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Section IV. Applications: (b) Trace element analysis and atomic physics

Atomic mass spectrometry of materials

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Texas Instruments and the University of North Texas (UNT) are collaborating on the design of an accelerator mass spectrometry (AMS) system dedicated primarily to the analysis of impurities in electronic materials and metals. An AMS beamline consisting of high-resolution magnetic ($M/dM > 350$) and electrostatic ($E/dE > 700$) analysis followed by a surface barrier detector has been installed on the NEC 9SDH pelletron at UNT, and a "clean" ion source is under development. An existing ion source (NEC Cs sputter source) has been used in conjunction with the AMS beamline to generate computer controlled molecule-free mass analyses of solid samples. Through a careful choice of isotopes and charge states a robust algorithm can be developed for removing molecular interferences from the mass analysis for essentially all materials. Examples using graphite, Si and CdZnTe are discussed.

1. Introduction

The detection of impurities in solid materials is important for a variety of modern technologies, including electronics and electro-optics. The presence of impurities at trace levels (10^{-6} to 10^{-12}) can affect the performance of devices constructed from these materials [1], and control of the accidental introduction of these elements during the manufacturing process is therefore required. Conventional mass spectrometric methods (secondary ion mass spectrometry (SIMS), spark source mass spectrometry) for detection of these elements are often unable to detect the impurity due to the presence of competing signals, primarily from molecular ions. Although techniques exist for resolving molecular and atomic ions of similar mass [2], this discrimination is often accomplished at the cost of reduced yield, which reduces the bulk sensitivity of the method. In addition, many samples of interest in the electronics industry consist of thin layers of patterned structures with correspondingly small sample volumes ($1-100 \ \mu m^3$). In these cases a severe reduction in system yield is unacceptable due to the limited number of impurity atoms available in the sample under study.

Accelerator mass spectrometry (AMS) has historically been utilized as an ultrasensitive method for measuring isotopic ratios involving rare radioisotopes of interest for dating applications [3]. A major reason for its success is the ability to couple the small sample size required by mass spectrometric methods with the removal of most of the common sources of interference in conventional mass spectrometry (molecules, scattered particles, detector noise). In many cases an extension to

other radioisotopes or stable isotopes is complicated by the sophisticated detection methods required to separate the isotope of interest from competing isobaric interferences, which often necessitates unique hardware for analysis of a new radioisotope. An extension of the AMS method to the detection of impurities in materials is not in general susceptible to this problem, however, since all elements except indium have at least one isotope with no stable isobars which can be used for analysis. Since the impurities in materials are often unknown, however, application of the AMS method requires the ability to sequentially search for all elements, preferably under computer automation. In addition the need for sensitivity to all elements places constraints on design of the ion source, since impurities from the sputtering beam, sample chamber, sample holder, electrodes, etc., must all be minimized.

This paper describes progress towards the development of a fully automated multi-element AMS detection system devoted primarily to the study of impurities in materials. The results described here were obtained using conventional ion source technology (NEC-SNICS source). A custom ion source under development specifically for materials applications is described elsewhere [4]. Examples of AMS multi-element mass scans from several materials systems are presented and discussed.

2. Experimental

The AMS measurements described here were performed on the 3 MV tandem accelerator at the Univer-

sity of North Texas (9SDH pelletron made by National Electrostatics Corporation). The facility is described elsewhere [5,6]. Solid samples were mounted in an NEC Cs sputter source (5×10^{-8} Torr pressure during analysis), and negative secondary ions were magnetically analyzed (momentum resolution $P/dP \sim 200$) through $90°$ before injection into the accelerator. After acceleration the resultant positive ions were magnetically ($45°$, $P/dP \sim 360$) and electrostatically ($45°$, energy resolution $E/dE \sim 700$) analyzed before detection. Computer controlled Faraday cups were placed after each analytical element, and a surface barrier detector was used for energy detection after the last cup. The magnets and electrostatic analyzer are computer controlled and for a given teminal voltage and charge state the electrostatic analyzer was set and the magnets were simultaneously ramped during a mass scan. To provide large dynamic range during the scan and still protect the surface barrier detector, Faraday cup detection was used for currents above $\sim 10^{-14}$ A, and particle counting in the surface barrier detector for lower level signals. All measurements were made using a terminal voltage of 2 MV, and impurities with charge states of $3 +$ or $5 +$ were monitored. (A charge state of $5 +$ was required on the CdZnTe sample due to the high magnetic rigidity of Te.) The terminal potential is not under computer control at present, and loading therefore distorts the signal for some high-intensity beams from the matrix material (Si, C). In these cases the transmitted intensity was measured manually.

SIMS analyses were performed on a Cameca IMS-3F system in low mass resolution mode ($P/dP \sim 300$) using Cs sputtering and negative ion detection. System pressure during analysis was 5×10^{-8} Torr. Computer control of a Faraday cup/electron multiplier combination allowed high dynamic range during analysis. The minimum measurable rate was ~ 0.1 Hz due to electron multiplier noise, and the maximum Cs current delivered to the sample was $\sim 10^{-6}$ A.

For the AMS measurements, the graphite and CdZnTe samples were mounted in an Al/Cu holder. The Si measurements were made using float-zone Si which had been machined in the shape of the holder, which removed the Al/Cu as a primary impurity source. In order to establish system background levels for the Si measurements, the Si was presputtered for several hours to attempt to coat existing surfaces with Si and reduce contamination from secondary processes.

3. Discussion

Fig. 1 shows an example of the ability of AMS to simplify the impurity analysis of CdZnTe, a compound semiconductor material used in the preparation of infrared detectors. In this figure the raw ion ratio between
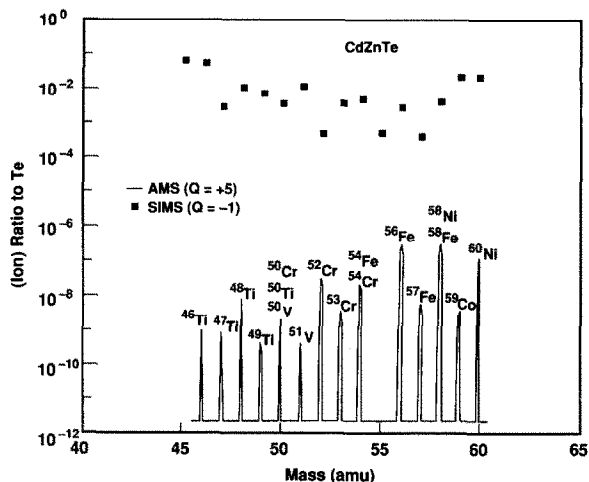

Fig. 1. AMS (2 MV, $Q = +5$) and SIMS analyses of bulk CdZnTe for masses 45–60. In each case the ratio of the raw ion intensity to the total Te signal is displayed. For clarity, only the peak values in the SIMS spectra are displayed.

the impurity of interest and the matrix (total Te signal) is plotted for various masses. The AMS data is shown in a typical mass scan format, but for clarity only the peak ratio (at each mass) in the SIMS spectra is displayed. The AMS baseline represents a count rate of 10^{-2} Hz. The ^{130}Te count rates for these analyses were 3×10^{5} (SIMS) and 1.3×10^{-9} A (AMS). The SIMS spectrum is dominated by the presence of various molecular species at high concentrations, while the AMS data shows removal of these interferences to ratios near 10^{-12} and allows the detection of the actual impurities. Although conventional high mass resolution methods are useful in discriminating against specific molecular interferences, they can be problematic in a general survey analysis of a sample such as CdZnTe due to the proliferation of high-intensity molecular signals of unknown composition and mass. Many high-resolution methods require some knowledge of the molecular impurity to help identify the atomic peak during high-resolution scans, since the instrument accuracy may be insufficient to assign an absolute mass. The AMS analysis solves these problems by removing the molecular contribution from the signal and thereby providing a more timely and reliable analysis.

The analysis of graphite is demonstrated in fig. 2, which once again compares AMS and SIMS data over the mass range from 10–65 amu. Peak count rates for these analyses were 10^{6} Hz (SIMS) and 5×10^{-8} A (AMS), and the SIMS values at 10^{-7} represent a background rate in the Cameca of 0.1 Hz. The SIMS data for graphite is dominated by the polyatomic C series (12, 24, 36, etc.) plus various hydrides, and once again these signals mask evidence for many impurities. The variations from natural abundance for the ^{13}C/^{12}C
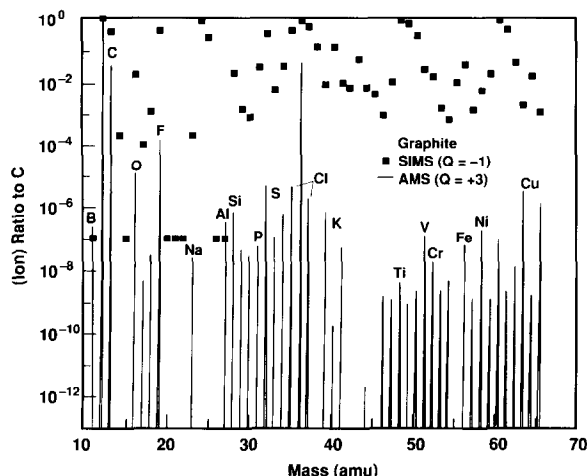
Fig. 2. AMS (2 MV, $Q = +3$) and SIMS analyses of bulk graphite for masses 10–65. In each case the ratio of the raw ion intensity to the total C signal is displayed. For clarity, only the peak values in the SIMS spectra are displayed. The signal at mass 36 is due to dissociation products for C_3 injection.
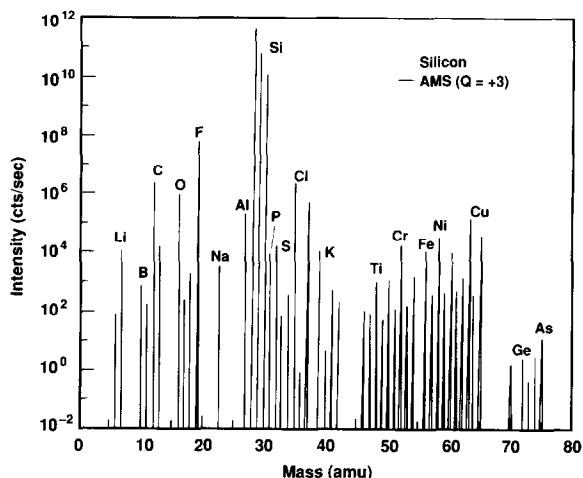

Fig. 3. AMS analysis (2 MV, $Q = +3$) of bare Si in the mass range 5–75. The signal at mass 42 is due to pulse pileup in the detector from SiN dissociation products. Negative ions are not detected for elements with electron affinities ≤ 0.

ratio are probably due to a combination of accelerator loading as well as a slight uncertainty in magnet calibration.

Although most signals in the AMS scan can be easily identified with an elemental impurity, the large peak at mass 36 is an example of a possible background signal in analyses of this type. Coupled magnetic and electrostatic analysis determines a mass to charge ratio M/Q rather than a mass directly, and energy analysis is therefore required to discriminate against off-mass ions with the same M/Q as the impurity of interest. In general this is done by using a surface barrier detector for energy windowing, but this is not possible for the high signal levels shown at mass 36. This signal is due to the injection of $^{12}C_3^{1-}$ which dissociates at the terminal and forms a $^{12}C^{1+}$ ion with the same kinematic parameters as the element of interest ($^{36}S^{3+}$). The problem can be avoided by choosing a charge state for analysis which is relatively prime to the mass of interest, and this will be incorporated in future algorithms.

Fig. 3 shows the raw AMS data from a Si sample which was pre-sputtered in the ion source for several hours in an attempt to reduce system backgrounds. There are several features of interest in this spectrum, which was collected using $Q = +3$ and a terminal voltage of 2 MV. Si is a material of great technological importance, and the detection of impurities is often greatly restricted by the presence of molecules such as SiH, SiO, Si_2, SiO_2, Si_2O, etc. These molecules obscure two of the major dopants of Si (^{31}P versus ^{30}SiH, $^{28}Si^{29}Si^{16}O$ versus ^{75}As) as well as various transition metals (Si_2 and SiO_2 versus Fe, Ni, Co) which have significant electrical effects. The AMS signals are all

well below normal molecular background levels and for multi-isotopic elements such as Fe and Ni the ratios lie close to the natural abundances. (Variations in the Li and B signals can be traced to isotopically enriched targets which have been used previously in the ion source.) The presence of S at masses 32 and 34 confirms the origin of mass 36 in this scan, but a plot of the energy spectrum gathered in the surface barrier detector (fig. 4) demonstrates the need for energy analysis due to the $^{12}C_3$ breakup product $^{12}C^{1+}$ ($E \sim 2.67$ MeV) seen previously in the graphite AMS scan. Although the C
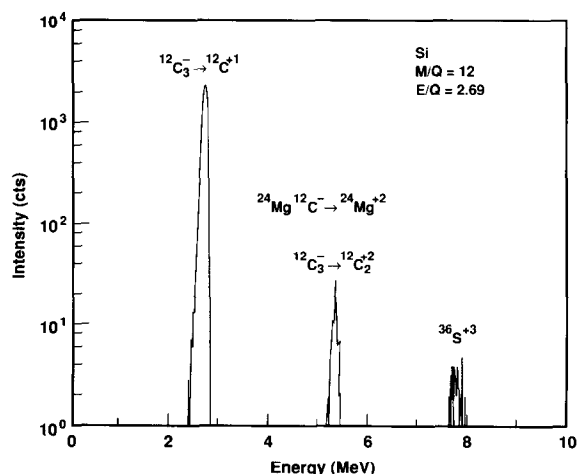

Fig. 4. Energy spectrum of particles with nominal mass 36 in the Si scan of fig. 3. An energy window was set from ~ 6.5–8.5 MeV to reject dissociation fragments. The peaks at 2.7 MeV and 5.4 MeV are due to breakup of C_3 and possibly MgC molecules.

levels in the source are much lower than during the graphite analysis, residual gases are always present at some level and will contribute some background if not rejected through energy analysis. There is also a signal at ~ 5.33 MeV due either to $^{24}Mg^{2+}$ dissociation products from MgC injection or $^{12}C_2^{2+}$ molecular ions from C_3 injection.

There are several elements in this mass range which do not form negative ions, and all are absent from the mass spectrum except for a signal at mass 42. This has been shown previously [7] to be due to pileup in the surface barrier detector from $^{28}Si^{14}N$ dissociation products. The strength of this signal suggests that injecting a Si-bearing molecule into the accelerator and looking for the dissociation products may allow analysis of some materials otherwise inaccessible, in a similar fashion to BeO$^-$ injection in conventional AMS. Fig. 5 shows such a scan in which molecular negative ions of the form $M^{28}Si^-$ were injected from the Si sample into the accelerator (M is the mass of the element of interest), and the analytical elements were tuned to look specifically for the dissociation fragments of mass M. Elements such as N, Mg, Ca, Mn and Zn are now evident in the spectrum at moderate levels. Analysis of elements with electron affinities ≤ 0 requires investigation of this procedure to identify the optimum molecule for a particular analysis (i.e. BeO$^-$ versus BeSi$^-$ for Be in Si analysis).

It is possible to estimate system contamination levels in the Si analysis by utilizing relative sensitivity factors (as determined by SIMS) for various elemental and molecular (MSi$^-$) ions. In each case the impurity of interest was ion implanted at a known dose and energy into a Si sample and subsequently profiled by SIMS
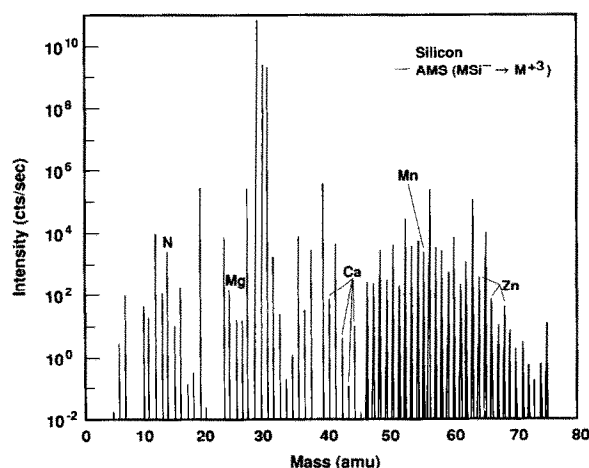
Table 1
Calculated contamination levels for the data displayed in figs. 3 and 5. SIMS relative sensitivity factors for Cs sputtering of Si were used to calculate the concentrations. These calculations do not correct for charge state variations.

Element	Injected ion	Calculated concentration [atoms/cm^3]
N	NSi	1×10^{15}
Mg	MgSi	2×10^{15}
Al	Al	6×10^{18}
P	P	2×10^{15}
S	S	2×10^{14}
Ca	CaSi	1×10^{16}
Mn	MnSi	6×10^{16}
Fe	Fe	2×10^{18}
Ni	Ni	6×10^{16}
Cu	Cu	2×10^{17}
Zn	ZnSi	4×10^{16}
Ge	Ge	3×10^{12}
As	As	1×10^{13}

using Cs sputtering and negative ion detection [9]. The peak concentration of the implant can be determined from knowledge of the implant parameters, and a measurement of the relative ion yields for Si and the elemental or molecular ion of interest provides a calibration factor for subsequent analysis of an unknown sample. (This is a routine method in SIMS and will also be available as a calibration method on AMS systems with shallow (~ 100 nm) depth profiling capabilities.) Transmission through the accelerator system will not be constant as a function of mass, and variations in the charge-state stripping probability will impose an uncertainty of about a factor of three on these values (in addition to uncertainties in the SIMS data). The results of these calculations are presented in table 1 for several impurities and represent the estimated concentrations as determined from the data shown in figs. 3 and 5 and published SIMS information [9]. Many of the elements with high background (Al, Fe, Cu) are known contaminants in the ion source. At present the sensitivity is limited due to contamination from the ion source materials, memory effects, etc., but these numbers and comparison with figs. 3 and 5 show a "detectability" limit in the ppt range for most elements (10–100 s collection time). Improvements in system transmission and the choice of injected molecular ion should provide ppt sensitivity for essentially all elements.

Fig. 5. AMS analysis (2 MV, $Q = +3$) of bare Si in the mass range 5–75 for "silicide" dissociation products. Negative molecular ions of the form MSi$^-$ are injected into the accelerator, and the dissociation fragments of mass M are detected.

4. Conclusion

Accelerator mass spectrometry has been used to generate atomic mass scans of several materials over a

broad mass range. The molecular ions associated with more conventional mass spectrometry methods are completely removed during AMS analysis. Careful choice of injection species allows access to elements with low electron affinities. Present sensitivities with this method are limited primarily by impurities in the ion source, but a "clean" ion source currently under construction should allow sensitivities in the parts-per-trillion range to be realized for most elements.

Acknowledgements

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