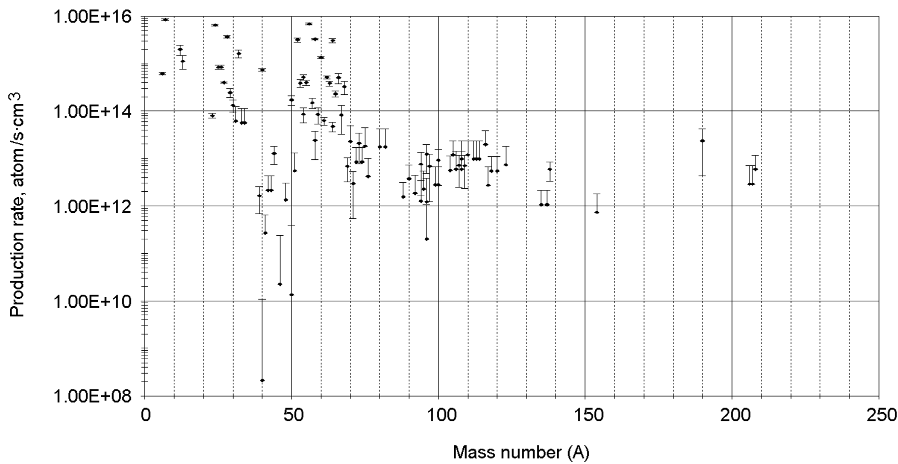

Fig. 4. Production rate of elements in the Ti coating

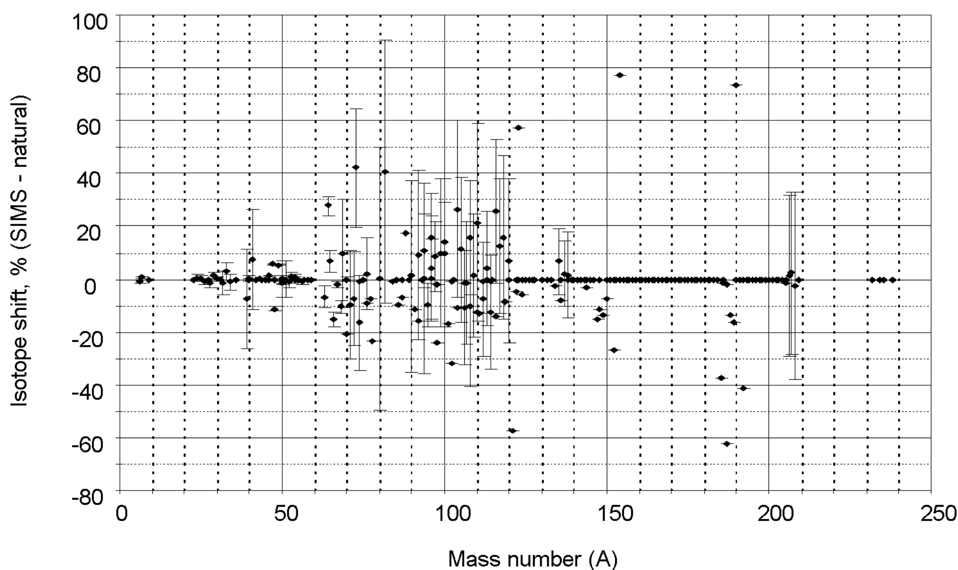

Fig. 5. Isotope shifts with error bars

Thirty-nine elements have isotopic shifts that deviate significantly from natural abundance, even when the statistical error bars (1σ) and isotope fractionation effects (max. error 4%) are included.

The isotope production rates plotted in Fig. 4 follow the "four peak" distribution of isotopes over characteristic mass range zones found earlier.[1] While the metal coatings used earlier were different, this agreement in trends provides more confidence in the present results. Beyond the element identification itself, a key concern with the overall interpretation is the possibility that the elements observed are not reaction products but impurities from components in the electrolytic cell. However, there is a significant quantity of material involved in the higher yield elements, e.g., ^{56}Fe with a production rate of $6.84 \cdot 10^{15}$ atom/s·cm^3 over a 10^6 s run gives 0.6 atom/cm^3. This level is well above the total amount Fe impurities that could accumulate from all of the various components of the system, which were analyzed individually in the earlier work.[1] Other high yield elements also fall above measured impurity limits. The data showing isotope shifts away from natural abundance is another confirming observation. Such deviations seem unlikely if an impurity source was the cause of these elements. In addition, in earlier work, "control" runs with sulfonated polystyrene microspheres showed little accumulation of impurities on the microspheres,[1] most impurities ending up on the cathode support grid. A full discussion of this impurity issue is beyond the scope of the present paper, but further details are provided in Reference 1.

While the experiment explained here represents a specialized research experiment, the combined NAA-SIMS technique described is quite general. This approach should be applicable to a wide range of samples arising in a variety of research and industrial processes.

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The NAA analysis was carried out in collaboration with Professor S. LANDSBERGER, now at the University of Texas. The SIMS analysis was performed using the facilities of the University of Illinois, Materials Research Laboratory.

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