SIMS Quantification Round-Robin Study at Evans Analytical Group

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Abstract–**Bulk-doped silicon wafers were measured at four EAG (Evans Analytical Group) site laboratories in a round-robin study of the calibration of SIMS measurements of dopant concentrations in silicon. Mean B, P, and As concentrations were determined for several bulk-doped silicon reference wafers. Absolute concentration calibration scales are determined by NIST Standard Reference Materials (B, As) or accepted Consensus Reference Materials (P). At any single EAG measurement site, the average repeatability of an individual dopant concentration measurement was about 0.7% for B, 2.1% for P, and 2.3% for As. Across the four sites, the best reproducibility for concentration measurements was found when bulk-doped standards were used for calibration. Average reproducibility of dopant concentration measurements across the EAG was 0.9% for B, 2.5% for P, and 2.6% for As.**

I. Introduction

Consistency of analytical measurements for Failure Analysis (FA), Quality Control (QC), and Research & Development (R&D) is very important to companies as they expand their manufacturing activities globally. To meet required process deadlines, it may be necessary to obtain analytical results from supporting laboratories at several different site locations. In this case, it is essential that all quantitative results have been placed on the same absolute calibration, and that measurements have been made to the same level of precision (repeatability and reproducibility). In other words, the actual site location of the analytical service provider must be transparent to the end user of the data. A group of laboratories can meet these requirements by the use of appropriate calibration standards and tightly controlled analysis protocols.

This paper presents results of a secondary ion mass spectrometry (SIMS) round-robin study conducted by the Evans Analytical Group (EAG), comprised of four analytical laboratories. The importance of this study is to show that SIMS can characterize dopant concentration and hence the dose and distribution of ion implants in silicon with good accuracy and precision using multiple instruments at multiple locations.

The specific goals of this round-robin were:

1. To provide calibration of common standards for use at all sites,
2. To establish uniform calibration scales for SIMS measurement of B, P, and As concentrations in silicon,
3. To characterize the reproducibility of SIMS measurements across the EAG.

Samples were B, P, and As bulk-doped silicon wafers. At least four separate wafers or distinct wafer locations were analyzed for each dopant. Calibration was to the boron NIST SRM-2137, arsenic NIST SRM-2134, and a phosphorus Consensus Reference Material (CRM). The SIMS measurements were made using both magnetic sector and quadrupole mass spectrometers (Table 1).

II. Procedures

Silicon samples were selected and distributed by Charles Evans & Associates (Sunnyvale, CA). Unknown samples were all bulk-doped (approximately 10^{19} cm^{-3}). Two configurations of samples were distributed:

1. Small pieces from adjacent areas of a single wafer selected to insure uniform doping.
2. Quarters of single wafers. After quartering, individual samples were selected from analogous radial locations within each quarter to investigate possible center-to-edge doping variations.

SIMS analyses were carried out using precision measurement protocols including multiple repeat analyses of individual unknown and standard samples. For magnetic sector instruments, a single sample-holder-window protocol was generally used. For quadrupole instruments, samples were mounted in close proximity on a single mount, and accessed using restricted sample stage motions. All sites used the same calibration samples:

1. B: Bulk-doped working reference material (1.05×10^{19} cm^{-3} B), concentration traceable to NIST SRM-2137,
2. P: Consensus Ion Implant (100keV 8.5×10^{14} cm^{-3} P),
3. As: Consensus Ion Implant, same lot as NIST SRM-2134 (100keV, 7.27×10^{14} cm^{-3} As).

TABLE 1
EAG PARTICIPATING LABS AND SIMS INSTRUMENTATION

	SIMS Instrumentation Used (M = magnetic sector, Q = quadrupole)		
EAG Site	Boron	Phosphorus	Arsenic
Charles Evans & Associates	M, Q	M	M
Evans Texas	Q	M	M
Evans East	Q	Q	Q
Evans Europa	Q	M	Q

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III. RESULTS

Representative data from the round robin are listed below in the tables. Tables 2, 3, and 4 give individual B, P, and As measurements for the first sample configuration. Each lab analyzed three pieces of a single bulk-doped wafer with the same dopant concentration. For each lab, the mean of the repeat measurements for each piece, and the mean concentration for all pieces of the wafer are listed on the right in the table. The relative standard deviation (%RSD) is for all of the repeat measurements considered as a set. The relative standard deviation of the mean (%RSD_{mean}) is the standard deviation of the three values of the mean obtained for the separate pieces of each wafer. At the bottom of each table are listed average values of these two relative standard deviations over the EAG labs.

Tables 5, 6, and 7 list the mean B, P, and As concentration values obtained at the different lab sites for all the different wafers and distinct wafer locations. Each entry in these tables is the mean value of at least three repeat measurements. For example, the 'all-sample' mean values listed in Tables 2-4 are repeated in Tables 5-7. As stated, the mean values for these three wafers were obtained from 9-12 measurements spread over three pieces. For the quartered wafers, measurements were made on one piece from the original wafer center, and two pieces (right and left sides) for both the R/2 and edge locations. No significant azimuthal variations were found in the data, so the individual measurements for the right-hand and left-hand pieces at each radial distance were combined for the mean value calculations. For the other wafers, each lab measured a single piece per wafer.

TABLE 2
BORON CONCENTRATION MEASUREMENTS, WAFER (SIBB2B)

Wafer Piece	^{11}B Concentration measurements (10^{18} cm^{-3})				Mean of Each Piece	Mean of All, %RSD, *%RSD_{mean}*
Evans East						
24	9.72	9.78	9.73		9.74	9.739
27	9.63	9.70	9.66		9.66	0.70%
31	9.80	9.83	9.80		9.81	*0.75%*
Evans Europa						
21	9.71	9.81	9.72		9.75	9.743
25	9.74	9.70	9.73		9.72	0.41%
30	9.71	9.78	9.79		9.76	*0.19%*
Evans Texas						
23	9.69	9.85	9.83	9.94	9.83	9.873
28	9.89	9.88	9.84	9.89	9.88	0.74%
32	9.85	9.89	9.98	9.94	9.92	*0.44%*
Charles Evans & Associates, Quadrupole						
22	9.79	9.78	9.90		9.82	9.758
26	9.74	9.78	9.81		9.78	0.94%
29	9.56	9.71	9.75		9.67	*0.79%*
Charles Evans & Associates, Magnetic Sector						
22	9.77	9.78	9.86		9.80	9.795
26	9.78	9.77	9.69		9.75	0.55%
29	9.87	9.84	9.79		9.83	*0.43%*
Average Single Measurement %RSD =						**0.67%**
Average Single Piece %RSDmean =						**0.52%**

TABLE 3
PHOSPHORUS CONCENTRATION MEASUREMENTS, WAFER (SIPP1A)

Wafer Piece	^{31}P Concentration measurements (10^{19} cm^{-3})				Mean of Each Piece	Mean of All, %RSD, *%RSD_{mean}*
Evans East						
66	4.730	4.750	4.770		4.750	4.808
65	4.950	4.820	4.780		4.850	2.07%
53/63T	4.990	4.790	4.690		4.823	*1.08%*
Evans Europa						
63B	4.890	4.700	4.760		4.783	4.826
56	5.130	4.940	4.900		4.990	3.19%
35	4.760	4.72	4.630		4.703	*3.07%*
Evans Texas						
44	4.834	4.921	4.766	4.934	4.864	4.815
65	4.766	4.732	4.841	4.893	4.808	1.62%
67	4.671	4.804	4.781	4.836	4.773	*0.95%*
Charles Evans & Associates, Magnetic Sector						
75	4.910	4.882	4.887	5.020	4.925	5.007
46	5.067	5.048	5.120	5.081	5.079	1.59%
53T	5.073	5.036	4.979	4.984	5.018	*1.55%*
Average Single Measurement %RSD =						**2.1%**
Average Single Piece %RSDmean =						**1.7%**

TABLE 4
ARSENIC CONCENTRATION MEASUREMENTS, WAFER (SIAS1B)

Wafer Piece	^{75}As Concentration measurements (10^{19} cm^{-3})			Mean of Each Piece	Mean of All, %RSD, *%RSD_{mean}*
Evans East					
57C	2.280	2.230	2.320	2.277	2.229
36R/2	2.190	2.120	2.190	2.167	2.70%
76	2.240	2.210	2.280	2.243	*2.53%*
Evans Europa					
66C	2.440	2.440	2.470	2.450	2.482
37R/2	2.400	2.460	2.460	2.440	2.55%
77	2.560	2.510	2.600	2.557	*2.61%*
Evans Texas					
67C	2.192	2.226	2.229	2.216	2.246
86	2.322	2.279	2.309	2.303	2.30%
47	2.233	2.258	2.165	2.219	*2.22%*
Charles Evans & Associates, Magnetic Sector					
87R/2	2.273	2.210	2.285	2.256	2.300
46	2.308	2.316	2.336	2.320	1.83%
75	2.347	2.335	2.294	2.325	*1.68%*
Average Single Measurement %RSD =					**2.3%**
Average Single Piece %RSDmean =					**2.3%**

On the right side of Tables 5-7, the concentration data are recast as concentration ratios, with the center location of the quarter-wafer samples used for normalization. The radial variations in the quartered wafers range from about 2-3% for B and P, to 8% for As.

IV. DISCUSSION

We can use the standard deviations calculated for subsets of the round-robin data to characterize the repeatibility and reproducibility of the dopant concentration measurements. The probability that a repeat determination of a particular quantity will fall within ± one standard deviation of the mean value for the quantity is about 67% (assuming the values are normally distributed,

TABLE 5
BORON CONCENTRATION MEASUREMENTS (MEAN VALUES) IN FOUR BULK-DOPED SILICON SAMPLES

	Wafer Sample							
	SIBB2F (center)	SIBB2F (edge)	SIBB2B	SIBB2A	SIBB2F (center)	SIBB2F (edge)	SIBB2B	SIBB2A
Measurement Site	Site Mean ^{11}B Concentration (10^{18} cm^{-3})				Site Average Boron Concentration Ratio			
EEAST	7.810	7.695	9.739		=1.000	0.985	1.247	
EEUROPA	7.940	7.787	9.743	8.350	=1.000	0.981	1.227	1.052
ETEXAS	8.053	7.935	9.873	8.440	=1.000	0.985	1.226	1.048
CEA Quad	7.945	7.765	9.758	8.492	=1.000	0.977	1.228	1.069
CEA Mag	8.004	7.812	9.795	8.395	=1.000	0.976	1.224	1.049
Mean (all sites)	7.950	7.799	9.781	8.419	=1.000	0.981	1.230	1.054
%Relative Std Dev	1.15%	1.13%	0.57%	0.72%		0.44%	0.76%	0.92%

TABLE 6
PHOSPHORUS CONCENTRATION MEASUREMENTS (MEAN VALUES) IN FOUR BULK-DOPED SILICON SAMPLES

	Wafer Sample							
	SIPP1D (center)	SIPP1D (edge)	SIPP1B	SIPP1A	SIPP1D (center)	SIPP1D (edge)	SIPP1B	SIPP1A
Measurement Site	Site Mean P Concentration (10^{19} cm^{-3})				Site Average Phosphorus Concentration			
EEAST	1.050	1.027		4.81	=1.000	0.978		4.58
EEUROPA	1.093	1.042	3.42	4.83	=1.000	0.953	3.13	4.41
ETEXAS	1.033	1.014	3.34	4.81	=1.000	0.982	3.23	4.66
CEA Mag	1.187	1.163	3.82	5.01	=1.000	0.980	3.22	4.22
Mean (all sites)	1.091	1.061	3.528	4.846	=1.000	0.973	3.19	4.47
%Relative Std Dev	6.29%	6.44%	7.32%	1.97%		1.40%	1.73%	4.35%

TABLE 7
ARSENIC CONCENTRATION MEASUREMENTS (MEAN VALUES) IN FIVE BULK-DOPED SILICON SAMPLES

	Wafer Sample									
	SIAS1C (center)	SIAS1C (R/2)	SIAS1C (edge)	SIAS1B	SIAS1A	SIAS1C (center)	SIAS1C (R/2)	SIAS1C (edge)	SIAS1B	SIAS1A
Measurement Site	Site Mean As Concentration (10^{19} cm^{-3})					Site Average Arsenic Concentration Ratio				
EEAST	3.47	3.42	3.14	2.23	1.54	=1.000	0.983	0.903	0.642	0.444
EEUROPA	3.70	3.74	3.47	2.48	1.73	=1.000	1.011	0.938	0.671	0.467
ETEXAS	3.39	3.18	3.03	2.25	1.53	=1.000	0.937	0.894	0.662	0.451
CEA Mag	3.46	3.47	3.31	2.30	1.58	=1.000	1.003	0.956	0.665	0.458
Mean (all sites)	3.505	3.450	3.235	2.314	1.596	=1.000	0.983	0.922	0.660	0.455
%Relative Std Dev	3.78%	6.64%	5.92%	5.01%	5.62%		3.36%	3.16%	1.95%	2.12%

at least approximately).

A. *Repeatibility of a Single Measurement*

Tables 2-4 provide information about the average repeatability of SIMS dopant concentration measurements made at a single EAG site laboratory.

For each lab, all nine (or twelve) individual concentration measurements from the three wafer pieces are assumed to be statistically equivalent, and a single %RSD characterizing the entire measurement set is calculated. For each lab, this value is listed on the right in each table, just below the mean concentration value obtained for all pieces. The four or five individual site RSDs are then combined, and an average EAG value listed at the bottom of each table.

For B, the EAG average single measurement %RSD is 0.7%. The averages are somewhat larger for P and As (2.1% and 2.3%) reflecting an increase in variance due to increased sensitivity to instrumental set-up (high mass resolution ion optics) and other technical aspects (e.g. relative variations in kinetic energy spectrum of dopant and matrix secondary ions).

B. Repeatibility of Mean Concentration Values for Single Wafer Pieces

Since the data for each wafer piece in Tables 2-4 consists of three or more repeat measurements, we can also calculate and compare the mean values for the pieces. If the fluctuations in the individual measurements are random and normally distributed, then statistically, the standard deviation of the mean (%RSD_{mean}) should be smaller than the single measurement standard deviation by the square root of the number of measurements, or about 1.7 for three measurements. From the averages at the bottom of each table, we see that for B and P, the %RSD_{mean} is somewhat less than the single measurement %RSD. For As, there is however no difference. This discrepancy implies that for the As data, the variations in the individual measurements are not random. Inspection of the data confirms that there are systematic variations in the concentration values from piece-to piece. Some degree of systematic variation is also probably present in the P data, and perhaps the B data, since the reduction in the %RSD_{mean} is less than the ideal factor of 1.7 to 2 expected from the number of individual measurements.

C. Reproducibility of Mean Concentration Values across the EAG

The mean concentrations that are listed on the left side of Tables 5-7 are based on data calibrated with the original standard samples (bulk-doped wafer for B, ion implants for P and As). On the right side of each table, the mean concentrations have been renormalized to one of the bulk-doped samples and expressed as concentration ratios. *For P and As, this is basically equivalent to recalibration with respect to a bulk doped reference sample.* For both elements, a significant decrease in the average %RSD occurs. (For B, the original calibration standard was bulk-doped, and renormalization to the second bulk-doped sample has little effect on the average %RSD).

For P and As, the larger scatter in the results when calibrated using the ion implanted standards appears to be due to additional variance in the sensitivity factors caused in part by uncertainties in the depth scale (profilometer depth measurements), and in part by other factors, possibly including detector saturation at the peak of the ion implant profile.

V. CONCLUSIONS

Although we have concentrated our discussion on the issue of the repeatibility and reproducibility of the SIMS measurements, the other goals of the round robin were met.

Mean B, P, and As concentrations were determined for several bulk-doped silicon reference wafers, and the concentrations were calibrated on absolute concentration scales determined by accepted NIST Standard Reference Materials (B, As) or Consensus Reference Materials (P). These bulk doped standards provide for convenient and precise SIMS dopant concentration calibration.

Good repeatability and reproducibility of dopant concentration measurements was attained across the four EAG laboratories. Using bulk doped standards, the EAG group-wide dopant measurement reproducibility is similar to the measurement repeatability at a single site.

Repeatability at a single site

At a single EAG site laboratory, the typical repeatability of precision dopant concentration measurements is characterized by relative standard deviations of:

Boron	±0.7% (67% confidence level)
Phosphorus	±2.1% (67% confidence level)
Arsenic	±2.3% (67% confidence level)

Reproducibility among all sites

Using ion-implanted calibration standards, the reproducibility of precision dopant concentration measurements among the four EAG site laboratories is characterized by relative standard deviations of:

Phosphorus	±5.5% (67% confidence level)
Arsenic	±5.4% (67% confidence level)

Using bulk-doped calibration standards, the reproducibility of precision dopant concentration measurements among the four EAG site laboratories is characterized by relative standard deviations of:

Boron	±0.9% (67% confidence level)
Phosphorus	±2.5% (67% confidence level)
Arsenic	±2.6% (67% confidence level)

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