
Sir: There has been considerable interest in quantifying secondary ion mass spectrometry (SIMS) results. Techniques utilizing theoretical and semitheoretical models of secondary ion emission have been proposed for this purpose but typically yield only "order of magnitude" results (1-3). Empirical calibration methods employing external or internal standards have also been shown to give excellent results (4, 5). However, the required SIMS standards are difficult to obtain since they must be homogeneous on the microscale and must closely approximate the chemical composition of the material to be analyzed.

Recently, the technique of ion implantation has been adopted to fabricate SIMS standards (6). Ion implants are well understood, and by utilization of the known implanted dosage, accurate conversion of secondary ion intensity to concentration can be achieved (7). Moreover, these ion implant standards can be tailor-made for a particular analysis requirement. Solid-state standard addition, the use of ion implantation to perform a conventional standard addition analysis to a solid sample, has been used to determine bulk dopant concentration in steel and semiconductor samples with good results (8). One handicap of this approach is that the residual concentration to be measured must be relatively high. Most realistic dopant concentrations in semiconductor materials are too low for the direct use of this standard addition approach.

In order to improve the sensitivity of this technique, we have investigated the use of computerized signal integration to increase the signal-to-noise ratio. This technique utilizes the known Poisson statistics of the ion counting circuitry. For this case, the noise associated with a particular number of counts, \( n \), is equal to the square root of \( n \). Therefore, the signal-to-noise ratio can be improved by a factor of 10 by increasing the number of counts by 100 times. This has been experimentally demonstrated in the field of vidicon spectrometry (9). A computerized integration method was adopted by our laboratory for the analysis of gelatin standards for quantitative SIMS analysis of biological tissues and was found to give improved detection limits (10).

In this study, the method of solid-state standard addition combined with computerized signal integration is applied to the quantitative analysis of a silicon wafer doped with a very low concentration of boron (approximately 10\(^{15}\) atoms/cm\(^2\)). Because of the existence of systematic errors in ion counting, there is deviation from the linear signal-to-noise vs. square root of time improvement. The experimental procedures are modified accordingly to obtain an optimal signal-to-noise ratio. The method is found to yield an accuracy of 12% and precisions of 17-25% depending upon measurement conditions. This boron concentration is almost an order of magnitude below the detection limit found previously by the usual solid-state standard addition method. Any laboratory for the analysis of gelatin standards for quantitative SIMS analysis of biological tissues and was found to give improved detection limits.

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**Literature Cited**


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profile data were then transferred to the PDP-11/34A for processing by a peak integration program. This program allows the operator to subtract out the background level of the unimplanted region from the implant signal and then outputs the integrated ion intensity of the implant peak.

Procedure. A commercially available polished boron doped silicon (100) wafer was used in this experiment. The boron concentration in the wafer was determined by four point probe electrical measurement to be $2.6 \times 10^{15}$ atoms/cm$^3$. The wafer was cut, cleaned ultrasonically with trichloroethylene, acetone, methanol, and deionized water, and mounted on an aluminum disk with conductive silver paint. The sample was then implanted with $1 \times 10^{13}$ atoms/cm$^2$ of $^{11}$B at 100 kV. The single crystal Si was tilted at an angle of 7° to reduce implant channeling.

After implantation, the sample was depth profiled for $^{11}$B. The depth profile was terminated and stored when the boron signal dropped to the constant residual level. The sample was then sputtered for another 5 min, thus removing an additional 200 nm of material to ensure complete removal of implanted boron. At this point the integration routine was run with an integration time of 3 s/cycle. The schematic of the experiment is shown in Figure 1. The depth of the sputtered crater was measured by a Taylor-Hobson Talystep stylus type surface profiler with a resolution of 5-10 nm to enable conversion of the implant fluence to concentration. To determine the noise of the electron multiplier, we ran the integration program with the exit slit of the mass spectrometer closed completely and the primary ion extraction voltage turned off.

To calculate the concentration of the background boron dopant, we divided the total residual signal accumulated by the integration value to give the residual signal, $S$, in counts/s.

**RESULTS AND DISCUSSION**

Figure 2, a depth profile of the $^{11}$B implant, shows the residual boron signal obscured by noise. The usual solid-state standard addition technique using the same primary ion current density and a 5-s acquisition time per analysis point yielded a noise limited detection limit for boron in silicon of approximately $2 \times 10^{14}$ atoms/cm$^2$, which is the detection limit of B in Si published in literature (7). With the present computerized integration approach, integrating each analytical point for 600 s (200 cycles), a boron concentration of $2.3 \times 10^{15}$ atoms/cm$^3$ was calculated with a standard deviation of $\pm 4 \times 10^{14}$ atoms/cm$^3$. This value agrees within 12% with the electrical measurements and is an order of magnitude below the detection limits using the conventional technique. This increase coincides with the expected $S/N$ improvement using a 100-fold increase in counting time.

The degree of improvement in sensitivity possible with the use of signal integration was evaluated by repeating the experiment using increasing integration times. Figure 3 gives the $S/N$ ratio plotted against the square root of the integration time. As shown the $S/N$ ratio begins to level off beyond 300 s integration, instead of continuing along the straight line. The time of 600 s (200 cycles) was chosen in the analysis as this time gave the best results within a reasonable analysis time. The leveling off of the curve in Figure 3 suggests that the maximum improvement to be gained by using this technique is approximately an order of magnitude.

The signal-to-noise ratio becomes constant with an increasing number of cycles for two reasons. For low-level signals, a long integration time tends to result in deterioration of the apparent signal, but the most significant reason is that a systematic error derived from computer ion counting is not accounted for. Owing to the logarithmic nature of the data display, any signal below 1 count/cycle is counted as 1 count/cycle. However, it is not necessary to remove this systematic error to obtain accurate results. Figure 3 shows that a constant signal-to-noise ratio of about 1 is obtained for 200 scanned cycles or more. Statistically, the signal is reliable because it is twice the background noise (systematic and random). Further comparison with the electrical value confirms the accuracy of this methodology. Since any signal with a lower signal-to-noise ratio would be unreliable statistically, the concentration measured in this experiment is concluded to be the detection limit of boron in silicon by the present method. Further increases in sensitivity beyond that will have
to come from improved ionization efficiency, increased collection of secondary ions by the mass spectrometer, and improved detectors. The technique of computerized signal integration however has shown its ability to improve the sensitivity of the solid-state standard addition method to more realistic concentration levels. An analysis time of several minutes instead of several seconds does not seem unreasonably long to provide an order of magnitude higher sensitivity. One caution, however, is that the sample to be analyzed by this technique must be homogeneous enough in depth to sputter through several hundred nanometers of material while integrating a reliable signal intensity.

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LITERATURE CITED


Determination of Ethylenediamine in Aqueous Solutions by Ion Chromatography

Sir: In a recent publication, Wimberley suggests an alternative eluent for the determination of divalent cations by ion chromatography (1). As an extension of this work, we have investigated the determination of ethylenediamine in aqueous solutions. Using ZnCl₂ and HCl in the eluent, we were able to successfully chromatograph ethylenediamine and demonstrate a linear response with conductometric detection. Our experiments substituted ZnCl₂ and HCl for Zn(NO₃)₂ and HNO₃ because the chloride causes less suppressor column degradation (2).

EXPERIMENTAL SECTION

Apparatus. A Dionex Model 18 ion chromatograph with a 0.1-mL sample loop was used for all experiments. A 4 × 50 mm cation precolumn (Dionex part no. 030800) and a 6 × 60 mm cation suppression column (Dionex part no. 030834) were used for the separation. A Shimadzu C-R1A integrating recorder was used to record and integrate the signal. A Hewlett-Packard 5995A gas chromatograph/mass spectrometer was used to confirm that the eluting species was ethylenediamine.

Chemicals. All chemicals were reagent grade and dissolved in grade 3 (18 MΩ/cm) deionized water.

RESULTS AND DISCUSSION

Attempts to separate ethylenediamine by using the conditions established by Small et al. were unsatisfactory because ethylenediamine is strongly retained to cation exchange resins (3). Retention times were too long to be practical and peak shapes were unsuitable for quantitation. The chromatographic system, as described by Jaworski, is also unsuitable because a 2 N HCl mobile phase would expel the suppressor during the course of one determination (4).

In a solution containing 0.004 N HCl and 0.0025 M Zn²⁺ the ethylenediamine is complexed to form the Zn(\(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\))²⁺ chelate (5, 6). This complex changes the free energy of solvation for the ethylenediamine and changes the partition coefficient between the complex in solution and that bound to the resin. This change allows the ethylenediamine to be chromatographed with acceptable peak shapes. After separation, the complex enters the suppressor column where Zn²⁺ is precipitated and HCl is stripped by the hydroxide form resin; hence, the ethylenediamine enters the conductivity detector as the free base in a background of deionized water. We determined that suppressor column regeneration as described by Wimberley proved generally adequate (5). However a more thorough regeneration was achieved by first washing the exhausted suppressor for one-half hour with a solution containing 0.0025 M HCl and 0.0025 M m-phenylenediamine dibydrochloride, followed by a regeneration cycle with 1 N NaOH.

Several experiments were run in an attempt to optimize the chromatogram. Initially both a precolumn and an analytical column were used for the separation. This produced acceptable results with retention times of approximately 25 min. Methanol and 2-propanol were separately added to the eluent in 5% and 20% concentrations (v/v) to reduce adsorption. The addition of organic solvents to the eluent produced tailing of the peak and reduced the detector response. Finally, the analytical column was removed and the separation performed on the precolumn only. This decreased the retention time of ethylenediamine to approximately 7 min.

Using only a precolumn, all alkaline earth cations were eluted before 4 min and were only slightly resolved from one another. All monovalent cations and amines (Li⁺, Na⁺, NH₄⁺, K⁺, Rb⁺, Cs⁺, methyamine, trimethylamine, ethylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, and triethanolamine) were found to elute near the dead volume. Nine standard solutions of ethylenediamine (0.1, 0.5, 10, 15, 20, 50, 75, and 100 ppm) were prepared from

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