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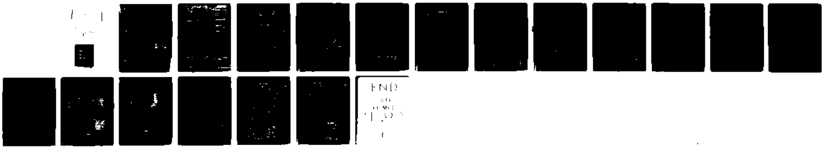

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SOLID STATE STANDARD ADDITION METHOD IN SECONDARY ION MASS SPECTROMETRY FOR IMPROVEMENT OF DETECTION LIMITS

by

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The technique of solid state standard addition is inadequate for the determination of low dopant concentrations present in real semiconductor samples. An extension of the solid state standard addition method using computer controlled signal integration is shown to lower the detection limit of boron in silicon by an order of magnitude. The precision and accuracy of this method were found to be 25% and 12%, respectively.

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ABSTRACT: The technique of solid state standard addition is inadequate for the determination of low dopant concentrations present in real semiconductor samples. An extension of the solid state standard addition method using computer controlled signal integration is shown to lower the detection limit of boron in silicon by an order of magnitude. The precision and accuracy of this method were found to be 25% and 12%, respectively.

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There has been considerable interest in quantifying secondary ion mass spectrometry (SIMS) results. Techniques utilizing theoretical and semi-theoretical 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 utilizing 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^3). Because of the existence of systematic errors in ion counting, there is deviation from the linear signal-to-noise versus 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.

EXPERIMENTAL SECTION

Instrumentation: Ion implantation was performed using an ACCELERATORS INC. 300R ion implanter (11). The SIMS analysis was carried out using a CAMECA IMS-3f ion microscope equipped with an electron multiplier for signal detection (12). The instrument is interfaced to a Hewlett Packard 9845T microcomputer for control and data acquisition. The IMS-3f was also interfaced with a Digital PDP-11/34 minicomputer for data processing. A 5.5 kV O_2^+ primary beam was rastered over a 250x250 μm^2 area at a current density of 1.60mA/cm^2. The sampled area was resticted to 150x150 μm^2 and positive secondary ions were monitored. All analyses were performed at 2×10^{-8} torr.

Software: The integration routine used to acquire the residual dopant signal repeatedly scans across a given mass for an operator-defined number of cycles, a cycle being one scan. The time allotted to each cycle is also under operator control. The data from each scan is added to a buffer containing the summation of all previous scans until the specified number of scans have been completed. At this time, the contents of the buffer are output.

Depth profiling of the ion implanted region was performed using the standard software supplied by the manufacturer. The depth 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 $2.6\text{x}10^{15}$ atoms/cm^3. The wafer was cut, cleaned ultrasonically with trichloroethylene, acetone, methanol, and deionized water and mounted on an aluminum disc with conductive silver paint. The sample was then implanted with $1\text{x}10^{15}$atoms/cm^2 of ^{11}B at 100kV. The single crystal Si was tilted at an angle of 7 degrees to reduce implant channelling.

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 minutes thus removing an additional 200 nm of material to ensure complete removal of implanted boron. At this point the integration routine was run using an integration time of 3 seconds/cycle. The depth of the sputtered crater was measured by a Taylor-Hobson Talystep stylus type surface profiler with a resolution of 5-10 nanometers to enable conversion of the implant fluence to concentration. To determine the noise of the electron multiplier, the integration program was run 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, the total residual signal accumulated by the integration routine was divided by the total time of integration. The noise signal of the electron multiplier (one count per cycle) was then subtracted from this value to give the residual signal, S_r, in counts/sec.

The following equation was used to calculate the residual concentration:

$$C_r = \frac{S_r \times T \times F}{I \times D \times A} \qquad (1)$$

where C_r is the residual elemental concentration to be determined in atoms/cm^3, S_r is the residual isotopic signal in cps as defined previously, T is the time of analysis in seconds, F is the fluence of the implant (1x10^{15} atoms/cm^2), I is the integrated sum of the implanted ion intensity in counts (typically about 1 million counts), D is the depth of the crater in centimeters (about 2 x 10^{-4} cm. typically), and A is the isotopic abundance.

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 second acquisition time per analysis point yielded a noise limited detection limit for boron in silicon of approximately 2×10^{16} atoms/cm^3, 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 seconds (200 cycles), a boron concentration of 2.3×10^{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 as a function of the square root of the integration times. As shown the S/N ratio begins to level off beyond 300 seconds integration, instead of continuing along the straight line. The time of 600 seconds (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 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 cps is counted as 1 cps. 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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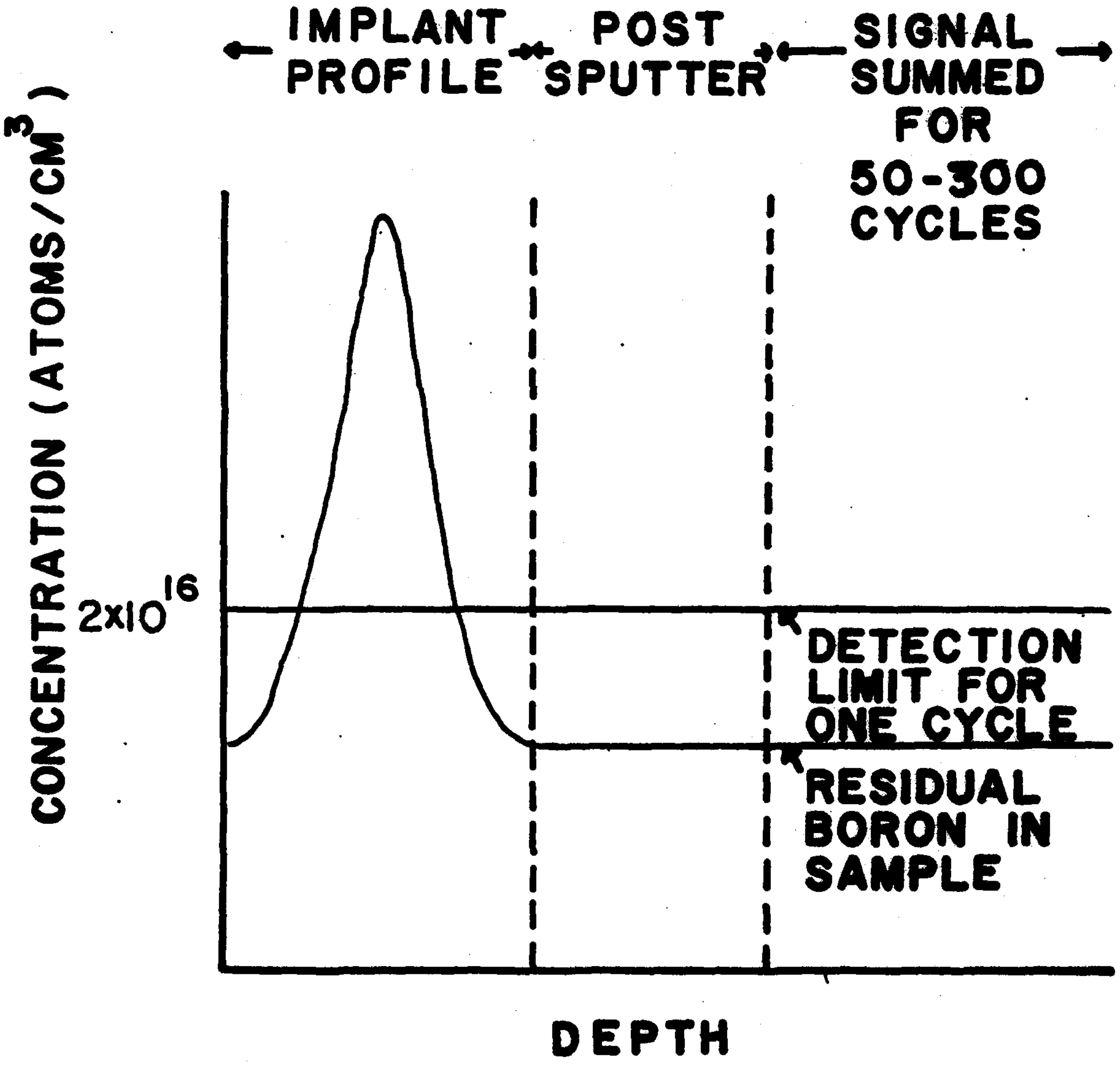
FIGURE CAPTIONS

Figure 1. Schematic of the experiment.

Figure 2. Depth profile of ^{11}B in silicon.

Figure 3. Signal to noise ratio plotted against the square root of the integration time.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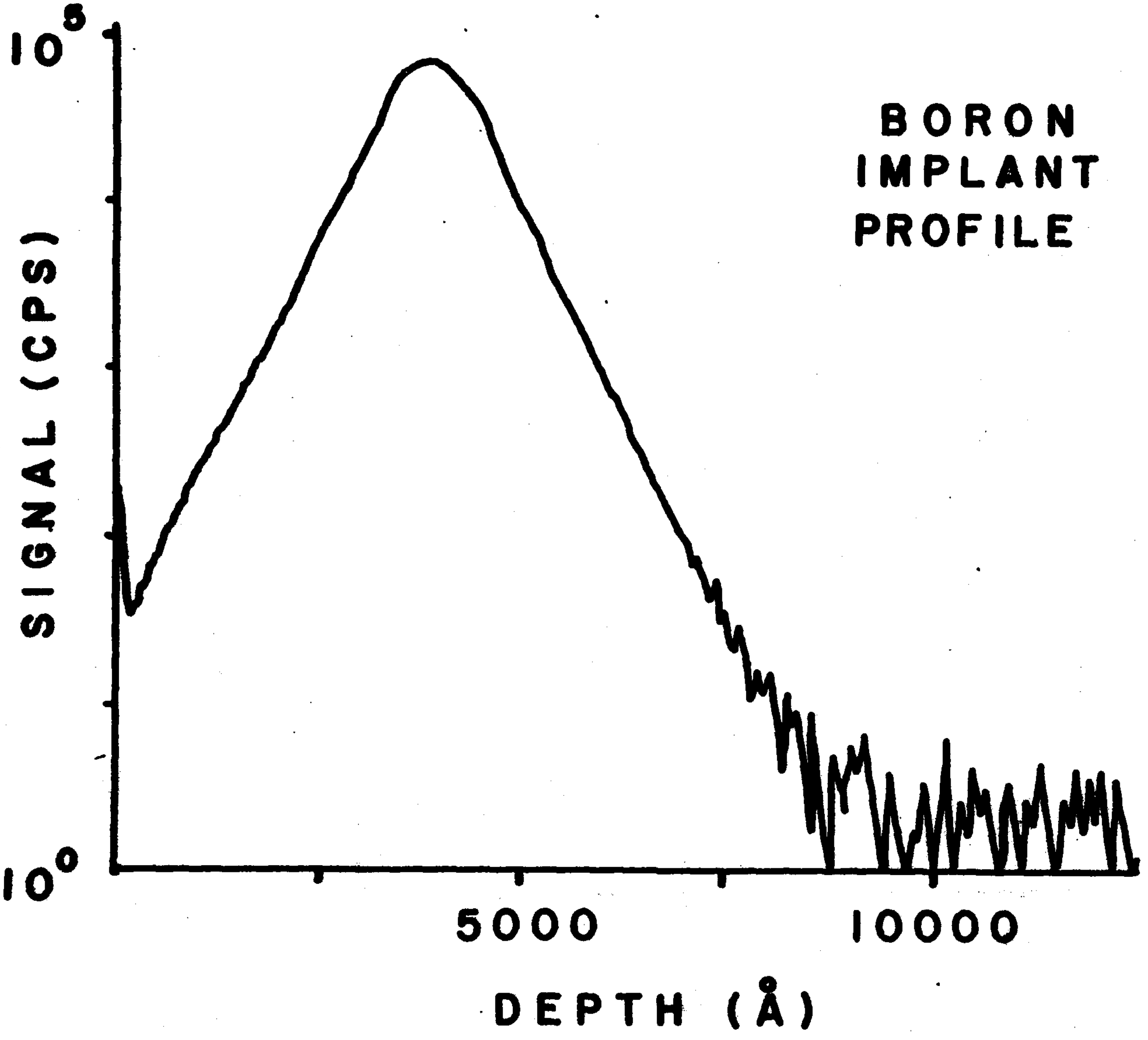
RESIDUAL BORON IN SAMPLE
DEPTH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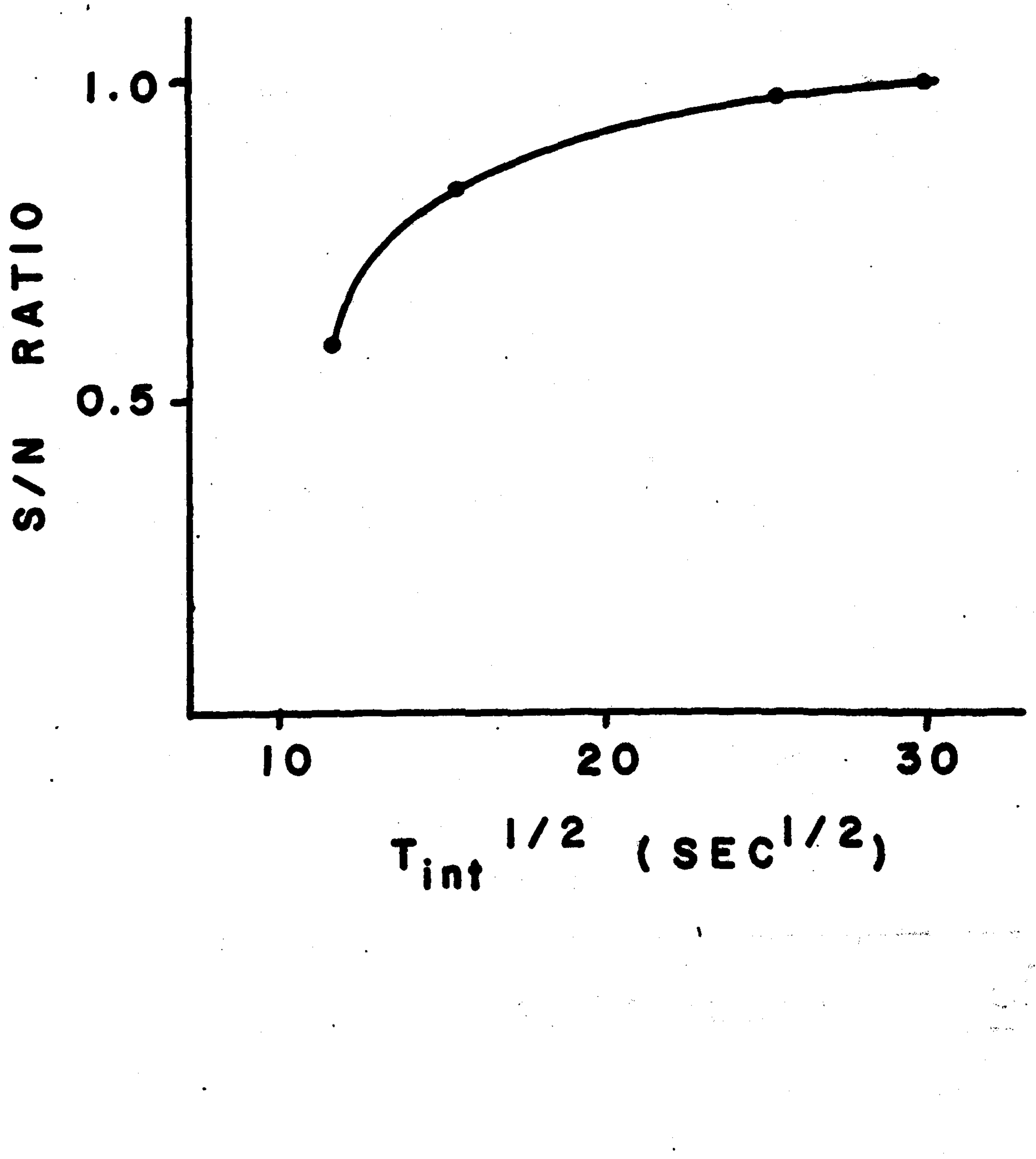
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