

CERTIFICATION OF AN ION-IMPLANTED ARSENIC IN SILICON STANDARD REFERENCE MATERIAL

The secondary-ion mass spectrometry (SIMS) community in the United States recently undertook a round-robin study to calibrate the implanted dose of arsenic in silicon by consensus. Variations in dose determination among laboratories were as high as 30 %, reflecting primarily the errors of the respective in-house standards. By contrast, in an international round-robin exercise sponsored by the International Standards Organization (ISO) the U.S. laboratories achieved a relative standard deviation of 4 % for nine independent determinations of the boron content in an unknown boron-doped silicon sample. This level of agreement was only possible because all the laboratories used SRM 2137 Boron Implant in Silicon as a common reference material. These results demonstrate the need for a common arsenic reference material to improve inter-laboratory reproducibility. Furthermore, SEMATECH (a consortium of semiconductor manufacturers) recently listed SRM implants of phosphorus and arsenic in silicon as high priority industrial needs. Consequently, a Standard Reference Material (SRM 2134 Ion-Implanted Arsenic in Silicon) was produced at NIST, using a wafer from the SIMS intercomparison. The material for this SRM was provided by a major ion implanter manufacturer who supplied three 200 mm diameter wafers that had been implanted with arsenic at an energy of 100 keV (in the same batch). One of the wafers was diced and distributed to 12 participating laboratories for the arsenic round-robin study described above. Each of the remaining wafers could provide 221 SRM units, enough for an estimated 10 year supply. One of the remaining wafers was therefore diced into 1 cm x 1 cm pieces with a wafer saw for use as SRM 2134. Because of the specificity and matrix independence of instrumental neutron activation analysis (INAA), this technique was chosen as the primary method for certification of the arsenic implanted dose.

Ten analytical specimens of silicon were selected from among the 221 pieces cut from the wafer to determine arsenic content and test for homogeneity. Two blank chips of silicon were analyzed in parallel. Pre-irradiation handling was done on a class 100 clean bench. In a Teflon TFE beaker, the specimens and blanks were rinsed together in ultrapure (UP) water, rinsed with 95 % ethanol, cleaned ultrasonically for one minute in ethanol, and rinsed twice with UP water. The samples and blanks were then agitated for one minute in UP water, blotted on Whatman 41 filter paper, and

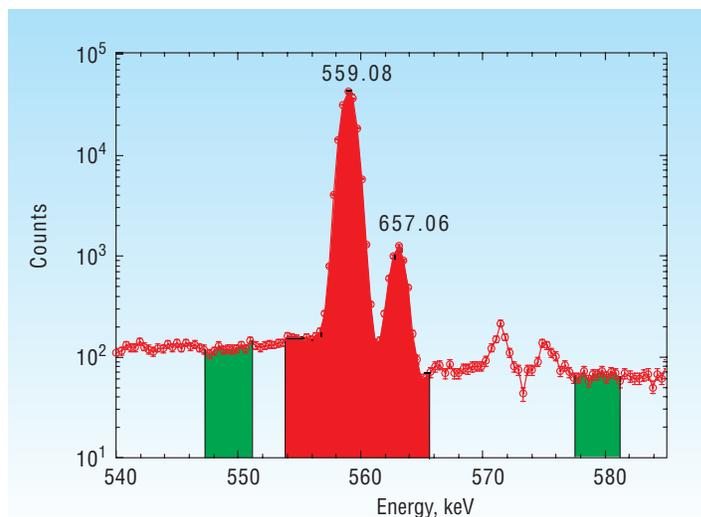


FIGURE 1. Region of the gamma-ray spectrum for analysis of As in SRM 2134. Limits of peak and baseline areas are indicated by vertical lines.

air-dried. Each was weighed and heat-sealed in a polyethylene bag that had been cleaned in high purity nitric acid.

A dilute solution standard was prepared by gravimetrically diluting a 10 mg/g solution of As₂O₃ in dilute ammonia to about 2 mg/kg. Another solution was prepared similarly from SRM 3103a Arsenic Spectrometric Solution. Aliquants of both solutions were weighed from a polyethylene pipette onto 1-cm disks of acid-leached Whatman 41 filter paper and dried to produce standards with about 200 ng arsenic each. Two standards from each solution were irradiated with the samples. A blank filter paper was shown in a separate experiment to contain no significant arsenic (<< 0.01 % of the amount in the standards).

Samples, standards, and blanks were stacked in the irradiation container in the following sequence: standard, blank, five samples, two standards, five samples, blank, and standard. The stack was irradiated for four hours in the RT-1 pneumatic tube of the NIST research reactor, at a thermal fluence rate of 7.7×10^{13} cm⁻²s⁻¹. The container was inverted halfway through the irradiation to equalize to the first order for the axial fluence rate gradient along the container.

After irradiation the silicon samples were cleaned ultrasonically for one minute in de-ionized water, blotted dry, and heat-sealed in clean conventional polyethylene bags for counting.

Gamma-ray activity was assayed at 10 cm from a germanium detector with a 1.71 keV resolution and 40 % relative efficiency at 1333 keV. Each sample and standard was counted at least twice, after the 2.62 h ^{31}Si matrix activity had substantially decayed. The 559 + 563 keV doublet of ^{76}As in each spectrum was integrated with the SUM computer program [1]. See Fig. 1. No evidence indicating significant heterogeneity among samples could be seen when the observed sample-to-sample precision was compared to what was expected from counting statistics combined with other sources of analytical variability.

NIST currently certifies elemental concentrations in SRMs using one of three modes: (1) a primary method at NIST with confirmation by other method(s); (2) two independent critically evaluated methods at NIST, and (3) one method at NIST and different methods by outside collaborating laboratories [2].

Table 1. Individual Uncertainty Components for Determination of Arsenic in SRM 2134.

Source of Uncertainty	Individual Uncert. (1s) %
Basis Measure - Sample Area / Micrometer Accuracy	0.012
Basis Measure - Sample Area / Precision (n = 26) ¹	0.0089
Concentrations of Comparators (Standards)	0.106
Mass Determination - Comparators	0.041
Isotopic Variability	0
Blank and Blank Correction (n = 10 ²) ¹	0.013
Irradiation Geometry Differences	0.039
Neutron Self - Shielding/Scattering Differences	0.024
Timing	0
Irradiation Interferences	Negligible
Measurement Replication (n = 9) ¹	0.081
Counting Statistics - Standards (n = 10 ⁵) ¹	0.073
Counting Geometry Differences	0.009
Pulse-Pileup	0.066
Dead-Time Effects (inadequacy of LT extension)	Negligible
Decay Timing Effects (Half life related)	0.053
Gamma-Ray Self Shielding	0.004
Gamma-Ray Interferences	0.00004
Peak Integration Method	0.033
Overall	0.189

¹ "n" indicates degrees of freedom which are listed for Type A sources of uncertainty.

Certification using a primary method is only possible when all potentially significant sources of uncertainty have been evaluated explicitly for the application of the method and the matrix under investigation. In addition, confirmation of measurements by a primary NIST method may be accomplished by one or more of the following: determination of certified constituents in other SRM(s) or CRM(s) of similar matrix and constituent concentration range; a second NIST technique with appropriate controls; or results of measurements from selected outside collaborating laboratories with appropriate experience.

In order to certify the arsenic concentration in SRM 2134 using INAA as a primary method it is therefore necessary to evaluate all significant sources of uncertainty explicitly. For this set of measurements, we considered sources of uncertainty greater than 0.01 % relative to be significant. The results of a complete evaluation of all sources of uncertainty are listed in Table 1. This evaluation yielded an expanded relative uncertainty of 0.38 % (as defined by ISO and NIST) and gives an approximate level of confidence of 95 %. The arsenic concentration observed was 91.20 ng/cm² ± 0.35 ng/cm².

In conclusion, we have successfully applied INAA as a primary method for the certification of this new SRM. The observed relative expanded uncertainty of 0.38 % is considerably smaller than the 1 % value desired by the semiconductor industry. This new SRM should greatly enhance the U.S. semiconductor industry's ability to achieve accurate and reproducible analytical results for this key dopant in silicon.

REFERENCES

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- [2] W. May, R. Parris, C. Beck, J. Fassett, R. Greenberg, F. Guenther, G. Kramer, S. Wise, T. Gills, J. Colbert, R. Gettings, B. MacDonald, *NIST Spec. Pub.* 260-136, 2000.